

International Mine Water Association

2013 Annual Conference

-

VOLUME

MINE WATER TECHNOLOGY



RELIABLE MINE WATER TECHNOLOGY VOLUME I

Reliable Mine Water Technology

Volume I

Proceedings of the International Mine Water Association Annual Conference 2013

August 6 — 9, 2013

Golden, Colorado, USA

Editors Adrian Brown Linda Figueroa Christian Wolkersdorfer International Mine Water Association. Anual Conference (2013 : Golden, CO) Reliable Mine Water Technology – Volume I International Mine Water Association Annual Conference, 2013, Golden, Colorado, USA / Adrian Brown, Linda Figueroa, Christian Wolkersdorfer, editors.



ISBN 978-0-615-79385-6 - Volume I

© International Mine Water Association 2013

Cover Design & Karoline Wolkersdorfer Layout and Typesetting & Prof. Dr. habil. Christian Wolkersdorfer

Cover Photographs front Stephen W. Oachs ↔ Henk Coetzee ↔ Carleton R. Bern ↔ Arabella M. L. Moorhouse ↔ Christian Wolkersdorfer ↔ back Matthew T. Bailey ↔ Henk Coetzee ↔ Christian Wolkersdorfer

Themes Photographs 1 Susan Wyman ∞ 2 Emmannuele Gagné ∞ 3 Robert Netshitungulwana ∞ 4 Christian Wolkersdorfer

Typeset with QuarkXPress in TheAntiqua, TheMix, and TheSans from Lukas de Groot

Printed in the USA on recycled paper



www.IMWA.info

Organizers



International Mine Water Association



Colorado School of Mines

International Scientific Committee

Joel Adams, USA Sandra Ainsworth, USA Lena Alakangas, Sweden Bert Allard, Sweden Lee C. Atkinson, USA Mattias Bäckström, Sweden Jeff Bain, Canada Andre Banning, Germany Carleton R Bern, USA Nico Bezuidenhout, South Africa Colin I. Booth, USA Hanna Braden, USA Adrian Brown, USA John Chahbandour, USA Rosa Cidu, Italy Wilhelm Georg Coldewey, Germany David Dettrick, Australia Enrico Dinelli, Italy Craig Divine, USA Scott Effner, USA Linda Ann Figueroa, USA

Kay Florence, United Kingdom Jennifer N. Geroni, United Kingdom Ieff Gillow. USA Jordi Guimera, Chile James Edward Hanley, USA Robert S Hedin, USA Roger Lynn Howell, USA Amy L. Hudson, USA Ryan Jakubowski, Peru Frans Knops, Netherlands Natalie Alyssa Kruse Daniels, USA Jorge Loredo, Spain John Foriyes Lupo, USA Clint McCullough, Australia Broder Merkel, Germany Thomas Metschies, Germany Jacek Motyka, Poland Kevin Myers, USA Robert W. Nairn, USA James Navratil, USA Carmen Neculita, Canada

Nora Hilda Paños, Argentina Walter Pohl, Austria Volker Preuss, Germany Naďa Rapantova, Czech Republic Pierre Rousseau, Australia Martin Schultze, Germany Robert Seal, USA Alison Sinclair. Australia Kathleen S. Smith, USA Mark Vancook, Canada Rens Verburg, USA Danie Vermeulen, South Africa John Waterhouse, Australia Daniel Weber, USA Walter Weinig, USA Phillip Whittle, Australia Frank Winde, South Africa Andrzej Witkowski, Poland Christian Wolkersdorfer, Germany Magdalena Worsa-Kozak, Poland

Local Organising Committee

Co-Chairs

Adrian Brown PE Dr. Linda Figueroa

Members

Dr. Lee Atkinson Dr. Carleton Bern Dr. Raymond Johnson Dr. Robert Kleinmann Dr. John Lupo PE Dr. Mei Lin Shelp Dr. Kathy Smith Liz Swaim John Waterhouse Daniel Weber PG Dr. Christian Wolkersdorfer

Administration

Melody Francisco Timothy O'Leary President, International Mine Water Association, Denver, Colorado USA Associate Professor, Colorado School of Mines, Golden, Colorado USA

Atkinson Mine Water Consultants, Inc., Golden, Colorado USA United States Geological Survey, Lakewood, Colorado USA United States Geological Survey, Lakewood, Colorado USA CH2M Hill, Pittsburgh, Pennsylvania USA Newmont Mining Corporation, Fiddlers Green, Colorado USA Barrick Mining Corporation, Toronto, Canada United States Geological Survey, Lakewood, Colorado USA Itasca Denver, Lakewood, Colorado USA Golder Associates, Perth, Western Australia Montgomery & Associates, Denver, Colorado USA International Mine Water Association, Freiberg, Germany

CSM Special Programs and Continuing Education, Golden, Colorado USA CSM Special Programs and Continuing Education, Golden, Colorado USA

IMWA 2013 Sponsors

Silver Sponsor



Bronze Sponsors





Cripple Creek & Victor Gold Mining Company www.ccvgoldmine.com









Other Sponsors







Aber da der unterste Theil der Erden sich an Ertzen durch so viel Mühe und Unkosten hat offenbahr machen lassen, da will nun Mangel vorfallen an Holtz und Kohlen dieselbe gut zu machen; Wird derhalben die größte Kunst, Wissenschaft, Fleiß, und Einrichtung hiesiger Lande darinnen beruhen, wie eine sothane Conservation und Anbau des Holtzes anzustellen, daß es eine continuierliche beständige und **nachhaltende** Nutzung gebe, weiln es eine unentberliche Sache ist, ohne welche das Land in seinem Esse nicht bleiben mag. Denn gleich wie andre Länder und Königreiche, mit Getreide, Viehe, Fischereyen, Schiffarthen, und andern von GOtt gesegnet seyn, und dadurch erhalten werden; also ist es allhier das Holtz, mit welchem das edle Kleinod dieser Lande der Berg-Bau nehmlich erhalten und Ertze zu gut gemacht, und auch zu anderer Nothdurft gebraucht wird.

Now that the ores in the lowermost part of the earth, through effort and expenses, were revealed, a shortage of wood and coal for their beneficiation occurs. Thus, the greatest skills of art, science, diligence, and institutions of the local states will examine how a conservation and cultivation of wood shall be done so that a continuous, lasting, and **sustainable** use is given, because it is an indispensable thing, without which this state will not continue to exist. Since other countries and kingdoms are blessed by God with crops, cattle, fishing, ships, and others, and survive because of that; so, here it is wood that is the precious jewel of these local states: it allows mining to stay alive and ore to be beneficiated, and also used for other affairs.

Hannss Carl von Carlowitz

Sylvicultura Oeconomica, Capter VII. Von Nothwendigkeit und Nutzen des Holtz-Anbaues, p. 105–106; Leipzig 1713

Welcome Message from the Conference Organizers

Welcome to IMWA 2013, the International Mine Water Association conference at the Colorado School of Mines in Golden, Colorado USA. At this conference we are presenting the state of the art and the practice in Reliable Mine Water Technology, because for mining to be sustainable the mine water technology it is based on must be reliable and verifiable, for all stakeholders.

IMWA 2013 takes place in a period when global mining is expanding to meet growth in mineral demand. Emerging nations are making the benefits of modern technology available to their citizens. And established nations are seeking to reduce the footprint of technology on their environments with new and often mineral-intensive advances in transportation, agriculture, energy, and environmental protection.

As mining takes place within the hydrologic cycle, and is water consumptive, this increased mineral extraction also expands mine water use, water treatment, water discharge, and potential for environmental impacts to water. To meet these challenges, sustainable mining requires a reliable and verifiable demonstration that the minimum quantity of water will be utilized, and the maximum protection of water resources will be achieved. This requires:

- Reliable investigation and evaluation at mine-design and mine-permit time;
- Reliable operation of water management systems during mining; and
- Reliable implementation of water protection systems after mine closure.

In addition, mining takes place under stringent regulations, and under the scrutiny of a highly informed and internationally connected public. Today, mining can only go forward with the support of all stakeholders, requiring independently verifiable assurance by regulators, miners, and the public that mining will meet their resource and environmental protection goals.

Mine water reliability requires reliable technology. Mining companies, researchers, engineers, geologists and scientists have developed and are refining the technology needed to meet the challenge to minimize mine water use, to control mine water flow and pressure, and to protect mine water quality. The first class program presented at IMWA 2013, comprising 200 papers and posters, short courses, and exhibits, showcases our mine water technical knowledge, and demonstrates that we know how to evaluate, use, extract, treat, discharge, and protect mine water. The program has been designed to provide ample opportunity for exchange of ideas and best practices with colleagues from around the world.

It is with great pride that Conference co-chairs Adrian Brown of IMWA and Linda Figueroa of the Colorado School of Mines welcome you at IMWA 2013: Reliable Mine Water Technology, to share the remarkable progress that has been achieved in making mine water use and protection reliable and mining hydrologically and geochemically sustainable.

Adrian Brown PE, President, International Mine Water Association Linda Figueroa PhD, Professor, Colorado School of Mines

300 years of "sustainability" - A word from the Editor-in-Chief of these Proceedings

Dear Colleagues and Friends,

After having now edited three sets of IMWA proceedings in four years, I have the feeling that something is on the move in mine water treatment and management. Evolving technologies are being presented and implemented in mine water treatment schemes. It is a little bit as if a James Watt of mine water is somewhere within our community, watching and collecting various pieces of information as well as existing technologies and putting them together in a brand new incremental way – just as James Watt did when he improved the Thomas Newcomen steam engine technology.

I am currently sitting in Freiberg/Saxony, just 200 meters away from the place where, 300 years ago, Hannß Carl von Carlowitz coined the term sustainability in his outstanding book *"Sylvicultura oeconomica"* (see page 11). He said that we need to maintain our forests in a sustainable way to ensure that mining can proceed. In 1713, the availability of wood was a key component of mining and smelting; today, sound environmental management during the entire mine lifecycle is just as critical. The treatment and management of mine water is one part of a responsible mining project – but it is the one that lasts long after mining has ceased. Therefore, it is essential that we develop technologies that will enable us to treat mine water as economically and reliably as possible.

But why not change the paradigm? Both Watt and von Carlowitz had a mining-related problem: Watt had too much water that needed to be pumped and von Carlowitz observed that forests were shrinking, limiting the supply of mine timber and fire wood for the smelters. Both of them initiated a paradigm shift, which is is what we need today in mine water management. Quite simply, in the future, we must see and use mine water as a resource instead of a waste. To cite one example, the abandoned South African gold mines in the Witwatersrand will potentially discharge about 180 ML/d of acidic to circumneutral mine water. This mine water contains 300 t of Ni, 290 t of Zn, 90 t of Co, 25 t of U, and 4 t of Li – a total value of 3 Million USD annually for just those metals (30 % of market price used)! Why not extract them?

As in the case of James Watt's optimised steam engine, the technology is available. We are incrementally improving it; now, what we need is for somebody (perhaps you?) to put all that knowledge together into a new technique for mine water winning. This year's IMWA proceedings might contain the key you need, hidden somewhere within its 200 papers, to be the one who initiates that paradigm shift – exactly 300 years after "sustainability" was brought to light. Please, when you listen to the presentations and read these papers, open your mind to new possibilities!

I wish you a wonderful IMWA 2013 conference and I look forward to seeing you during one of the coffee breaks, social events, or field trips.

Glückauf and all the best!

Christian Wolkersdorfer Freiberg/Saxony, July 7th 2013

Contents

VOLUME I THEMES 1-4

1 RELIABLE MINE WATER PERMITS AND REGULATION

Bek	esi, Gabor; Tyler, Murray; Niejalke, Darren; Waterhouse, John	
	Improved Regulation of Water Supply for the Olympic Dam Mine, South Australia	29
Bitt	ner, Arnold; Zingelmann, Markus	
	Groundwater Use and Protection as Part of the Namibian Mining Application	35
Her	nandez, Aurora Maria	
	Mine Closure Regulations – Case Scenario in Northern Quebec	41
Küll	s, Christoph; Bittner, Arnold; Marx, Vera	
	Strategic Assessment of Water Resources for the Erongo Uranium Province	47
Log	don, Mark J.	
	What Does "Perpetual" Management and Treatment Mean? Toward a Framework for Determining an	
	Appropriate Period-of-Performance for Management of Reactive, Sulfide-Bearing Mine Wastes	53
Nicł	olson, Andrew Dow; Williams, Les; Rudnick, Deborah; Ortega, Jennifer	
	Spatial and Temporal Assessment of Ecological Risks at a Gold Mine Pit Lake	59
Sch	penbacher, Jeff	
	Managing Water Permits with GIS at Questa Mine	63
Tim	ns, Wendy A; Leong, Shane; Taplin, Ros; Hazelton, James; Laurence, David	
	Mine site water information disclosures in the context of watersheds and reporting frameworks, eastern	
	Australia	69
Vinl	r, Sue; Hoey, Dave; Robbins, Sarah; Roux, Estelle; Wolhuter, Alexandra	
	Regulating mine water releases using water quality trading	71
Whi	ttle, Phillip; Smith, Ross E.W.	
	Development and application of water quality criteria for reliable management of off-site risk	77
Wyı	nan, Susan; Harmon, Makinsey	
	Management of Mine Water Quality Data from Permitting to Compliance to Closure	83
I	2 RELIABLE MINE WATER HYDROLOGY	
B. G	agné, Emmanuelle; Rouleau, Alain; Chesnaux, Romain; Roy, Denis W.; Cloutier, Vincent; Daigneault, Réal	
	Underground Mine Site Investigations for Estimating Hydrogeological Properties of Regional Fractured Roc	k
	Aquifers	91
Bick	ford, Fred Eric; Breckenridge, Larry	2
	Simulated Mining, Backfilling, and Artificial Recharge of the Corani Open Pit	97
Bred	lenkamp, Brendon	51
	Numeric model calibration against both flux and head targets to determine reliable groundwater inflow	
	predictions	103
Cast	iglia, Peter; Lane, Terre; Foote, Randy; Linderfelt, William; Cheng, Cheng; Jordan, David; Wilson, Daniel;	5
	Tinklenberg, Annelia	
	A deep, non-potable water supply for the Ochoa Sulphate of Potash (SOP) Mine Project, Lea County. New Me	xico.
	U.S.A.	105
		2

Cottingham, Christopher Todd; Vitale, Matt; Selker, John; Lupton, Sarah; Selker, Frank	
Using Fiber Optics and Vibrating Wire Piezometers to Characterize an Aquifer in Preparation for Ground	
and Aquifer Freezing	111
Digges La Touche, Gareth; Sraj, Nina; Yungwirth, Grace	
The application of ecohydrology to mine water impact assessment	117
Dowling, Jeremy; Beale, Geoff; Bloom, Jack	
Designing a Large Scale Pit Slope Depressurization System at Bingham Canyon	119
Dowling, Jeremy; Zimmerlund, Ben; Kennealy, Jamie; van den Berg, Elmer	
An Integrated Model for Mine Dewatering at the Bagdad Mine	125
Everett, Brent; Effner, Scott; Kaminsky, Jon; Kramer, David	
Hydrogeologic Characterization and Numerical Modeling of Groundwater Inflow to Support Feasibility	
Studies for Underground Mining – a Case Study in the Southeast Idaho Phosphate District	133
Gale, John Edward; Seok, Eunjeong	
Field and laboratory coupled fracture deformation-pore pressure-permeability experiments that provide	
insight for depressurization of fractured rock slopes	139
Howell, Roger Lynn	
Airlift Testing in Exploration Coreholes	145
Li, Xiangquan; Hou, XinWei; Liu, Lingxia; Wang, Zhengxing; Gao, Ming	
The General Scheme for Hydrogeological and Environment Geological Investigation of Large Scale	
Coal Bases, in China	151
Liu, Houmao; Nel, Elaine; Kotze, Johanita; Ding, Dong	
Mine Dewatering in a Compartmentalized Hydrogeologic Setting at Sishen Mine in South Africa	157
Luscz, Emily Catherine; Le, Vinh-Luu	
Managing High Altitude Bog Deposits: An Investigation of the Hydrogeologic and Geotechnical	
Challenges associated with Andean Bofedal Sediments	163
Moleiro Cabrera, Manoel Camilo; Youlton, Cristian; Wendland, Edson	
Quantification of water evaporation by open pit mining lake using lysimeters	169
Pedder, Rosalind Katherine; El Idrysy, Houcyne	
The combined use of spinner flow logging and geotechnical information to investigate the hydraulic	
properties of fractured rock mass	175
Rapantová, Naďa; Wolkersdorfer, Christian; Krzeszowski, Światosław; Grmela, Arnošt	
Methodology of Quantitative Assessment of Mine Water Inflows	181
Sui, Wanghua	
Grouting for ensuring coal mining safety above limestone aquifers with high water pressure	189
Swanson, Eric E.; Titone, Brian C.	2
Packer Testing Program Design and Management	200
Szczepinski, Jacek Jozef	
Stream-aguifer interaction in mining conditions using a groundwater flow model	206
Thompson, Keith Steven: Cadle, Sonva	
Integrating Less-Common Data Sources to Improve Groundwater Model Calibration	212
Thompson, Randi Lee: Johnston, Katherine Sylvia: Crozier, Trevor Wade: Wilbur, Stephen Crawford	
Groundwater Modelling and Site Investigations to Evaluate Groundwater Supply Availability	
and Withdrawal Impacts for a Proposed Gold Mine in Yukon Canada	218
Wang, Changshen: Bai, Haibo: Mao, Xianbiao: Liu, Shucai: Liu, Jingcun: Liu, Yong	210
Integrated methods to determine the optimal underlying grouting strata against hazardous	
water inrush (China)-a case study	222
mater in aon (ennia) a case study	222

Wi	ilton, N	Aichael John; Lupo, John	
	Wate	er Balances and their Role in Operational Mine Water Management	223
Yu	ngwirt	th, Grace; Preene, Martin; Dobr, Michal; Forero Garcia, Felipe	
	Prac	tical Application and Design Considerations for Fully Grouted Vibrating Wire Piezometers in	
	Min	e Water Investigations	229
Zh	an, Gu	iosheng; Milczarek, Mike; Keller, Jason; Giraudo, Joe	
	The	AA leach pad cover design – a successful reclamation project at a Nevada gold mine	237
	3	Reliable Mine Water Geochemistry	
An	naral F	ilho, Juarez; Weiler, Jéssica; Schneider, Ivo; Broadhurst, Jennifer	
	Usir	ng Humidity Cells Tests to Evaluate an ARD Minimization Approach in Santa Catarina Coal Field, Brazil	245
Be	ddoes,	, Paul; Herrell, Michael; Vandenberg, Jerry	
	Role	of Professional Judgement and Scaling in Interpretation of Water Quality Model Results	251
Be	zkorov	vajny, Andrzej; Czop, Mariusz; Stochel, Bernadetta; Worsa-Kozak, Magdalena	
	Hyd	rogeochemistry of the Mine Water from "Bochnia" Salt Mine (Kraków Region, South Poland)	257
Bh	attach	arya, Jayanta; Das, Bidus Kanti	
	Proc	cess sustenance in an organic carbon exhausted chemo-bioreactor by sweetmeat waste dosing	263
Bre	eckenr	idge, J. Larry; Bickford, Fred. E; Luscz, Emily	
	Asse	essing the Reliability of an Unlined Tailings Storage Facility for Protecting Water Resources	269
Bro	oadhu	rst, Jennifer Lee; Bryan, Christopher; Becker, Megan; Franzidis, Jean-paul; Harrison, Sue	
	Cha	racterising the Acid Generating Potential of Mine Wastes by means of Laboratory-scale	
	Stat	ic and Biokinetic Tests	275
Ca	mden-	Smith, Bronwyn P; Johnson, Raymond H; Richardson, Robert; Billing, David G; Tutu, Hlanganani	
	Inve	stigating the potential impact of efflorescent mineral crusts on water quality:	
	com	plementing analytical techniques with geochemical modelling	281
Ca	mpbel	l, Kate Marie; Alpers, Charles; Nordstrom, D. Kirk; Blum, Alex; Williams, Amy	
	Cha	racterization and Remediation of Iron(III) Oxide-rich Scale in a Pipeline Carrying Acid Mine	
	Drai	inage at Iron Mountain Mine, California, USA	287
Ch	apin, 1	Thomas; Progess, Christina; Todd, Andrew	
	Min	iSipper: A New, High-capacity, Long-duration, Automated In Situ Water Sampler for	
	Acid	l Mine Drainage Monitoring	295
Ch	atwin,	Terrence Doyle; Williams, Dean; Creek, Mike	
	Acid	l Rock Drainage Challenges and a Path Forward	301
Со	etzee,	Henk; Kotoane, Mpho; Atanasova, Maria; Roelofse, Frederick	
	Inte	ractions between dolomite and acid mine drainage in the Witwatersrand: results of field	
	and	laboratory studies and the implications for natural attenuation in the West Rand Goldfield	307
Со	sta, M	aria Rosário; Ávila, Paula; Ferreira, Adelaide; Fereira da Silva, Eduardo	
	Avai	lability of trace elements in the abandoned Freixeda gold mine area, NE Portugal	313
Cra	avotta	, Charles	
	Арр	arent Rates of Fe(II) Oxidation and Associated Hydrogeochemical Interactions in an	
	Exte	ensively Mined Watershed, Pennsylvania, USA	319
De	v, Sub	habrata; Das, Bidus Kanti; Bhattacharya, Jayanta	
	Sulf	ate Reduction Performance of Sulfate Reducing Bacteria Using Marine Waste Extract as Nitrogen Source	325
Do	orey, Ro	obert; Breckenridge, Larry	
	Min	e Waste Geochemistry Assessment, Corani Project, Puno, Peru	331

Fricke, James Ross; Dean, Daniel Miller	
Use of a Biological Polishing Step to Improve Bioassay Test Results	337
Gautama, Rudy Sayoga; Kusuma, Ginting Jalu; Abfertiawan, Sonny; Wiedhartono, Arief; Gunawan, Firman;	
Lestari, lin; Simbolon, Reynaldi; Diana, Melinda Rose	
Study on capping options for overburden encapsulation to prevent acid mine drainage in	
Lati coal mine, East Kalimantan, Indonesia	341
Gillow, Jeff; Griffin, Adam; Christoffersen, Lee; Divine, Craig; Hay, Michael; DeDycker, Phil	
Control of Tailing Seepage through Reactive Chemical Amendments	347
Greer, Briana; Helgen, Steve; Nicholson, Andrew; Kosinski, Sean	
Incorporating Wall Rock Runoff into Pit Lake Water Quality Modeling in the Arid Western United States	353
Harley, Andrew	
The adoption of the soil chemical equilibrium approach to solving hydrogeochemical problems	359
Helgen, Steven O.; Greer, Briana; Nicholson, Andrew	
Addition of a Rate Limit to a Shrinking Core Oxidation Model for Predictive Modeling of Mine Water Quality	365
Jiang, Jianhua; Auckland, Adam; Long, Dejiang; Mackenzie, Ian; Bender, Michael	
Numerical Simulation of Total Suspended Solid Concentration in Oil Sands Tailings Ponds	371
Johnson, Raymond H.; Tutu, Hlanganani	
Reactive transport modeling at uranium in situ recovery sites: uncertainties in uranium	
sorption on iron hydroxides	377
Jones, Ashley; Rogerson, Micheal; Greenway, Gillian; Mayes, William Matthew	
Controls on zinc uptake from circum-neutral mine drainage in freshwater biofilms	383
Karlsson, Lovisa; Karlsson, Stefan; Allard, Bert; Sjöberg, Viktor; Bäckström, Mattias	
Release of metals from unprocessed and processed black shale due to natural weathering	391
Kruse Daniels, Natalie Alyssa; Breckenridge, Larry; Kruse, Colin	
A simple modeling approach for an acid generating, backfilled mine pit	397
Loredo, Jorge; Ordoñez, Almudena; Alvarez, Rodrigo	
Holistic View of Water Affection in the Mercury Mining District of Asturias (Spain)	399
Lyle, Sarah Louise; Barnes, Andrew; Stewart, Michael David	
Hydrological Impact Assessment within a Natura 2000 Protection Area in Northern Scandinavia	405
Mahoney, John J	1 2
Sensitivity of Database Selection in Modeling the Transport of Uranium	411
Makgae, Mosidi; Maree, Jannie; Annandale, John	•
Neutralised Mine Water For Irrigation – Cost And Feasibility Study	417
Mavunganidze. Taimos: Tutu. Hlanganani	1,
The role of humic substances in metal attenuation in leachates emanating from abandoned	
gold tailings footprints	425
Netshitungulwana, Robert; Yibas, Bisrat; Novhe, Obed Ntshengedzeni; Motlakeng, Tshepo	1 2
Stream sediment geochemistry of the areas impacted by mining around Emalahleni (formerly known as	
Witbank), South Africa: Fingerprinting AMD potential point sources	429
Pint. Tina: Hinck. Peter	1 5
Use of an integrated source-to-receptor model to facilitate rapid assessment of water quality	
impacts during mine planning	435
Raman, Chandra Devi: MacSween, Jessica: Shea, Joe: Kaliaperumal, Raiendran: Oakes, Ken: Mkandawire, Martin	155
Prediction of hydrogeochemical changes due to surface water seepage into 1B Mine Pool	
of Cape Breton, Canada	441
Rue, Garrett; Crouch, Caitlin; McKnight, Diane	
Increasing ARD and rare earth metal concentrations in an alpine watershed	447

Sackey, Michael Amplini ; Kuma, Jerry S. 1; Anornu, Geophrey; Kortatsi, Ber K.	
Attenuation Potential of Clay Liner Carbon-in-Leach Tailings Storage Facilities:	
A Case Study at Gold Fields Ghana Limited, Tarkwa Mine (GFGL).	451
Sackey, Michael Ampim; Kuma, Jerry S, Y; Anornu, Geophrey; Kortatsi, Ben	
Cyanide Decay and Metal Speciation in Decant Ponds of Carbon-in-Leach Tailings Storage Facilities:	
A Case Study at Gold Fields Ghana Limited, Tarkwa Mine (GFGL)	457
Sartz, Lotta; Bäckström, Mattias	
Impact of temperature on weathering rates – a long-term kinetic study on waste rock	
from Bergslagen, Sweden	463
Song, Xin; Leone, Gaston	
Modeling Application in Evaluating Environmental Impact due to Phosphate Mining Activities	469
Tlowana, Supi; Coetzee, Henk; Makgae, Mosidi	
Realistic simulation of acid mine drainage generation in the gold mines of the Witwatersrand, South Africa	475
Warren, Bartholomew James	
Selenium in mine waters: a review	481
Whitmore, Christa; Kauffman, Mary; Effner, Scott	
Application of Column Leaching Tests to Predict Seepage Water Quality from Waste Rock in	
the Southeast Idaho Phosphate District	487
Williams, George P.; Gammons, Chris H.; Parker, Stephen R.	
Natural acid rock drainage in the Judith Mountains, Central Montana, USA	493
Williamson, Jacob; Pastorinho, Ramiro; Ranville, James; Meyer, Joseph; Santore, Robert; Ryan, Adam; Gorsuch,	
Joseph; Rogevich-Garman, Emily; Schlekat, Christopher; Dwyer, Robert	
Toxicity of Metal Mixtures to Daphnia magna: Comparison of Laboratory and Field Investigations	499
4 RELIABLE MINE WATER TREATMENT	
4 RELIABLE MINE WATER TREATMENT	
4 RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia	507
 A RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Böcketzöm Mattiac: Satz, Lotta 	507
 A RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta 	507
 A RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey Matthewa T. Maerhawa, Arabella M. L. Byram A. James, Korchaw, Staven 	507 513
 A RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T.; Moorhouse, Arabella M. L.; Byrom, A. James; Kershaw, Steven 	507 513
 A RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T.; Moorhouse, Arabella M. L.; Byrom, A. James; Kershaw, Steven Applications for Hydrous Ferric Oxide mine water treatment sludge: A Review 	507 513 519
 A RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T.; Moorhouse, Arabella M. L.; Byrom, A. James; Kershaw, Steven Applications for Hydrous Ferric Oxide mine water treatment sludge: A Review Brown, Adrian 	507 513 519
 A RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T.; Moorhouse, Arabella M. L.; Byrom, A. James; Kershaw, Steven Applications for Hydrous Ferric Oxide mine water treatment sludge: A Review Brown, Adrian Low-cost Long-term Passive Treatment of Metal-Bearing and ARD Water using Iron Rich Material 	507 513 519 525
 A RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T.; Moorhouse, Arabella M. L.; Byrom, A. James; Kershaw, Steven Applications for Hydrous Ferric Oxide mine water treatment sludge: A Review Brown, Adrian Low-cost Long-term Passive Treatment of Metal-Bearing and ARD Water using Iron Rich Material Conroy, Kevin W; Huff, Brian D; Gallagher, Neal T 	507 513 519 525
 A RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T.; Moorhouse, Arabella M. L.; Byrom, A. James; Kershaw, Steven Applications for Hydrous Ferric Oxide mine water treatment sludge: A Review Brown, Adrian Low-cost Long-term Passive Treatment of Metal-Bearing and ARD Water using Iron Rich Material Conroy, Kevin W; Huff, Brian D; Gallagher, Neal T Development of Treatment Solutions for the Central City/Clear Creek Superfund Site in Colorado 	507 513 519 525 533
 A RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T.; Moorhouse, Arabella M. L.; Byrom, A. James; Kershaw, Steven Applications for Hydrous Ferric Oxide mine water treatment sludge: A Review Brown, Adrian Low-cost Long-term Passive Treatment of Metal-Bearing and ARD Water using Iron Rich Material Conroy, Kevin W; Huff, Brian D; Gallagher, Neal T Development of Treatment Solutions for the Central City/Clear Creek Superfund Site in Colorado Conroy, Kevin W; Moderski, Anna M 	507 513 519 525 533
 A RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T.; Moorhouse, Arabella M. L.; Byrom, A. James; Kershaw, Steven Applications for Hydrous Ferric Oxide mine water treatment sludge: A Review Brown, Adrian Low-cost Long-term Passive Treatment of Metal-Bearing and ARD Water using Iron Rich Material Conroy, Kevin W; Huff, Brian D; Gallagher, Neal T Development of Treatment Solutions for the Central City/Clear Creek Superfund Site in Colorado Conroy, Kevin W; Moderski, Anna M Water Management and Treatment for the Copperwood Mine Project 	507 513 519 525 533 539
 A RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T.; Moorhouse, Arabella M. L.; Byrom, A. James; Kershaw, Steven Applications for Hydrous Ferric Oxide mine water treatment sludge: A Review Brown, Adrian Low-cost Long-term Passive Treatment of Metal-Bearing and ARD Water using Iron Rich Material Conroy, Kevin W; Huff, Brian D; Gallagher, Neal T Development of Treatment Solutions for the Central City/Clear Creek Superfund Site in Colorado Conroy, Kevin W; Moderski, Anna M Water Management and Treatment for the Copperwood Mine Project Eger, Paul; Kairies Beatty, Candace 	507 513 519 525 533 539
 A RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T.; Moorhouse, Arabella M. L.; Byrom, A. James; Kershaw, Steven Applications for Hydrous Ferric Oxide mine water treatment sludge: A Review Brown, Adrian Low-cost Long-term Passive Treatment of Metal-Bearing and ARD Water using Iron Rich Material Conroy, Kevin W; Huff, Brian D; Gallagher, Neal T Development of Treatment Solutions for the Central City/Clear Creek Superfund Site in Colorado Conroy, Kevin W; Moderski, Anna M Water Management and Treatment for the Copperwood Mine Project Eger, Paul; Kairies Beatty, Candace Constructed Wetland Treatment Systems for Mine Drainage– Can They Really Provide Green 	507 513 519 525 533 539
 A RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T.; Moorhouse, Arabella M. L.; Byrom, A. James; Kershaw, Steven Applications for Hydrous Ferric Oxide mine water treatment sludge: A Review Brown, Adrian Low-cost Long-term Passive Treatment of Metal-Bearing and ARD Water using Iron Rich Material Conroy, Kevin W; Huff, Brian D; Gallagher, Neal T Development of Treatment Solutions for the Central City/Clear Creek Superfund Site in Colorado Conroy, Kevin W; Moderski, Anna M Water Management and Treatment for the Copperwood Mine Project Eger, Paul; Kairies Beatty, Candace Constructed Wetland Treatment Systems for Mine Drainage– Can They Really Provide Green and Sustainable Solutions? 	507 513 519 525 533 539 545
 4 RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T.; Moorhouse, Arabella M. L.; Byrom, A. James; Kershaw, Steven Applications for Hydrous Ferric Oxide mine water treatment sludge: A Review Brown, Adrian Low-cost Long-term Passive Treatment of Metal-Bearing and ARD Water using Iron Rich Material Conroy, Kevin W; Huff, Brian D; Gallagher, Neal T Development of Treatment Solutions for the Central City/Clear Creek Superfund Site in Colorado Conroy, Kevin W; Moderski, Anna M Water Management and Treatment for the Copperwood Mine Project Eger, Paul; Kairies Beatty, Candace Constructed Wetland Treatment Systems for Mine Drainage– Can They Really Provide Green and Sustainable Solutions? Fahlqvist, Anna Linnéa; Bäckström, Mattias; Sartz, Lotta; Allard, Bert 	507 513 519 525 533 539 545
4 RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T.; Moorhouse, Arabella M. L.; Byrom, A. James; Kershaw, Steven Applications for Hydrous Ferric Oxide mine water treatment sludge: A Review Brown, Adrian Low-cost Long-term Passive Treatment of Metal-Bearing and ARD Water using Iron Rich Material Conroy, Kevin W; Huff, Brian D; Gallagher, Neal T Development of Treatment Solutions for the Central City/Clear Creek Superfund Site in Colorado Conroy, Kevin W; Moderski, Anna M Water Management and Treatment for the Copperwood Mine Project Eger, Paul; Kairies Beatty, Candace Constructed Wetland Treatment Systems for Mine Drainage– Can They Really Provide Green and Sustainable Solutions? Fahlqvist, Anna Linnéa; Bäckström, Mattias; Sartz, Lotta; Allard, Bert Removal of uranium from a neutral mine water using uncoated and iron oxyhydroxide coated iron tailings	507 513 519 525 533 539 545 545
 A RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T.; Moorhouse, Arabella M. L.; Byrom, A. James; Kershaw, Steven Applications for Hydrous Ferric Oxide mine water treatment sludge: A Review Brown, Adrian Low-cost Long-term Passive Treatment of Metal-Bearing and ARD Water using Iron Rich Material Conroy, Kevin W; Huff, Brian D; Gallagher, Neal T Development of Treatment Solutions for the Central City/Clear Creek Superfund Site in Colorado Conroy, Kevin W; Moderski, Anna M Water Management and Treatment for the Copperwood Mine Project Eger, Paul; Kairies Beatty, Candace Constructed Wetland Treatment Systems for Mine Drainage– Can They Really Provide Green and Sustainable Solutions? Fahlqvist, Anna Linnéa; Bäckström, Mattias; Sartz, Lotta; Allard, Bert Removal of uranium from a neutral mine water using uncoated and iron oxyhydroxide coated iron tailings Florence, Kay; Morgan, Philip 	507 513 519 525 533 539 545 551
4 RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T.; Moorhouse, Arabella M. L.; Byrom, A. James; Kershaw, Steven Applications for Hydrous Ferric Oxide mine water treatment sludge: A Review Brown, Adrian Low-cost Long-term Passive Treatment of Metal-Bearing and ARD Water using Iron Rich Material Conroy, Kevin W; Huff, Brian D; Gallagher, Neal T Development of Treatment Solutions for the Central City/Clear Creek Superfund Site in Colorado Conroy, Kevin W; Moderski, Anna M Water Management and Treatment for the Copperwood Mine Project Eger, Paul; Kairies Beatty, Candace Constructed Wetland Treatment Systems for Mine Drainage– Can They Really Provide Green and Sustainable Solutions? Fahlqvist, Anna Linnéa; Bäckström, Mattias; Sartz, Lotta; Allard, Bert Removal of uranium from a neutral mine water using uncoated and iron oxyhydroxide coated iron tailings Florence, Kay; Morgan, Philip A Novel Electrochemical Process for Aqueous Oxidation of Acid Mine Drainage Using Advanced Power	507 513 519 525 533 539 545 551
4 RELIABLE MINE WATER TREATMENT Adeniyi, Amos; Maree, Jannie; Mbaya, Richard; Popoola, Patricia HybridICE™ filter design in freeze desalination of mine water Bäckström, Mattias; Sartz, Lotta Fly ash injection into weathered mine waste Bailey, Matthew T;, Moorhouse, Arabella M. L; Byrom, A. James; Kershaw, Steven Applications for Hydrous Ferric Oxide mine water treatment sludge: A Review Brown, Adrian Low-cost Long-term Passive Treatment of Metal-Bearing and ARD Water using Iron Rich Material Conroy, Kevin W; Huff, Brian D; Gallagher, Neal T Development of Treatment Solutions for the Central City/Clear Creek Superfund Site in Colorado Conroy, Kevin W; Moderski, Anna M Water Management and Treatment for the Copperwood Mine Project Eger, Paul; Kairies Beatty, Candace Constructed Wetland Treatment Systems for Mine Drainage– Can They Really Provide Green and Sustainable Solutions? Fahlqvist, Anna Linnéa; Bäckström, Mattias; Sartz, Lotta; Allard, Bert Removal of uranium from a neutral mine water using uncoated and iron oxyhydroxide coated iron tailings Florence, Kay; Morgan, Philip A Novel Electrochemical Process for Aqueous Oxidation of Acid Mine Drainage Using Advanced Power Electronics and Real time Control	507 513 519 525 533 539 545 551 557

Fornarelli, Roberta; Mullett, Mark; Ralph, David	
Factors influencing nanofiltration of acid mine drainage	563
Govender-Ragubeer, Yageshni; Gericke, Mariekie	
Chromium (VI) removal from effluents using zeolite	569
Gusek, James Joseph	
A Periodic Table of Passive Treatment for Mining Influenced Water - Revisited	575
Gusek, James Joseph; Buchanan Jr., Ronald J.; Sorells, Duff	
Infiltration-Diverting Cap and Full-Scale Biochemical Reactor Operation at the Iron King/Copper	
Chief Mine, Arizona	581
Hamai, Takaya; Ikeda, Manami; Furuya, Hisatoshi	
Research on applicability of anaerobic passive bioreactor to acid mine drainage treatment in Japan	587
Harrison, Anna Lee; Power, Ian Malcolm; Dipple, Gregory M	
Strategies for enhancing carbon sequestration in Mg-rich mine tailings	593
Hedin, Robert S	
Temperature Independent Removal of Iron in a Passive Mine Water System	599
Hedin, Robert S; Hedin, Benjamin C	
Carbon Sequestration Through Oceanic Fe Fertilization: Opportunity for Mine Water?	605
Jeschke, Christina; Knöller, Kay; Simon, André; Gast, Martin; Hoth, Nils	
Assessment of glycerol-enhanced bacterial sulfate degradation in lignite mining sediments by	
stable isotope investigations	611
Kamika, Ilunga; Momba, Maggy	
Bioremediation of V5+ and Ni2+ by indigenous Marinobacter Goseongensis isolated from	
South African Vanadium Mine Waste	613
Kamika, Ilunga; Momba, Maggy	-
Effect of nickel to nutrient removal by selected indigenous protozoan species in wastewater systems	619
Karlsson, Stefan; Sjöberg, Viktor; Grandin, Anna; Allard, Bert	2
Leaching pattern of metals from historic sulphidic mine waste upon addition of bark compost	625
Kinser, Karla; Sansom, Stephanie; Oliver, Douglas S.	5
A Global Perspective on Boron Removal: Treatment Technologies and Practical Applications	633
Kruse Daniels, Natalie Alyssa; Bowman, Jennifer R; Mackey, Amy L; Lopez, Dina	55
A comparative study of lime doser treatment	639
Kruse Daniels, Natalie Alyssa; Johnson, Kelly S; Bowman, Jennifer R	
Habitat and watershed characteristics that limit stream recovery after acid mine drainage treatment	643
Lillev. Tim	15
Optimising mine pit dewatering treatment techniques to meet production deadlines	649
Malisa, Rejoice; Maree, Johannes P; Hardwick, Ed; Oosthuizen, Frederick	15
Resin Freeze Desalination Process for Acid Recovery	655
Moore, Lucas Ryan; Durand, Jean Robert; Strickland, Forrest	
Metals Removal from Mine Effluents – Understanding the Chelant is Key	661
Moorhouse, Arabella M. L.; Wyatt, Lee M.; Watson, Ian A.; Hill, Steve	
A high surface area media treatment trial of a circum-neutral, net alkaline coal mine	
discharge in the South Derbyshire Coal Field (UK) using hydrous ferric oxide	667
Nairn. Robert W.	
Carbon dioxide impacts both passive treatment system effectiveness and carbon footprint	673
Nairn, Robert W.	
Successful Passive Treatment of Iron-Rich Lead-Zinc Mine Waters and an Effective Method to	
Address Nuisance Constituents	679
	, , ,

Nason, Peter	
Advances in using sewage sludge to remediate sulfidic mine tailings - An overview from pilot- and	
field-scale experiments, northern Sweden	681
Paños, Nora Hilda; Gutierrez, Luis Ventura; Senese, Ana Alicia	
Influence of temperature in sulphate-reducing anaerobic bacteria (SRB) development and metal	
removal efficiency	687
Peer, Rebecca A. M.; Strosnider, William H. J.; Winfrey, Brandon K.; Nairn, Robert W.	
Passive Co-Treatment of Acid Mine Drainage and Municipal Wastewater: Removal of Less	
Commonly Addressed Metals at Cerro Rico de Potosí, Bolivia	691
Pinto da Costa, João; Girão, Ana; Lourenço, João; Monteiro, Olinda; Trindade, Tito; Costa, Maria Clara	
Integrated synthesis of nanosized semiconductors in a bioremediation system for the treatment	
of AMD using biologically produced sulfide	693
Pluta, Irena	
Removing barium from saline waters in coal mines of the Upper Silesia (Poland)	699
Ramos, Renato Giani; Cunha, Osmar; Rodrigues, Fabio; Scassiotti, Walter; Ribeiro, Mauricio; Aerts, Peter;	
Stephen, Smith	
Remediation of Environmental Impact of Acidic Dam of Mines Through Membrane Process	705
Rutkowski, Tom; Hanson, Rachel; Conroy, Kevin	
Mine water treatment options for meeting stringent selenium regulatory limits	711
Rutkowski, Tom; Rhodes, Melissa; Smith, Jessa; Conroy, Kevin; Bratty, Mike	
Treatment of high total dissolved solids and acidity in Cerro de Pasco mining wastewater, Peru	717
Sanders, Laura; Moore, Lucas R.; Durand, Jean Robert	
Selenium Removal from Effluents in Industrial Mineral Processes	723
Smith, Kathleen S.; Figueroa, Linda A.; Plumlee, Geoffrey S.	
Can treatment and disposal costs be reduced through metal recovery?	729
Stewart, David	
Water Filtration Innovation to Optimize Recovery and Costs	735
Strzodka, Michael; Preuss, Volker; Thürmer, Konrad	
Underwater Nozzle Pipelines (UNP) – A new Process for in-lake Liming	741
Walters, Evan Robert; Behum, Paul T.; Lefticariu, Liliana	
Sulfate Reducing Bioreactor Dependence on Organic Substrates for Long-Term Remediation of	
Acid Mine Drainage: Field Experiments	747
Wyatt, Lee M.; Moorhouse, Arabella M. L.; Watson, Ian A.	
Full scale pilot test of a novel technology to remediate alkaline coal mine water using high-surface	
media at Acomb Mine Water Treatment Scheme, UK	749
Zinchenko, Dmitriy; Schauer, Patrick Jordan; Migchelbrink, Joel; Liang, H. C.; Tamburini, Joe R.; Nketia, Michael;	
Rolston, Nathan; Hatley, James; Lau, Tony; Willis, Jeremy	
Evaluation of High-Rate Clarification for Water Treatment at a Uranium Mine – A Case Study	755

I

Volume II 👁 Themes 5 – 8

5 RELIABLE MINE WATER OPERATIONS

Broschek, Ulrike; Lobos, Jorge; Cornejo, Jorge; Bravo, Luis; Lagos, Josué; Volker, Karien	
DROP Project: Leaching process optimization for reducing water consumption in copper mining	807
Chahbandour, John	
Reliable Mine Water Management; Connecting the Drops to Operate "Water Smart" Mines	813
Clements, Nathan; Noske, Craig	
Dugald River Tailings Storage Facility and Process Water Dam – Robust Options Analyses	819
de Wet, Louis Daniel; Sidu, Sibusiso	
Water Quality and Compliance Monitoring of Treated Underground and Surface Water at the Grootvlei	
Proprietary Mines and the Blesbokspruit Wetland, Springs, South Africa	825
Dong, Shuning; Wang, Hao; Liu, Zaibin; Shi, Xianxin	
Practical Technologies and Equipment for Preventing and Controlling Coal Mine Water Hazards in China	831
Fernández Rubio, Rafael; Lazarim, Helio Alexandre; Fernández Lorca, David; Ribeiro, Vinícius Viera	
Surface water control in the bauxite mines of Porto Trombetas (Pará, Brazil)	837
Fosso-Kankeu, Elvis; Mulaba-Bafubiandi, Antoine Floribert; Barnard, Tobias; Campana, Patricia	
Indirect implication of bacterial proteins in the biouptake of metals from aqueous solution	843
Hudson, Amy L.; Meyer, Troy	
Consideration of Thermal Conditions in Year Round Heap Leach Operation in the Northern Desert Climates	849
Kasedde, Hillary; Bäbler, Matthäus; Kirabira, John Baptist; Tilliander, Anders; Jonsson, Stefan	
Mineral recovery from Lake Katwe brines using isothermal evaporation	855
Klaus, Reinhard	
Glass Bead Filter Packs in Water Wells for Higher Efficiency and Reduced O $\mathfrak S$ M costs	861
Lotfiazad, Farshad; de Bary, Alejandro	
Assessing Water Availability for Life of Mine Operation Using Probabilistic Water Balance Model	867
Lupo, John Foriyes	
Considerations for Mine Water Management in Operations	873
Novhe, Ntshengedzeni Obed; Ogola, Jason Samuel; Maree, Jannie	
Characterization of potential acid leachate from raw coal, discard coal, and slimesfrom a Colliery	
in the Witbank Coalfield, Mpumalanga Province, South Africa	875
Pan, Guoying; Lin, Yun; Wu, Yazun	
The hydrogeological exploration and test technology to precisely determine the location of groundwater	
recharge channel in mining area	881
Steyl, Gideon; van Tonder, Gerrit; Chironga, Lordrif	
Dewatering strategy for a copper mine in the Democratic Republic of Congo	887
Sun, Yajun; Sui, Wanghua; Dong, Guiming; Liu, Shucai; Yu, Jincun	
Evaluation and Depressurization of an Ordvician limestone confined aquifer in Xingcun coal mine	893
Wallace, Michael Gary; Johnson, Kathryn Olive; Osnes, John Dorwin; Krantz, Eric Lee; Hocking, Crystal Marie	
Hydrogeological and Geochemical Evaluations in Support of Mine Water Management for the	
Jurong Rock Cavern Project, Singapore	899
Weidner, Christoph; Henkel, Sebastian; Schüttrumpf, Holger; Rüde, Thomas R.; Klauder, Wiebke	
Assessing the Applicability of Quaternary Sediments as Gravel Pack Material for Dewatering Wells	905

"Reliable Mine Water Technology"

\ A /	Vazu	n Lin Yun Dan Cupying	
vvu	, razu	n; Lin, Yun; Yan, Guoying	011
	Disc	miniation of bursting water source by hydrochemical and stable isotope method	911
I	6	Reliable Mine Water Closure	
Ben	thaus	s, FriedrCarl; Lucke, Beate	
	Innc	ovative Mine Water Treatments in Post-Mining-Areas of Germany	919
Bru	eckne	r, Friedemann; Ceranski, Helena; Mansel, Holger; Uhlig, Christiane	
	Imp	acts of Re-Rising Groundwater Levels in Rehabilitated Opencast Mining Areas,	
	Pred	liction Tools and Potential Measures of Damage Limitation	925
Cid	u, Ros	a; Biddau, Riccardo; Dore, Elisabetta; Vacca, Andrea	
	Anti	mony and arsenic uptake by vegetation growing at abandoned mines	931
Coe	tzee,	Henk	
	Floo	ding of the underground mine workings of the Witwatersrand Gold Fields	937
Coe	tzee,	Henk	
	Rapi	d field based analytical techniques for the environmental screening of abandoned mine sites	943
Cra	votta,	Charles; Geroni, Jennifer	
	Effeo	rts of CO2 Degassing on pH and Fe(II) Oxidation Rates in Coal Mine Effluents	949
Dav	vis, An	dy; Lengke, Maggy	
	New	Insights on Factors Controlling Pit Lake Chemistry	955
Der	nnis, S	tefanus Rainier; Dennis, Ingrid; Johnstone, Andrew	
	Min	e flooding prognosis making use of EPANET	961
Div	ine, C	raig; Griffin, Adam; Christoffersen, Lee; Preston, Kelli; DeDycker, Phil	
	Trac	er Testing to Evaluate Tailing Pile Hydrogeologic Characteristics to Support Closure and Reclamation	967
Dur	en, Sa	abre Miel; McKnight, Diane Marie	
	Wetl	and Photochemistry as a Major Control on the Transport of Metals in an Acid Mine Drainage	
	Imp	acted Watershed	973
Firp	o Vas	quez, Beatriz Alicia; Schneider, Ivo André Homrich; Trein, Camila Maria	
	Fabr	icated Soil Using Coal Mine Waste	977
Fra	u, Frai	nco; Podda, Francesca; Da Pelo, Stefania; Ardau, Carla	
	Arse	nic contamination in the Baccu Locci mine watershed (Sardinia, Italy) after remediation	983
Frip	piat,	Christophe; Veschkens, Mathieu; Pacyna, Daniel	
	Mon	itoring the shallow subsurface for gas emission from abandoned underground mines	989
Frip	piat,	Christophe; Veschkens, Mathieu; Pacyna, Daniel; Funcken, Luc	
	Non	-conclusive time series analyses – what can we learn on the behavior of the groundwater system?	
	Und	erstanding what caused the collapse of an abandoned drainage tunnel	995
Joh	nston	e, Andrew Clifford; Dennis, Ingrid; McGeorge, Norman	
	Grou	andwater Stratification and Impact on Coal Mine Closure	1003
Kirk	, Alla	n R; Bogert, Henry; Marks, Mary Beth; Curiel, Eli	
	Sten	nming Flow using Hydraulic Adit Plug Closure, a Comparison: Glengarry Mine,	
	New	World District, Montana and World's Fair Mine, Patagonia, Arizona	1009
Kirk	, Lisa	Bithell; Bozeman, Lauren R.; Kirk, Allan R.; Marks, Mary Beth	
	Geo	chemistry of Improved Groundwater Quality Resulting from Adit Plugging, Glengarry Mine,	
	New	World District, Cooke City MT USA	1011
Kül	s, Chi	istoph; Bittner, Arnold	
	Pass	ive barriers for long-term containment of Uranium and Vanadium	1017

Landkamer, Lee L.; Lee, Ilsu; Drennan, Dina; Sharp, Jonathan O.; Figueroa, Linda A.	
Substrate and biogeochemical design considerations for sulfate reducing bioreactors	1023
Lund, Mark Andrew; Van Etten, Eddie J.B.; McCullough, Clint D	
Importance of catchment vegetation and design to long-term rehabilitation of acidic pit lakes	1029
MacSween, Jessica Pearl; Raman, Chandra; Kaliaperumal, Raj; Oaks, Ken; Mkandawire, Martin	
Modeling potential impact of geothermal energy extraction from the 1B Hydraulic System of the	
Sydney Coalfield, Nova Scotia, Canada	1035
McGivern, Amber L.; Gammons, Christopher H.; Duaime, Terence E.	
Aqueous geochemistry of the "other" pit lake in Butte, Montana, USA	1041
Metschies, Thomas; Laubrich, Jan; Müller, Jürgen; Paul, Michael; Barnekow, Ulf	-
Management of water collection and treatment in the remediation of an uranium mill tailings site	1047
Müller, Mike	
Modeling Pit Lake Water Quality – How Do We Solve Multi-Disciplinary Problems?	1055
Musiolik, Aleksandra; Pluta, Irena	
Some problems concerning determination of barium in mine waters of the Upper Silesia (Poland)	1061
Novhe, Ntshengedzeni Obed; Netshitungulwana, Robert; Yibas, Bisrat; Motlakeng, Tshepo; Sakala, Emmanuel	
Metal pollution sources and transport in mined watershed: an insight from Ermelo Coalfield, South Africa	1067
O'Hayre, Arthur; Kos, Paul; Morr, Dennis	
Reclamation of a Pit Lake at a Coal Mine in the Pacific Northwest	1073
Paul, Michael; Meyer, Jürgen; Jenk, Ulf; Baacke, Delf; Schramm, Andrea; Metschies, Thomas	
Mine Flooding and Water Management at uranium underground mines two decades	
after decommissioning	1081
Perzoff, Tania; Banning, Jessica; Kingston, Scott; Hoos, Rick	
The challenges of re-opening historical Canadian mine sites with respect to water quality	1089
Piatak, Nadine M.; Woodruff, Laurel G.; Seal, Robert R.; Jones, Perry M.	
Baseline geochemical characterization of trace elements in stream sediments in mineralized	
watersheds of the Duluth Complex, northeastern Minnesota	1095
Rapantova, Nada; Licbinska, Monika; Grmela, Arnost; Lusk, Karel	
Mine Water Quality at Abandoned Uranium Mining Sites in the Czech Republic	1097
Richers, Dave; Richardson, Charles Doc; Hudson, Amy	
A Rational Approach to Pit Lake Chemistry Modeling	1105
Rowe, Jerry	
Innovative Systems for Mine Closure at the Haile Gold Mine	1111
Seal, Robert R.; Jones, Perry M.; Piatak, Nadine M.; Woodruff, Laurel G.	
Implications of high dissolved organic carbon concentrations on potential copper toxicity in surface	
waters in the vicinity of Cu-Ni-PGM deposits of the Duluth Complex, northeastern Minnesota	1117
Sjöberg, Viktor; Karlsson, Stefan; Grandin, Anna; Allard, Bert	
Vegetation of historical mine waste from the Ljusnarsberg deposit with Agrostis capillaris –	
Impact on leaching of copper	1119
Spurlin, Matthew S.; Rogoff, Eric; Cichy, Dan M.; Divine, Craig E.	
Enhanced 3-D Visualization as a Powerful Data Analysis and Stakeholder Communication Tool	
During Mine Closure	1125
St. Louis, Robert Michael	
Assessment of Legacy Contaminant Remediation at the Phoenix Mine, Nevada	1131
Stochel, Bernadetta; Czop, Mariusz; Krzywański, Zenon; Worsa-Kozak, Magdalena	
Hydrogeochemistry of the Mine Water from "Rudna" mine (Lubin Region, South Poland)	1139

Strosnider, William H. J.; Llanos Lopez, Freddy S.; LaBar, Julie A.; Palmer, Kelsea J.; Peer, Rebecca A. M.;	
Nairn, Robert W.	
Cerro Rico de Potosí, Bolivia: Broader Impacts from Unabated Acid Mine Drainage	1143
Tshivhase, Victor Makondelele; Mathuthu, Manny	
Radiological effect of mine dumps on surrounding water resources	1145
Vermeulen, Danie; Wessels, Lize; Lukas, Eelco	
Development of a 3-D electrical conductivity image for a colliery in South Africa to determine post-closure	
management options	1151
Walton-Day, Katherine; Mill, Taylor J; Adolph, Amundson; Dee, Kato T; Relego, Melissa R; Borbely, Caitlin	
The Water-Quality Effects of a Bulkhead Installed in the Dinero Mine Tunnel, near Leadville, Colorado	1157
Wolkersdorfer, Christian; Kahl, Sandra; Komischke, Holger; Hasche-Berger, Andrea	
Hydrodynamics in a flooded underground limestone mine	1165
Wyatt, Lee M.; Moorhouse, Arabella M. L.; Watson, Ian A.; Kershaw, Steven	
Methodology for assessing water pollution and risks associated with abandoned lead-zinc mining at	
Wanlockhead and Leadhills, southwest Scotland, UK	1173
Yibas, Bisrat; Netshitungulwana, Robert; Novhe, Obed; Mengistu, Haile; Sakala, Emmanuel; Thomas, Abraham;	
Nyabeze, Peter K	
A holistic approach towards best management practices of mine pollution impacts using a	
catchment area strategy, South Africa	1179
7 RELIABLE MINED HYDROCARBON WATER	
Bern, Carleton R; Engle, Mark A; Boehlke, Adam R; Zupancic, John W	
Low Salinity Hydrocarbon Water Disposal Through Deep Subsurface Drip Irrigation:	
Leaching of Native Selenium	1187
Bouzalakos, Steve; Timms, Wendy; Rahman, Priom; McGeeney, Dayna; Wheelan, Mark	
Geotechnical centrifuge permeameter for characterizing the hydraulic integrity of partially	
saturated confining strata for CSG operations	1193
Cath, Tzahi; Geza, Mengistu; Drewes, Jörg; Xu, Pei	
Decision support tool for management of produced and frac-flowback water	1199
Defossez, Anne-Julie; Londe, Louis; Cabon, François; Roux, Pierre	
Hydrogeological Aspects during Closure of an Underground LPG Storage	1205
Lachmar, Thomas; Randall, Kevin	
Suitability of Central Utah's Navajo Sandstone for Disposal of Mined Hydrocarbon Water	1211
Nowak, Neil; Briest, John	
High Density Polyethylene (HDPE) Lined Produced/Flow-back Water Evaporation Ponds	1217
O'Neil, Diane Elizabeth	
Addressing Legal, Regulatory, and Risk-Allocation Challenges for Water Reuse in Hydraulic Fracturing	1223
Veil, John	
Water Associated with Oil and Gas Production – Produced Water Management and Water Needs	1229

8 FIELD TRIPS

Joh	nson, Raymond H.	
	IMWA 2013 Mid-Conference Tour to Leadville, Colorado: August 7 th , 2013	1237
Johnson, Raymond H.		
	Mines, Mountains, and Hot Springs: IMWA 2013 Post-Conference Tour to Silverton, Colorado:	
	August 10–13, 2013	1241
I	LAGNIAPPE	
	Author Index	763

Keyword Index	770
IMWA Membership Application Form (English version)	779
IMWA Membership Application Form (Chinese version)	1265

RELIABLE MINE WATER PERMITS AND REGULATION REGULATION



Improved Regulation of Water Supply for the Olympic Dam Mine, South Australia

Gabor Bekesi¹, Murray Tyler², Darren Niejalke², John Waterhouse³

¹Australian Water Environments, 1/198 Greenhill Rd, Eastwood, 5006 South Australia, Australia, gaborbekesi@austwaterenv.com.au

²BHP Billiton, 55 Grenfell Street, Adelaide, 5000 South Australia, Australia, murray.tyler@bhpbilliton.com ³Golder Associates, 1 Havelock Street, West Perth, Western Australia 6005, Australia, jwaterhouse@golder.com.au

Abstract Groundwater use from the water supply wellfield in the Great Artesian Basin (GAB) is regulated according to its effect on aquifer pressure, not according to the volume of groundwater taken. Originally a maximum of 5 m pressure drawdown was set at five sites, each approximately 50–60 km from the wellfield. There was initially an unacceptably large uncertainty in drawdown estimation because 'noises' (the effects of antecedent pastoral use and temperature on measured wellhead pressures) were recognised as comparable in magnitude to the 5 m limit. A modified regulatory structure was developed, based on a whole of wellfield approach.

Keywords Artesian pressure, drawdown, Great Artesian Basin, Australia

Introduction

Wellfield B supplies an average of 30 ML/d of groundwater from the Great Artesian Basin (GAB) to the Olympic Dam mine and the town of Roxby Downs (Fig. 1) in South Australia (SA). Water use from Wellfield B was regulated by a drawdown criterion (a maximum of 5 m as pressure drawdown) set at five sites ("assessment sites") to preserve flows at GAB springs and pressure at pastoral wells. This regulation approach had been in place since 1996. Through analysis of extensive monitoring data collected since 1996, it has become apparent that antecedent pastoral flows and temperature had a larger influence on the measured pressures than originally anticipated (Bekesi *et al.* 2012a). As a result of recent investigations to improve pressure and drawdown calculations by incorporating temperature (Bekesi *et al.* 2012b) the true magnitude of errors/uncertainties became apparent. Disregarding temperature/antecedent flows resulted in signifi-



Fig. 1 The Great Artesian Basin of Australia (cross-section from www.gabcc.org.au).





cant errors in drawdown estimation; at one site drawdown was reported as up to 4 m before being corrected to just over 1 m in 2012 (Fig. 2, after Bekesi *et al.* 2012c). Reported drawdown at another assessment site was up to 4.4 m compared with the current estimate of drawdown of 2.3 m.

The high importance of the wellfield for mining and town water supply, and the magnitude of uncertainties being comparable to the maximum drawdown criterion of 5 m, meant that there was an unacceptably large uncertainty in point drawdown estimation. A new and improved regulatory assessment was required. In particular, the risk of an entire wellfield being non-compliant because of a single incorrectly reported drawdown value exceeding 5 m had to be minimised or eliminated.

Unique Hydrogeological Features of the Great Artesian Basin

Habermehl (1980) and Radke *et al.* (2000) provide comprehensive descriptions of the GAB. The GAB is one of the largest basins (\approx 1.7 × 10⁶ km²) in the world. In most places, the GAB is the sole source of reliable freshwater for drinking in an arid environment. The main GAB aquifers comprise of sandstones of Jurassic age and up to 2 km in depth (Fig. 1).

Four unique features of the GAB, important for this paper (high temperatures, low storativity, high wellhead pressures and continuously used pastoral wells) are discussed below.

- Groundwater temperature in the GAB varies between 22 °C in the recharge areas and 100 °C in the discharge areas (Radke *et al.* 2000, Habermehl and Lau 1997; Habermehl and Pestow 2002) and generally increases with increasing depth of burial. Groundwater near Wellfield B (depth ≈ 700 m) has a temperature of 60-80 °C.
- 2. The GAB aquifer consists of highly confined sandstones and siltstones with a horizontal hydraulic conductivity in the order 1–10 m/d with a very low storativity in the order of 10^{-5} . Because of the highly confined nature of the GAB (low storativity) the assessment sites were located some 50–60 km from Wellfield B (Fig. 3) in an attempt to monitor both the effects of drawdown on pastoral supplies and, to the south of Wellfield B, on GAB springs.
- 3. Most wells near Wellfield B have high wellhead pressures, approximately +700 kpa (70 m H_2O) above ground level. To measure pressure, most GAB wells are shut in and surface pressure is measured after a predetermined wait/recovery time (Bekesi *et al.* 2012c).



Fig. 3 Drawdown around Wellfield B in June 2012. Contour interval is 2 m. Shaded region represents drawdown > 10 m with an area of 1930 km². Contours are based on 25 drawdowns calculated as difference between the contemporary wellhead pressure and a reference pressure pre-dating Wellfield B

4. The GAB is situated beneath arid land, and because of the large area of the pastoral properties, long water supply lines, remoteness of the area, and high drilling costs, some of these pastoral wells are used more or less continuously (Bekesi *et al.* 2012c).

The combination of continuously used wells, high pressures and hot water make flow and pressure measurements and the calculation of drawdown more challenging than in cold aquifers. Pressures measured at the well head often decrease during recovery (Bekesi *et al.* 2013) and the influence of density variations at high temperatures may introduce significant errors. Therefore groundwater temperature has to be incorporated into the drawdown calculations (Bekesi *et al.* 2013).

The Calculation of Drawdown

In 2012, the monitoring network around Wellfield B included both dedicated monitoring sites (28) and pastoral wells (26). Some pastoralist were allowed to tap to monitoring bores and, as a result, only about one-third of the bores were unused in 2012. The monitoring of private wells near Wellfield B serves to provide a large monitoring network and to confirm that artesian pressures are preserved in pastoral wells. Drawdown at each measuring point has traditionally been calculated as the difference between the contemporary wellhead pressure and an agreed reference pressure (judged to pre-date any effects of Olympic Dam water supply abstractions). Lately, temperature effects have also been incorporated to improve the estimation of drawdown. Despite these improved calculations, drawdown estimation is still subject to an estimated ±1.5 m uncertainty.

Improved temperature-inclusive drawdowns reported in 2012 at the five assessment sites varied between 0.7 and 3.4 m, still comparable to the estimated ±1.5 m uncertainty, presenting a considerable risk for reporting incorrect compliance or false alarms alike. The regulation measured the performance of the entire wellfield with (arguably) too much emphasis on the assessment sites. It was realised that a better way of assessing the broad impact of groundwater abstractions would be to develop a single measure of drawdown. Whilst drawdowns at some points are important, assessment at a few key points does not give a measure of the effects of the entire wellfield.

Negotiations with the Regulator

The high importance of the wellfield for mining and town water supply, and the pointbased drawdown approach meant that there was an unacceptably large risk associated with



Fig. 4 Reported (June 2012) and predicted 10 m drawdown contours. Drawdowns are calculated as difference between the contemporary wellhead pressure and a reference pressure pre-dating Wellfield B

any of the five individual site conditions. Since 2009, BHP Billiton has initiated several reviews of the hydrogeological aspects of wellfield sustainability, monitoring and modeling. As a result, negotiations with the SA regulator commenced in 2010 to review and improve the drawdown criteria for Wellfield B. Several options, ranging from the elimination of some of the assessment sites, to a single drawdown index (weighted average drawdown)representing the entire wellfield, have been investigated. Since 2011/12 investigations focused on deriving a single graphic representation of the interpreted drawdown.

The Area within the 10 m Drawdown Concept

The concept, eventually agreed, is to regulate by the size of the area within the 10 m drawdown contour. That is, drawdowns at individual sites are reported and contoured annually and the area contained inside the 10 m drawdown contour line (where drawdown \geq 10 m) is calculated (Fig. 3). Drawdown is calculated as described in page 3, on reference pressures that pre-date Wellfield B.

The choice for the contour value was a compromise between large drawdown (suppressing most of the ± 1.5 m errors) and the practicality of constructing a reliable contour line. Fig. 3 indicates that, in 2012, no drawdown was reported > 15 m in observation wells; three reported > 10 m and ten > 8 m. Therefore 10 m was seen as the most sensible value.

A criterion for the area inside the 10 m drawdown contour, *i.e.* 4450 km², was calculated from numerical modeling (Fig. 4). For the explicit protection of springs, mostly situated to the south of Wellfield B, individual drawdown criteria were also set at 4 m in two dedicated monitoring bores (S1 and S2 in Fig. 4).

Using the area footprint approach allows focus on resource sustainability that can be monitored by the area of drawdown footprint, contained within the 10 m drawdown contour of Wellfield B. The drawdown cone around Wellfield B is the measure of the depressurisation of the GAB Aquifer. Sustainability, or the availability of water for both current and future users, including the environment, is directly related to the size and pattern of the current drawdown and future rates of recovery of pressures once the mining activity and groundwater production ceases.

Conclusions

The new regulation relies on a simple, graphical and "whole-of-wellfield" measure and minimizes the risk of using incorrect drawdowns at individual sites. Notwithstanding, further opportunities exist to improve drawdown calculations at individual bores regardless of the way compliance criteria are set.

References

- Bekesi G, Tyler M, Waterhouse J (2012a) Improved Calculation of Groundwater Heads for Environmental Management in the Great Artesian Basin, Australia.
 Proceedings, International Mine Water Association (IMWA) 2012. 30 September 4 October 2012, Bunbury, WA.
- Bekesi G, Tyler M, Waterhouse J (2012b) Conclusions From Using an Active Production Well for Mine Drawdown Compliance. Proceedings, International

Mine Water Association (IMWA) 2012. 30 September – 4 October 2012, Bunbury, WA.

- Bekesi G, Tyler M, Waterhouse J (2012c) Lessons from the Use of an Active Production Well for Compliance Monitoring in the Great Artesian Basin, Australia. Mine Water and the Environment Journal of the International Mine Water Association (IMWA) 31(3):225-232.
- Bekesi G, Tyler M, Waterhouse J (2013) Groundwater Head in High Temperature Aquifers. Quarterly Journal of Engineering Geology and Hydrogeology 46:87–94
- Habermehl MA (1980) The Great Artesian Basin, Australia. BMR J Aust Geol Geop 5:9–38
- Habermehl MA, Lau JE (1997) Hydrogeology of the Great Artesian Basin, Australia. (Map at a scale 1:2,500,000). Australian Geological Survey Organisation, Canberra.
- Habermehl MA, Pestow I (2002) Geothermal Resources of The Great Artesian Basin, Australia. GHC Bulletin, 23(2):20-26.
- Radke BM, Ferguson J, Creswell RG, Ransley TR, Habermehl MA (2000) Hydrochemistry and Implied Hydrodynamics of the Cadna-Owie-Hooray Aquifer, Great Artesian Basin, Australia. Bureau of Rural Sciences, Canberra.

Groundwater Use and Protection as Part of the Namibian Mining Application

Arnold Bittner¹, Markus Zingelmann²

¹SLR Environmental Consulting (Namibia; Pty) Ltd., 8 General Murtala Muhammed Street, Windhoek, Namibia, abittner@slrconsulting.com ²Beak Consultants GmbH, Am St. Niclas Schacht 13, 09599 Freiberg, Germany, markus.zingelmann@beak.de

Abstract Water is a scarce commodity in semi-arid Namibia. Therefore water supply for towns, industry, and mines can often only be ensured through the utilization of groundwater resources. Conflicting interests between farmers and bulk users often cause severe problems. Two emerging mining projects are used as examples on how a timely transparent approach involving all stakeholders at an early stage of mine development and based on thorough scientific but easy to understand investigations, can result in a proper project implementation. This constructive participation during an early stage caused less negative effects during the process of mine development and construction later on.

Keywords groundwater use, groundwater protection, Namibia, flow and transport modeling, mining application, Omitiomire Copper Mine, Otjikoto Gold Mine

Introduction

The mining sector in Namibia has significantly increased during the past ten years. Groundwater quality and quantity impacts of mining projects are affected by a progressive rise of public awareness. This paper presents predictions of potential impacts on groundwater and delivers management plans designed to meet legal requirements and minimize impacts on groundwater associated with mining in a rural area. Special attention has been paid to reasonable applying numerical groundwater flow and transport models prior to the mining start. These models were developed as decision making tools, forecast and planning instruments, to initially describe the groundwater conditions for a Copper- and a Gold mine project that are located in commercial farming areas. Both models aim at synergizing groundwater abstraction for mining purposes with the water demand of local stakeholders.

The proposed Omitiomire copper mine is located approx. 150 km north-east of the Namibian capital Windhoek (Fig. 1). The regional geology dominated by a series of dome structures such as the Ekuja Dome, a structurally controlled 'window' of Irumide-age rocks (Steven et al. 2000) flanked by younger rocks of the Damara Orogen (900 Ma to 450 Ma pan-African rocks). The Ekuja Dome covering an area of approximately 15 by 12 km is economically important as it hosts the Omitiomire chalcocite deposit (Speiser 2010). Rainfall in the area of Omitiomire is extremely variable, but the mean annual precipitation since 2000 is 442 mm/a (cp. Zingelmann 2012). The model domain is characterized by shallow groundwater levels (< 10 m below ground level) in the vicinity of the Black Nossob River and its tributaries and relatively deep regional groundwater levels (on average 35 m below ground level), according to Bittner and Marx (2012). Groundwater recharge causes significant rising water levels during and after occasional floods in ephemeral rivers. The groundwater quality in the project area is generally good and classified to class B according to Namibian drinking water standards (Steven



2010). A proposed mining phase 1 will consist of three small test mine pits with a depth of approximately 50 m. During the mining phase 2 a larger mine pit with a total depth of 340 m will be created.

Another project example, the proposed Otjikoto project, is located 300 km north of Windhoek (Fig. 1). Schist and quartzite of the Damara Sequence in alternating sequences with marble and ortho-amphibolite of the Karibib Formation are dominating local geological conditions. The project area is situated on the eastern margin of the Platveld Basin, which is dipping to the Northern Zone of the northeast trending limb of the Damara Orogen extending from Swakopmund to Grootfontein (Klock 2001). Rainfall distribution follows an irregular pattern with a mean annual average of approximately 475 mm/a (Bittner & Winker 2012). The aquifer systems of the study area are consisting of three major units: 1) marbles of the Karibib Formation, 2) the surrounding and underlying quartz biotite and graphitic schists of the Okonguarri Formation, and 3) the calcrete layer covering the Okonguarri Formation (Klock 2001). Groundwater levels in the project area range between 10 and 50 m below ground level. Most groundwater samples taken within the study area are characterized as predominantly Ca-bicarbonate water types.

Methods

Public meetings were held during the initial phases of the mining application process, following the protocol of the Environmental Impact assessment process. Stakeholders such as surrounding commercial famers, water supply utilities, environmental groups and municipalities were invited to express their concerns and recommendations. This public participation process together with groundwater specialist investigations and in consideration of mining interests were taken as basis to develop numerical groundwater flow simulations and subsequent groundwater abstraction and mine pit dewatering scenarios (Fig. 2). The stakeholders were involved in the development of a groundwater monitoring network, and were informed on a regular basis on the outcome of the studies. For both projects, mitigation measures were implemented according to the recommendations derived from model based risk assessments.

Numerical groundwater flow and transport models were utilized to calculate water


Fig. 2 Work flow and progress of groundwater issues for a transparent mining application as part of an Environmental Impact Assessment process.

volumes, determine flow paths, and estimating groundwater characteristics. Both projects are located within fractured basement rocks with major linear structures such as faults and ephemeral rivers, but different hydrogeological units. To thoroughly consider this environment and to acceptably display the permeable and groundwater relevant layers, a finite element modeling approach using FEFLOW has been selected for both projects. Both flow models were calibrated as a steady-state solution and were expanded to transient models later.

For the Omitiomire project in a first step a conceptual model has been developed to describe the baseline conditions and create a basis for the numerical flow solution. Manifold data, such as monitoring results, existing hydrogeological reports (Simmons 2008), and aquifer testing data (Bittner 2007), were integrated into a project database. Efficiently realized calibration of the transient flow solution produced a variety of different flow scenarios. Each scenario is computing a 10-year transient flow solution (Table 1), simulating: 1) a conservative dry period with 25 % less rainfall, 2) a conservative wet period with 25 % of additional rainfall, 3) a wet period with 50 % of additional rainfall, and 4) a period with no rainfall. Table 1 shows fluxes of the entire model domain.

Recharge (indirect and direct) has been simulated as 0 to 5.5 % of the calculated rainfall, depending on hydrogeological units (Zingelmann 2012). Due to the fact that rainfall and subsequent recharge in Namibia is extremely variable but sometimes zero, a conservative approach simulating a period of no rainfall has been chosen. Predictions were given on how much groundwater could be assumed as maximum inflow into the mine pit. Simulated water levels show rising tendencies in scenarios 2 and 3, on average by 3.5 m and 12.0 m, respectively. Scenario 1 and 4 are showing dropping water levels during the 10-year period.

Shallow water levels can be observed shortly after recharge/runoff events in the ephemeral Black Nossob River and in underlying basement aquifers. It is evident that the porous alluvial aquifer acts as leakage or recharge channel (Bittner & Marx 2012). The radius of influence from the river channel is variable and depends on the local geology but is usually not larger than 1,000 m (Fig. 3). Recharge in the vicinity of the Black Nossob River changes the local groundwater flow pattern, especially after flood events as can be seen in Fig. 3. Intensely fissured zones, fractures and faults influence the general groundwater flow conspicuously. To avoid over ab-

No.	Scenario	Flux out [m ³ /a]	Flux in [m ³ /a]	Recharge [m ³ /a]	Mine pit dewatering [m³/a]	т
1	25% less	49,498,450	48,385,321	1,234,928	146,540	to
2	25% more	84,914,777	77,917,645	7,345,260	214,983	ic
3	50% more	103,273,637	94,436,734	9,849,383	285,927	10
4	no rainfall	41,948,390	41,827,285	0	109,262	

Table 1 Groundwater fluxes of scenarios 1, 2, 3, and 4 for the Omitiomire project.





straction and to keep impacts on groundwater levels as low as possible, it is recommended to utilize mainly groundwater from mine pit dewatering for production, unlike originally planned. The water demand for the Omitiomire project is estimated at 4 L/s or approximately 0.13 GL/a at the beginning. In summary, it was recommended to use mainly groundwater from the open cast pit and to avoid abstraction from water supply boreholes located in the vicinity of neighboring farms. In other modeling scenarios the best locations of potential dewatering wells were determined, in order to avoid negative groundwater drawdown effects. The generally low permeability of the local basement rocks and subsequently confined drawdown around the mine pit and water abstraction wells further reduces possible negative impacts on nearby groundwater users.

The Otjikoto project lies amidst commercial farmland, where substantial volumes of groundwater are abstracted to allow for cattle breeding and irrigation (Fig. 4). The water demand of the gold mine with an estimated 10 years life of mine was calculated at approximately 38 L/s or 1.2 GL/a. Subsequent groundwater model abstractions scenarios took this in consideration. Like for the Omitiomire Copper Mine project a combined mine pit dewatering and water supply well abstraction strategy was recommended as most efficient.

After a consultation process as part of the Environmental Impact Assessment and in cooperation with the main Namibian bulk water utility and other stakeholders, a mine water management plan has been developed to carefully ensure construction and production during the first years. The marble aquifer (Fig. 4) is one of the most efficient and productive but also vulnerable aquifers in the region and numerical modeling results showed that increasing the abstraction volume by 1.2 GL/a is acceptable for the medium term (Bittner & Winker 2012). To keep impacts on local freshwater sources as low as possible, a phased abstraction strategy was recommended changing from initially 100 % supply from water wells in the first years of mine development to recycled groundwater from mine pit dewatering after mine pit excavation progresses below the water table. One of the most important issues of the future numerical groundwater solution for the Otjikoto Gold Mine project shall



Fig. 4 Otjikoto aquifer scheme with proposed mine pit.

be the prediction of groundwater quality impacts. The mass transport model solutions and scenarios will consider potential seepage from mine infrastructure such as the tailings storage facility in order to avoid negative impacts on precious groundwater resources.

Conclusions

Groundwater dependent mining projects, like the Omitiomire copper and the Otjikoto gold projects, often cause conflicting interests between stakeholders. This can result in a considerable delay of the project implementation. It has been shown that a transparent hydrogeological management plan involving all parties prior to the start of the projects can reduce these effects. Furthermore, groundwater modeling and reasonable designed modeling scenarios can show whether the demand of freshwater/groundwater can be satisfied without over-abstracting local aquifers. Important modeling results shall be made available to the public as the public shall be involved continuously during the whole process of the mining application. It has been shown that private users in the vicinity of the proposed projects could benefit from groundwater investigations and were able to enhance their water supply system. All in all, less negative effects during the construction phase could be observed. Some original mine plans had to be adopted or modified, but did not cause a delay in the project implementation.

For the Omitiomire copper project, which is located in a farming area relying on groundwater supply, it has been shown that groundwater abstraction for the mine and pit dewatering would not have negative impact on surrounding farm boreholes. The mine should abstract only small volumes from boreholes tapping the local aquifer but should rather make use of recycled groundwater from mine pit dewatering.

The Otjikoto gold project plans to make use of groundwater from a nearby marble aquifer which is already utilized by the main Namibian bulk water supply utility and which is the only source of fresh water for the town of Otjiwarongo and local farmers. The groundwater investigations, including numerical models, showed that mine pit dewatering and sustainable abstraction of groundwater from production wells tapping the marble aquifer would not have negative impact on the water supply to the town and the farming community. A transparent approach and early stage involvement of stakeholders and the public, combined with thorough scientific but easy to understand groundwater investigations and models can help to implement groundwater dependent mining projects within a reasonable time frame, as well.

Acknowledgement

The authors thank Marco Roscher from Beak Consultants GmbH for critical comments. Furthermore, we thank Andreas Hamperl for the efficient quality assurance.

References

- Bittner A (2007) Hydrogeological Situation in the Omitiomire Copper Mine EPL near Steinhausen. Hydrogeological Report. Prepared for Craton Mining & Exploration (Pty) Ltd, Windhoek.
- Bittner A, Winker F (2012) Numerical Groundwater Flow Model, Otjikoto Gold Mine – Conceptual Model and Numerical Flow Model. Hydrogeological Report. SLR Environmental Consulting (Namibia; Pty) Ltd.
- Bittner A, Marx V (2012) Omitiomire Surface Water Study. Hydrological Report. Prepared for Craton Mining & Exploration (Pty) Ltd, Windhoek.
- Klock H (2001) Hydrogeology of the Kalahari in northeastern Namibia with special emphasis on groundwater recharge, flow modeling and hydrochemistry.

PhD-thesis, Julius-Maximilians-University of Würzburg.

- Simmons A (2008) Preliminary Groundwater Investigations for the Steinhausen Project. Hydrogeological Report. Namib Hydrosearch CC. Prepared for Craton Mining & Exploration (Pty) Ltd, Windhoek.
- Speiser A (2010) Scoping Report Social and Environmental Impact Assessment of the Proposed Copper Mine on Farm Groot Omitiomire. A. Speiser Environmental Consultants CC. Prepared for Craton Mining & Exploration (Pty) Ltd, Windhoek.
- Steven N, Armstrong RT, Smalley T, Moore TJ (2000) First Geological Description of a Late Proterozoic (Kibaran) Metabasaltic Andesite-hosted Chalcocite Deposit at Omitiomire, Namibia. In: Geology and Ore Deposits. The Great Basin and Beyond Proceedings. Vol. 2.
- Steven N (2010) Report on Nine Groundwater Samples from the Omitiomire Copper Mine Project Area, Namibia. Hydrogeological Report. Rockwater Consulting. Prepared for Craton Mining & Exploration (Pty) Ltd, Windhoek.
- Zingelmann M (2012) Numerical Groundwater Flow Model of the Proposed Omitiomire Copper Mine, Namibia – Mining Phase 1. Groundwater Specialist Input Report. Beak Consultants GmbH. Prepared for Craton Mining & Exploration (Pty) Ltd, Windhoek.

Mine Closure Regulations – Case Scenario in Northern Quebec

Aurora M. Hernandez

Grand Council of the Crees-Cree Regional Authoriy (GCC-CRA) 277 Duke Street, Suite 102; Montreal, Quebec, H3C 2M2, amhernandez@gcc.ca

Abstract Mine closure regulations have few provisions dealing with long-term monitoring or catastrophic events. Indigenous groups are usually left out in the process of restoration after the disaster. The northern Quebec dam failure causing tailings spill into the water stream is an illustration. Monitoring results compiled by the Cree first nation showed water and sediment quality impacted by elements not covered by government regulations. Tailings traces found up to 80 km downstream. Fish and fish habitat potentially impacted. To have sustainable development procedures for mine closure regulations, a review of long-term monitoring, catastrophic events responses and public engagement is required.

Keywords public participation, regulations, post-closure monitoring, catastrophic events, Northern Quebec

Introduction

In Canada, the provincial governments are responsible for the construction, management, reclamation and closure of mine sites. Federal involvement is specific in nature, limited to the list of acts for which the Quebec Ministry of Natural Resources (MNR) is responsible. Regarding mine restoration, the province of Quebec had a major reform in the mining act in 1995 which resulted in among other things obligating proponents to submit a restoration plan for approval before starting-up mining activities and the new act also requires proponents to deposit a financial guarantee for the restoration plan. The MNR is responsible for approving the restoration plans presented by the proponent. A guideline to prepare the mining rehabilitation plan was produced by MNR (Quebec 1997) in which general international components are included (Garcia 2008). For mines in operation and closure the evaluation of the environmental quality is restricted by directive 019 (Quebec 2012). Nevertheless, guidelines and legal frameworks for rehabilitation of abandoned sites as well as reclaimed sites do not include any participation of communities even if they are often directly impacted by the effects of mining activities. Furthermore, the legal framework is not clear for abandoned or reclaimed sites long-term monitoring policies such as inspection of the site, reporting, emergency responses procedures.

In 2003 the National Orphaned/Abandoned Mine initiative (NOAMI) produced a guideline pamphlet for community involvement in planning for rehabilitating abandoned and orphaned mines in Canada which could be used as a basis to develop a policy for citizen engagement plans and strategies for rehabilitation of such problematic sites, in order to provide equal opportunity for locals to contribute and participate in the decisions and processes that affect them. But in practice, the implementation of these guidelines for reclaimed sites or abandoned sites which need long term monitoring are almost inexistent.

The former Opemiska mine spill is the case scenario for this setting, located in the James Bay municipality, in operation from 1954 until 1991. The closure and rehabilitation phase finished in 2002 after government approval of restoration works, declaring its long term stability. Surprisingly, in 2008 the dyke of the tailing pond holding approximately 21 Mt

of tailings (Garon *et al.* 1992) broke. The mud carried down a section of route 113, the only municipal road in the area, it covered the nearby Slam Creek with tailings and traveled down the water network to the nearby Obatogamau River. Tailings where seen at the Cree First Nation of Waswanipi community, approximately 80 km downstream. MRN inspections on reclaimed and abandoned sites are planned to occur every two years but no inspection reports previous to the incident where shown after the dyke failure.

Methods

The Cree First Nation of Waswanipi is one of the ten Cree communities in James Bay municipality of Northern Quebec. The James Bay and Northern Quebec Agreement (JBNQA) is a treaty and the Cree rights in the agreement are protected by the Constitution of Canada. Under this agreement, administrative entities such as the Cree Regional Authority (CRA) where created in order to implement the dispositions therein. The Agreement establishes a system of three categories for the land, each having some preferential rights for traditional activities and other Cree rights. Fig. 1 shows the map of the traditional territory, the communities, the applicable agreement region and the different category lands.

Among other things an environmental and social protection regime to protect traditional activities for present and future generations was also established along with guar-



Wolkersdorfer, Brown & Figueroa (Editors)

anties provided for hunting, fishing and trapping. The environmental protection regime has a process under which the Crees have special rights to participation in the review process that is greater than the general public, whenever a development project is subjected to the environmental and social impact assessment (ESIA). The list of subjected projects is included in the agreement, as well as a list of projects not subjected to the ESIA. The projects not included in either list have to be reviewed on a project by project basis in order to determine if they are subjected or not to the review process. Rehabilitation mining sites as well as catastrophic events on reclaimed sites are not included on either list.

In order to avoid time delays often related to the ESIA process and budget constraints, an alternative method for the Cree first nation consented to include a working group with members representing the government and the Cree First Nation. Since there were no structured procedures and no clearly defined roles for this new approach the communication, inclusiveness and integration of Cree concerns on the decision-making process were very limited. Information dissemination and facilitation was inconsistent for the rehabilitation works and concerns from the community where not properly considered. Water quality, fish and fish habitat are the main concerns of the Cree First Nation. MRN results showed water quality was acceptable according to directive 019. But most of the concerns for the Cree Nation where not at or near mine site location but further downstream, and metal content associated to tailings larger than the directive 019 listing. Furthermore, already existing mistrust increased when concerns were not responded through regulations, forcing the Cree Nation to pursue a separate sampling campaign without any resources or assistance from governmental entities.

The sampling campaign was designed to answer the concerns of the Cree First Nation of Waswanipi. Fig. 2 shows the location of the mine site, the stations both from the government and the Cree first nation campaign near the mine site. Fig. 3 shows an overall sampling and monitoring region of the Cree First Nation sampling campaign covering a distance of more than 100 km downstream. The parameters sampled were more than those included in directive 019. Table 1 shows the different parameters analyzed for water quality. Sediments where also sampled at the different stations and an additional campaign for fish and fish habitat was conducted. The ministry of natural resources did not include any sediment sampling in their analysis.

MRN	CRA								
Directive 019 (2012)	Surface Water Quality								
Arsenic	Arsenic	Mercury	Manganese	Magnesium					
Copper	Copper	Uranium	Molybdenum						
Iron	Iron	Chlorine	Selenium						
Nickel	Nickel	Antimony	Sodium						
Lead	Lead	Aluminum Phosphoru							
Zinc	Zinc	Thallium	Boron						
Total Cyanide	Total cyanide	Chromium	Calcium						
Hydrocarbons	Hydrocarbons and PCB's	Cadmium	Beryllium						
Total suspended solids	Tot. suspended solids	Barium	Vanadium						
рН	pН	Silver	Tin						
	Turbidity	Cobalt	Potassium						

Table 1 List of parameters analyzed by MRN and CRA for surface water quality



Results

Five main sampling stations for water quality and sediments named CRA-01 representing the reference point, upstream from the Spill on Obatogamau River; CRA-02 closest station to the Opemiska site outflow after the road 113; CRA-03 on Slam Creek just before joint to Obatogamau River; CRA-04 on Obatogamau River about 10 km downstream of Slam Creek and CRA-05 near the Cree first Nation of Waswanipi community. In addition, different inspections on nearby lakes were done for sediments and two fish sampling areas are represented in bleu on Fig. 3.

pling stations and distance

Average and standard deviations calculations for each parameter where performed on the integrated data for surface water quality and sediments across all time points, Kruskal-Wallis Tests with post-hoc comparison of all stations to CRA-01, reference station upstream from the mine where included. Significant differences (when p < 0.05) are highlighted in the data. The area of greatest interest by the Cree nation was beyond Slam Creek. The last station measured by MRN was at the junction of Slam Creek and Obatogamau River (near station CRA-03). Graphs and tables are available in attachments (http://bitly.com/IMWA2013_531).

For surface water, parameters exceeding a single measurement or average concentrations to the reference station (CRA-01) are: turbulence, manganese, sodium, magnesium, potassium, sulfate, aluminum and calcium. Significant differences (when p<0.05) further downstream than Slam Creek are turbidity, sodium, magnesium and aluminum. Exceeding regulation standards for surface water quality are turbidity, aluminum, manganese, iron and naphthalene.

For sediments, parameters exceeding a single measurement or average concentrations to the reference station (CRA-01) are: nitrate-nitrite, barium, aluminum, copper, manganese, vanadium, iron, nickel, zinc, sodium, chromium, magnesium, potassium and calcium. Significant differences (when p < 0.05) further than the last Slam Creek (last station measured by MNR) are aluminum, copper, barium, manganese, vanadium, iron, nickel, zinc, sodium, chromium, magnesium, calcium and potassium. Exceeding regulations standards for probable or frequent effect level in sediments are mercury, arsenic and copper. Note that the regulation has no criteria for aluminum, manganese, molybdenum, sodium, zinc, molybdenum, iron, magnesium, potassium, vanadium and calcium which had which had concentrations in the hundreds and thousands mg/kg on the sediments measured.

Fish sampling program was conducted on Yellow Walleye and Lake Whitefish with the objective of evaluating metal levels in the dorsal muscle and comparing with data from nearby Lakes Chibougamau and Ouje-Bougamou study (Laliberté 2004), although those are areas also impacted by mining activities in the past, it was the only data available for comparison. Unfortunately the target of 10 male and 10 female walleye and whitefish was not attained. After an average of 105 hours of gill net fishing, the average catch per unit effort (CPUE) on average for both sampling stations was 0.86 for Yellow Walleye and 0.13 for Lake Whitefish. The objective to evaluate metal levels in the dorsal muscle was thus not accomplished due to the lack of fish. Historical data in Waswanipi Lake from 1989 was the only comparison available for CPUE in the area (Dion *et al.* 1992). The CPUE at the time was 15.7 for Yellow Walleye and 3.2 for Lake Whitefish.

MNR did a characterization of the Slam Creek to evaluate the impacts of the spill (Gagnon et al. 2008). The results revealed that the fish habitat was destroyed completely throughout Slam Creek but no further downstream studies where pursued even after the requested of the Cree First Nation of Waswanipi. Based on the results obtained by CRA, the Cree Nation Government requested Environment Canada (EC), federal entity responsible for fish and fish habitat to pursue a more detail study on the fish and fish habitat impacts due to the spill. EC prepared the guidelines for the study and mandated MNR to pursue it. The sampling campaign was finished in September 2011. The Cree Nation was not implicated in the sampling campaign nor have they access to the information or the results. The final study has not been shared and no date has been given to expect the results of the study.

Conclusion

The Opemiska spill occurred six (6) years after the site was reclaimed by the government. Today, there are still no regulations on the monitoring after the industry has been liberated from closing process. Furthermore, directive 019 does not request any monitoring on surface water quality, sediments and fish downstream from the final effluent, which makes it impossible to compare results when catastrophic events occur in order to relate its impacts on the environment. Most of the time, budget limitations regarding abandoned as well as reclaimed sites do not permit a thoughtful monitoring plan, including fish and fish habitat impacts further downstream from the mine area and long term treatment or monitoring (Chambers 2000), inspection measures and responses. Monitoring should be in place for reclaimed sites at least every season in order to have a periodical evaluation

of the reclaimed site. Communities should be involved in those plans.

Results based on past catastrophic events must be used to develop regulations on mining closure rehabilitation and monitoring, impacts related, and public participation implementation. If a collaborative approach would have been used as part of the rehabilitation plans after the Opemiska spill, the investment done by the Cree Nation on the sampling campaigned could have been used jointly for the benefit of all parties.

Although guidelines to work collaboratively with concerned stakeholders have been proposed worldwide, they are hardly implemented on abandoned or reclaimed sites. Nevertheless, to avoid conflict and to benefit from stakeholders resources, structured procedures and clearly defined roles for citizen participation are needed. Indigenous communities as well as municipalities can play an important role supporting rehabilitation plans if they are included in the decision-making process and their concerns are respected and integrated in the actions and final design of the site.

Indigenous communities need support to develop mechanisms to better participate in emergency responses and monitoring related to catastrophic events for closed as part of a skill transfer knowledge and capacity building system. It could be done in joint groups where industry, community, government & academics set goals, study options, plan together, develop monitoring plans, analyze results, share information and use it for implementation and development. These groups could not only focus on environmental aspects but social and economic as well, where knowledge is transferred to develop future generations and technical development is achieved under leading practices principles.

References

Quebec Government (1997) Guidelines for preparing a mining site rehabilitation plan and general mining site rehabilitation requirements. Ministère des Ressources naturelles du Québec and the Ministère de l'Environnement et de la Faune du Québec. www.mrn.gouv.qc.ca/english/publications/mines/ environment/guianmin.pdf

- Garcia DH (2008) Overview of International mine closure guidelines. American Institute of Professional Geologists
- Quebec Government (2012) Directive 019 sur l'industrie minière. Le ministère du développement durable, Environnement et Parcs. www.mddep. gouv.qc.ca/milieu_ind/directive019/
- Best Practices in Community Involvement Planning for Rehabilitating Abandoned and Orphaned Mines in Canada NOAMI Brochure (2003) www.abandoned-mines.org/publications-e.htm
- Garon M, Couture JM, Jean R, Hunt GG, Francoeur L, Rodrigue V, Côté D, Hamel A, Lowe DM, St-Arneault C (1992) Fermeture et restauration des sites – Opemiska. Minova Inc. Division Opemiska
- Quebec Government (2006) James Bay and Northern Quebec Agreement and Complementary Agreements. Les publications du Québec www.gcc.ca/ pdf/LEG00000006.pdf
- Laliberté D (2004) Metal concentrations in fish and sediments from Lakes Aux Dorés, Chibougamau, Obatogamau and Waconich in 2002. Environment Quebec
- Dion R, Simoneau M (1992) Developpement d'une peche commerciale a Waswanipi, synthese des données biologuiques 1988, 1989, 1990. Cree Regional Authority.
- Gagnon C, Lapierre G, Daneau S, Gagnon M, Marcoux L (2008) Caractérisation du ruisseau Slam à la suite de la rupture de la digue du basin de polissage de l'ancienne mine Opémiska
- Chambers DM (2000) A position paper on perpetual water treatment for mines. Center for Science in Public Participation

An electronic attachment can be found here: http://bitly.com/IMWA2013_531

Strategic Assessment of Water Resources for the Erongo Uranium Province

Christoph Külls¹, Arnold Bittner², Vera Marx²

¹IHF, Fahnenbergplatz, 79098 Freiburg, Germany, christoph.kuells@hydrology.uni-freiburg.de ²SLR Environmental Consulting (Namibia; Pty) Ltd., 8 General Murtala Muhammed Street, Windhoek, Namibia, abittner@slrconsulting.com

Abstract The development of uranium mining in the arid Erongo region of central western Namibia has increased pressure on limited water resources. An assessment of available water resources and demand from different stakeholders was carried out. An Integrated Geohydrological Model (IGHMS) was developed. IGHMS produces time series of key hydrological processes such as channel flow, evapotranspiration, transmission losses, lateral subsurface flow and water level of aquifers in key compartments used by mines and other stakeholders in the region. The model uses an explicit visual modelling approach. This approach facilitates model maintenance and integration of stakeholder actions. IGHMS is a framework model. For important aquifers or aquifer compartments more detailed numerical groundwater models have been developed. IGHMS assures the consistency of boundary conditions. The results of IGHMS have led to a new monitoring and licensing strategy in the uranium province of the Erongo Region.

Keywords strategic environmental impact assessment, integrated geohydrological model, aquifer compartment, regional/basin model, water resources allocation, new monitoring and licensing strategy.

Introduction

The current and planned mining activities in the Swakop River Basin and other areas in the Erongo Region of Namibia will have impacts on the availability and quality of water resources. The Erongo region in the central western part of Namibia receives 350 to less than 50 mm of rainfall per year, most of the mining areas are located in the arid part with rainfall of less than 150 mm per year. Groundwater resources in the crystalline basement are scarce and mostly constrained to shallow alluvial aquifers. In order to minimize negative impacts and to develop environmentally sound strategies for social and economic development it is of paramount importance to understand the distribution of water resources (Benito et al. 2009). The sustainable yield of alluvial aquifers needs to be estimated as a basis for water allocation to stakeholders and mines.

A Strategic Environmental Assessment (SEA), conducted by the Southern African Institute of Environmental Assessors (SAIEA) under the auspices of the Namibian Chamber of Mines,has assessed all sector development scenarios in the Namib Uranium Province. One part of this SEA was a Water Balance Study for the river catchments in the Namib Uranium Province which aimed at providing information on water balance and groundwater availability from alluvial aquifers (Külls *et al.* 2009). Recommendations about abstraction constraints were derived from the SEA to reduce the negative impact on ecosystems and existing agricultural users.

The Namibian Ministry of Mines and Energy appointed the Institute of Hydrology (Germany) and BIWAC (Namibia) to carry out the hydrogeological specialist study and water balance of both Khan and Swakop river catchments in the Erongo Region. The works pro-

gramme comprised the development of a conceptual model based on field investigations (groundwater sampling campaign) and exisiting database information, the implementation of numerical groundwater flow models of selected Swakop- and Khan river compartments (BIWAC 2010) and subsequently an Intergated Geohydrological Model of the Swakop/Khan river catchment as basis for an improved monitoring, decision support system and licensing procedure through the regulator. The Integrated GeoHydrological Model of the Swakop basin (IGHMS) integrates hydrological data, calculates key hydrological processes and state variables and thereby defines hydrological boundary conditions of recharge, lateral inflow and outflow for compartments in a hydrologically consistent manner. Numerical groundwater models can be plugged into IGHMS for a detailed and numerical modeling of specific compartments (BIWAC 2010).Results of the IGHMS are used to evaluate impact of water abstraction scenarios on other stakeholders, mines and farmers in terms of groundwater levels and groundwater flow. These components form a decision support system for water right allocation (Fig. 1).

Delineation of river compartments

Hydrogeological data, remote sensing data and information from field campaigns such as water level depths, river bed geometry and vegetation density were used to determine compartment boundaries. Altogether nine Swakop River compartments and 10 Khan River compartments were delineated and their respective sub-catchments calculated (Tab. 1, Fig. 2). These compartments represent surface and groundwater management units defined by natural boundaries. Most of the basin is characterized by crystalline bedrock composed of schist, granite and amphibolite. The fractured basement aquifer has low groundwater yields. Most of groundwater resources are found in alluvial aquifers that act as a linear subsurface drainage. Alluvial aquifers are recharged by transmission losses from infrequent floods. These alluvial aquifers are characterized by a pool-step sequence. Channel sections of several tens of kilometers are typically separated by basement highs where aquifer depth decreases from several tens of meters to few meters and groundwater re-surfaces. At these steps dense vegetation develops. Compartments are separated by these steps at their upper and lower boundaries. These channel sections were then characterized in several ways. Groundwater samples were taken from boreholes in the river alluvium and adjacent basement aquifers and analyzed for major ions, metals and rare elements as well as CFC samples for characterization of the groundwater residence times of all river sections/compartments in



Wolkersdorfer, Brown & Figueroa (Editors)

Compartment	Length of compartment km	Area of compartment km²	Average width compartment m	Average depth m	Average RWL m	
S1 WESTFALENHOF	53	8.6	162	8	2	-
S1 OTJIMBINGWE	26	7.7	296	10	4	
S3 POTBERG	42	15.7	374	13	6	
S4 HOREBIS	33	10.7	325	23	7	
S5 LANGER HEINRICH	26	10.4	401	17	6	
S6 HUSABBERG	25	5.3	212	13	5	
S7 IDA DOME	36	8.6	240	18	8	
S8 ETANGO	20	7.5	376	23	7	
S9 FARMING ZONE	29	13.0	449	15	7	
K1 SPES BONA	26	5.9	226	14	10	
K2 ONGUATI	17	1.6	92	15	8	
K3 GROOT ROOIBERG	8	2.1	262	15	8	
K4 KLEIN ROOIBERG	11	1.3	114	15	10	
K5 NAOB/USAKOS	30	7.5	250	7	3	Table 1 Information
K6 KHANBERGE	31	5.6	182	23	7	
K7 VALENCIA	5	0.8	162	12	4	on compartment
K8 RIO TINTO	14	1.4	102	18	8	characteristics:
K9 ROSSING	25	4.1	164	18	4	Swakon River (S)
K10 CONFLUENCE	17	3.6	213	22	14	and Khan river (K)



Fig. 2 Delineation of river compartments and subcatchments as basis for IGHMS

the Swakop/Khan catchment within the Erongo Region. For several of these compartments specific numerical groundwater models were developed: Compartments 07 (Valencia) and 08 (Rössing) of the Khan River and 02 (Otjimbingwe) and 05 (Langer Heinrich) of the Swakop River (BIWAC 2010). For these compartments specific hydrogeological investigations using geophysics and available borehole logs were carried out based on which aquifer geometry was defined. The hydrogeological information obtained from the models was incorporated in IGHMS.

Surface and sub-surface flow from each sub-catchment was modeled based on a daily rainfall records and catchment parameters. A unit runoff map of Namibia developed by Namwater based on existing runoff data was used to convert rainfall into direct runoff. Evaporation was calculated based on climate data including temperature and relative humidity using an approach specifically developed for Namibia and calibrated in the study area by Hellwig (1977).

Methods

IGHMS was developed with the software package SIMILE of Simulistics[®]. This software has been proposed for explicit environmental modeling, especially for integrating processes of different disciplines. The software allows visualizing the complete program structure. Non-programmers can follow the flow of water and resources and relate to different modules and compartments or processes of the model. This was an important aspect as the model will be used by local stakeholders and decision makers in situations of potential conflict.

The model consists of a sequence of compartments. For each compartment all inflows and outflows are calculated based on hydrological processes. Each sub-model (Swakop/Khan) represents all relevant geo-hydrological processes: channel flow, evapotranspiration, transmission losses and groundwater recharge, pumping, lateral groundwater inflow and outflow, and groundwater exchange with the basement aquifer.

Average runoff coefficient (r_c) defined as the percentage of runoff generated from rainfall is estimated as 4 % (DWA 1992). This percentage varies depending on geology, soils, antecedent moisture and vegetation. Runoff coefficient can be used as a calibration parameter to fit modeled to measured channel runoff. Channel inflow controls transmission losses and indirect recharge to the alluvial aquifer. Surface and groundwater flow are routed through all compartments. The time step of the routing module is hourly for surface and daily for groundwater flow. Water evaporates during rainy season from wet and moist sand as well as from groundwater (evaporation and transpiration). Evaporation was calculated based on the approach of Hellwig (1973) for wet sand and vegetated areas in terms of potential evaporation (ETp). Data on the extent of vegetated areas, sandy surface and permanently or temporarily wet areas



Fig. 3 Part of the model structure showing surface runoff, transmission losses, pumping and recharge: q=runoff, Cin=channel inflow, *C*_{out}=*channel outflow*, *r*_s=*surface runoff*. *TL=transmission losses depend on L=length of* the compartment (km), ecs=extinction coefficient $(m^3/s \text{ per } km)$ and are limited by storage (S) of the alluvial aquifer (A). The model also takes into account spill flow from an upstream reservoir (spill), while no, go and noc are indices for the compartment number. Pumping is controlled by pumping rate (pr), borehole depth (pd) and a *flexibility (pf) of pumping at low storage volume* (S) of the alluvial aquifer (A) resulting in a lower pumping rate (pv). Lateral groundwater inflow to the compartment depends on max. inflows calculated from Boussinesqs law and basin recharge (r).

were obtained from satellite images. Response of evapotranspiration (ET) to groundwater water level was accounted for by implementing parameters for extinction depth (ETd) and flexibility (ETf). ETd simply specifies the maximum evaporation depth. ETf introduces the adaptation of plant transpiration to declining water levels: When water levels drop resistance increases and evaporation rates decrease. In addition, some sub-segments of the river compartment fall dry and as a consequence, overall compartment transpiration decreases. Lateral inflow was calculated based on Boussinesq law for drainage of an unconfined aquifer with a sloping impermeable base. The maximum lateral inflow was estimated taking into account hydrogeological properties of basement

rock as well as compartment and sub-catchment characteristics. The average slope was derived from a digital elevation model for either side of the compartment. Transmissivity was derived from pumping tests. The alluvial module describes inflow and outflow as a function of actual storage of the alluvial aquifer (A). Time step is daily. Inflows consist of indirect recharge from floods, groundwater inflow from upstream compartment (and from the Khan compartment at the confluence) and lateral groundwater inflow from the basement. The outflows are: groundwater abstraction through pumping and flow to the downstream compartment (or the sea).Pumping rates can be included and specified for each single compartment. The module features a pumping depth (pd) and a pumping flexibility (pf). Pumping flexibility reflects the feedback between actual pumping rate and groundwater level. If no flexibility is specified, predetermined pumping rates are applied until the borehole is dry. This feature can be used to establish a quantitative relationship between adaptation to lower water levels and the reduction of no-production risks.

Scenario development and decision making

One of the main purposes of GHMS is to enable the mines and regulators (GSN/DWAF/SEMP) to predict the impact of potential groundwater abstraction from the Swakop and Khan rivers on downstream aquifer compartments. Changes in stored water volume, average water level and impacts on water quality can be calculated. Cumulative effects of abstraction from different river sections and the influence of one single borehole on a number of downstream compartments can be shown. The impacts can be calculated for a period of time that has to be defined by the user. Groundwater abstraction in a specific river compartment will not only lower the groundwater level but will also influence recharge rate, transpiration rate, outflow and transmission losses in that compartment as all these processes depend on groundwater level. All these resulting indirect impacts in the compartment and in all lower compartments are calculated and can be visualized. Environmental impacts can be quantified and their respective risks specified.

Results

Several abstraction scenarios were run and evaluated. The impact on downstream compartments was calculated in terms of runoff and groundwater level in compartments. In general impact of groundwater abstraction was found to be mainly local and constrained to the compartment. The propagation of impacts on downstream compartments was found to be low. Only if abstraction increases transmission losses from floods and thereby reduces the size and frequency of flow events in lower compartments, a significant reduction of water resources availability results. The time scale of system response was found to be at the scale of few years to few decades. Local impact of abstraction, however, is significant due to low recharge rates and limited aquifer volume. The model also revealed a significant impact of previous dam construction in the upper part of the basin on present water groundwater resources (CSIR 1997). Three different groundwater abstraction scenarios of 100,000, 200,000 and 500,000m³/year were modeled for Langer Heinrich (left) and the adjacent downstream compartment Husabberg (compartments 5 and 6, Fig. 4). The water level in the compartment strongly depends on flood recharge; the recession of aquifer water level is slightly affected by different pumping rates. Impact on the lower compartment is not significant; all three time series of water levels are superimposed and cannot be discerned (Fig. 4, right hand side).

Conclusions

A series of important recommendations were derived from a Strategic Environmental Impact assessment of the Erongo Uranium Mining Province including the need of a model based abstraction management for shallow



Fig. 4 Groundwater water level in the Langer Heinrich (5) and Husabberg (6) compartments for three pumping scenarios of 100,000, 200,000 and 500,000 m³/year.

groundwater resources. The total water demand of mines in the Erongo region was found to exceed natural resources in alluvial aquifers by far and the development of alternative sources of water was therefore encouraged. An integrated GeoHydrological model of the region was developed (IGHMS). IGHMS provides a DSS for groundwater management. Scenarios such as reduced/increased rainfall, adaptive dam management and impact of dam releases, vegetation management such as removal of invasive species can be modeled and evaluated.

References

- Benito, G., Rohde, R., Seely, M., Külls, C., Dahan, O., Enzel, Y., et al. (2010). Management of Alluvial Aquifers in Two Southern African Ephemeral Rivers: Implications for IWRM. Water Resources Management, 24(4), 641–667.
- BIWAC (2010): Numerical Groundwater Model and Water Balance of the Swakop/Khan River System.

Groundwater Specialist input to the Strategic Environmental Assessment of the Central Namib 'Uranium Rush', Windhoek.

- CSIR (1997): An Assessment of the Potential Environmental Impacts of the Proposed Aquifer Recharge Scheme on the Khan River, Namibia. Final Report by CSIR Division of Water, Environment & Forest Technology to Rössing Uranium Limited, Swakopmund, Namibia.
- DWA (1992): Unit Runoff Map for Namibia. Department of Water Affairs, Ministry of Agriculture, Water and Rural Development.
- Hellwig, D. H. R. (1973): Evaporation of water from sand, 3: The loss of water into the atmosphere from a sandy river bed under arid climatic conditions. Journal of Hydrology, 18(3–4), 305–316.
- Külls, C., Marx, V., Bittner, A., Ellmies, R., & Seely, M. (2009). Environmental impacts on the hydrology of ephemeral streams and alluvial aquifers. Geophys. Abstr., Vol. 11: 5517.

What Does "Perpetual" Management and Treatment Mean? Toward a Framework for Determining an Appropriate Period-of-Performance for Management of Reactive, Sulfide-Bearing Mine Wastes

Mark J. LOGSDON¹

¹Geochimica, Inc. 9045 Soquel Drive STE 2, Aptos, California,95003 USA, mark.logsdon@sbcglobal.net

Abstract Mine wastes, typically millions to billions of metric tonnes and occupying hundreds to thousands of hectares, will remain geochemically reactive for centuries to millennia. Establishing a coherent basis for determining how far into the future proposed mine-site closure must be effective has too often been neglected. Consideration of closure stages, closure risks, and engineering practice suggest that a planning period for management of mine wastes should be nominally 200 years. It should include a semi-quantitative assessment of whether or not major changes in performance are likely to occur between approximately 200 and 1,000 years.

Keywords Perpetual management; design-basis; extreme events; engineering plans *vs*. discounted costs; 200 to 500 and 1,000 years

Introduction

At the time of closure, hard-rock mine wastes, typically including waste rock/overburden and tailing, typically range in mass from a few millions of metric tonnes for small underground mines or heap-leach systems with modest lifetimes to billions of metric tonnes for large, long-term open-cut mines. The waste management units occupy hundreds to thousands of hectares of surface, with some structures at large, end-dumped rock piles extending over several hundreds of metres of vertical relief. If infiltration were 20 % of average annual precipitation of 1,000 mm/a over a waste-rock system covering 500 ha, the steady-state effluent would be 1×10^6 m³/a, a very substantial volume to be treated if the water is low-pH, high-SO₄ solution with a range of dissolved metals above discharge criteria. Even if a cover system were to reduce that net infiltration by 90 % and one were to allow for ranging flows associated with variable flow paths, for large waste-rock storage systems the water-treatment demand is very significant.

For mine wastes in which the pyrite content is greater than a few tenths of a weight percent, reaction rates for pyrite oxidation are so slow that pyrite will remain active for periods of hundreds to thousands of years, and in many cases much longer.

- Example 1: There is a record of sulfide mining in the Iberian Pyrite Belt that extends at least 4,500 years (Leblanc *et al.* 2000). Massive-sulfide copper deposits of the Eastern Mediterranean were major sources of copper in the Homeric Bronze Age, and they continue to be reactive today
- Example 2: In erosional scars exposed in Quartz-Sericite-Pyrite altered volcanic and intrusive rocks in the Red River Valley, northern New Mexico, the radiometric dating of jarosite and alunite formed by oxidation of pyrite in these scars indicates that pyrite has been reacting *in situ* for periods of 30,000 to 1.5 million years, yet such altered rocks still retain much of their original pyrite. Calculated depletion

times for waste rock there range from ca. 1,500 a to more than 100,000 a, based on plausible alternative models for the hydrodynamics of the waste-rock piles (Logsdon 2011)

Engineered Waste-Management Systems: Design Basis and Extreme Events *Background*

For waste-management units at mine sites, closure and reclamation of waste rock or tailing will be designed, built, and maintained to achieve specific reclamation goals. Performance of the engineering structures and related reclamation actions, including seepage, slope stability, erosion control, and re-vegetation, must be sustainable into the future. This section addresses the time frames that are expected for reclamation activities and proposes a design time frame for long-term period of performance of the reclamation.

Engineering structures, including mine structures, are designed to perform with respect to some specific design criteria related to the natural environment, often organized around response to external forces with statistically-defined probabilities of occurring per unit time (equivalently, as "return periods for an event of a given magnitude"). For example, it is usual for hydraulic structures for a specific catchment to be evaluated in terms of runoff resulting from a specified precipitation event (e.g. precipitation over a 24-hour period) with a specific return period, e.g. 100 years (equivalent to a probability of 0.01/a for such a flow). Similarly, it is common for seismic stability of embankments or rock-pile slopes to be assessed in terms of expected deformation for site-specific seismic events with defined recurrence intervals. In the terminology of geotechnical engineering, one speaks of "design-basis events" and also considers the risks from "extreme events", incorporating both into the detailed design criteria for an entire project that ultimately will be defined and, of course, executed.

To be useful for establishing design criteria, the return periods need to be considered (a) in terms of the duration of relevant activities at the mine and (b) in terms of the consequences if an event were to occur. For example, if a mine had a projected remaining operating life of 20 years, then the binomial probability of a 100-year event occurring in the remaining lifetime of the mine would be 18.2 %. To assess the need for considering large and extreme events, one must therefore consider the relevant time frames for the closure and reclamation activities associated with the waste-management facilities that are required on a site-specific basis. The implications are not often calculated. Suppose that it was decided that the mine reclamation activities needed to be fully functional for 200 years, with a less than 10 % probability of a failure over that period. From a simple binomial model, the design-basis events that need to be accommodated then amount to 2,500-year recurrence intervals, and it is clear that design-basis events such as one-in-a-hundred-year storms will be expected with probability = 1.

Timeframes for Reclamation and Post-Closure Maintenance

There are three reclamation periods that are relevant to establishing a design framework:

1. The period of construction and active reclamation. During this period, there would be active use of heavy equipment to construct the stable forms of the piles and to place any covers. This also is the period of active planting and cultivation essential to the phased re-vegetation of the rock pile surfaces. Based on consideration of the surface areas, volumes and terrains, and using industry-standard assumptions for equipment and manpower, it is expected that the active construction and reclamation period for significant wasterock piles would require up to 20 years, depending on detailed planning factors, such as how many rock piles can be reclaimed simultaneously. Because the mining company would have a substantial work force and a large and varied fleet of equipment on hand, maintenance requirements, even substantial rebuilding efforts if they were required, could be managed efficiently.

2. The final reclamation plans typically will require successful establishment of woody species to ensure shallow slope stability and to provide the effective evapotranspiration needed for the cover design to achieve a long-term goal of minimizing net infiltration. Based on experience with reclamation and re-vegetation on minedrock piles, it is expected that the development of the final, sustainable, vegetative cover would require a period of another 10 to 30 years after the end of the active construction period.

Following completion of the original resloping and reclamation activities, one would expect that equipment and personnel would gradually be reduced to an ongoing maintenance level. Such a team would be capable of handling the level of work associated with ongoing maintenance of the berms and benches on rock piles, however for a major rebuilding effort, if required, the mining company would have to contract outside services, including engineers and major earth moving equipment.

3. Beyond the period of reclamation of up to 50 years, the mining company should anticipate that there will be a period of long-term maintenance and monitoring that will document that the expectations for stable slopes with controlled water-quality performance have been met.

Consideration of Risk in Light of Maintenance Capabilities

The period of greatest vulnerability for the resloping and reclamation will be the early days of construction, before re-vegetation would be effective at stabilizing the shallow portion of the slopes. Fortunately, this is the period when the mining company will have the greatest capacity to respond, because the large-scale equipment and large work force will remain on site.

As the workforce and equipment inventory are drawn down, a more formal plan is required. During the longer-term reclamation and post-closure maintenance period, we consider it reasonable to evaluate conditions in terms of the consequences that would ensue from events, particularly hydraulic events, of certain magnitudes. If the events are ones that produce consequences that can be repaired as a matter of course by the maintenance approach, then this represents one set of conditions. If, on the other hand, the consequences of a specific event required a substantial or complete rebuild of the originally-designed closure facilities, then a major intervention would be required, and that would be another class of risk entirely.

We propose the following framework:

 If an event produces geotechnical and hydrological consequences that (a) remain entirely on the Mine property and (b) can be repaired by the available maintenance team in a period of ≤6 months or less, with minimal engineering supervision, then the consequence will be considered "amenable to maintenance".

For portions of reclaimed rock-pile slopes to have conditions "amenable to maintenance", we propose that the system and subsystems (*e.g.* surface-water conveyances on benches) be designed to control events with a recurrence interval of 100 years. This requires that the long-term maintenance capacity of the Mine's closure program must be equipped and trained to manage impacts to the designbasis slopes and covers from events with recurrence intervals up to 100 years. For example inter-bench surface-water conveyances would be designed to pass the 100-year event, because the expected consequence of failures (minor erosion from overtopping of a lift) would fall within the range of simple repairs that would be expected of maintenance.

• If an event produces geotechnical or hydrological consequences that (a) extend off the Mine property and (b) cannot be repaired within 6 months using the available equipment and manpower, then the consequences would require rebuilding.

The Mine presumably intends that, after all the work that will go into managing the rock piles to be "safe and stable," there would only be a very small probability of consequences off site. For the purposes of discussion, we propose that the designbasis events that would yield off-site impacts or major rebuilding would have a probability of occurrence of less than 10 % during the proposed 200-year period of performance. Based on a binomial model, this means that the design basis for critical structures that would limit consequences to off-site-only impacts must be the 2,500-year recurrence event.

For comparison to a time-frame analysis focused primarily on financial assurance rather than trictly on engineering, readers will wish to consult Kempton (2003).

Period of Performance

There is no industry standard for such a longterm performance of closed mine facilities, nor are there established regulatory criteria for rock piles. The only geotechnical systems for which there has been extensive analysis of long-term periods of performance is for the mining and milling residues controlled under the Uranium Mill Tailings Radiation Control Act (UMTRCA) of 1978 (P.L. 95–604). The regulatory standard requires that control of tailings "shall be effective for up to 1,000 years to the extent reasonably achievable and, in any case, for at least 200 years" (EPA, 1983). The UMTRCA time frames were established to consider periods over which climatological and geomorphic processes could reasonably be predicted, given current knowledge of earth science and engineering. In a review of the technical basis for the regulations, the National Research Council, the contracting-review arm of the U.S. National Academy of Sciences, concluded that the 200year period was consistent with our knowledge of the longevity of engineered systems, but that estimates looking forward 1,000 years must be thought of as qualitative and inherently uncertain.

The Academy has recently returned to this topic in an updated review of the performance of engineered barriers for waste management (NRC 2007). The general conclusion of the NRC is that up to 20 years of field observations indicate that engineered waste-containment systems designed, constructed and maintained appropriately meet or exceed their intended performance. However, NRC notes that the demonstrated period of performance for such systems remains only a few decades, and that longer-term monitoring will be needed to show that performance over hundreds of years can be achieved reliably across the range of waste-management alternatives currently in service. A key finding of the recent study is that on-going maintenance is required (Mitchell 2008).

Industry-standard practice by mining companies and their technical advisors considers that engineered covers, such as a stable, very low erosion slope with a low-net infiltration, sustainable re-vegetated cap can be established. Given the exploration, development and operation history of the mine and an expected construction and reclamation activity on the order of 50 years, there will be nearly 100 years of geologic and hydrogeologic data available for most modern mines. It seems entirely reasonable to project that time period forward and to establish a goal of 200 years performance for the engineered closure system at modern mines, in keeping with the rational of the National Academy.

Conclusions

Consideration of these periods, the scientific basis for understanding closure risk, and established engineering practice leads us to suggest that a reasonable, total planning period for management of mine wastes should be in the range of 200 years, and it probably should include a semi-quantitative assessment of whether or not major changes in performance are likely to occur between approximately 500 and 1,000 years. Plans should include (1) identification of risks to surface and groundwater in terms of adverse impacts to beneficial uses, (2) presentation of a case that mine-waste structures would be stable with respect to erosion by flooding or deep-seated shear failures, and (3) presentation of a case that reactive wastes as disposed for those periods will remain physically stable.

The mine waste will remain a hazard beyond routine monitoring periods, and mine sites may cease operations under one owner through abandonment, bankruptcy, mergers and acquisitions. Therefore waste management plans need to address how responsibilities will be executed in the future. If there is an expectation of a transfer of authority (e.q. to the State or a landowner), there should be an explanation of how and by whom this will be (a) funded and (b) physically executed. Furthermore, if original operators are no longer available, there must be clarity as to how and by whom closure obligations will be executed. The closure explanation should show that the proposed successors both understand the nature of the burdens and are capable of executing the management responsibilities over the design-basis time that is established for the specific project.

Although this discussion paper is framed scientifically in terms of sulfide oxidation, the geochemical consequences of concern for mine-waste management include all potential classes and outcomes of reactivity. This includes not only acid-rock drainage and metals leachability, but also neutral drainage with elevated metals or salinity, as well as special classes of geochemical reactivity such as release of nitrogen species from explosive wastes in mined rock, release of selenium from black shale, arsenic mobilization due to reductive dissolution of As-bearing ferric phases, airfall of soluble, smelter-produced solids to soils, and other matters. The nature of the geochemical hazards at a mine site needs to be evaluated in terms of the mineralogy of the rocks, tailing or other wastes (*e.g.* hydrometallurgical or water-treatment sludges), site climate and hydrology, and the nature of sensitive receiving environments (*e.g.* extremely clean site waters or national or traditional heritage sites adjacent to mining operations).

Acknowledgements

The author thanks many colleagues who have considered these issues with him over the last thirty years. Richard Dawson and Ed Redente contributed deeply to the current concepts. David Blowes, David Jacobs, Stuart Miller, Michael Portigal, Leslie Smith, James Veness, and G. Ward Wilson, all contributed to the formulation of these ideas. The paper also benefits materially from the comments of an anonymous reviewer, including insights from several papers that he brought to our attention.

The specific analysis and recommendations here remain my responsibility.

References

- Environmental Protection Agency 1(1983) Standards for Remedial Actions at Inactive Uranium Processing Sites. Federal Register 48/3, 590–606
- Kempton, H (2003) Addressing the Dilemmas of Long-Term Mining Impacts Using a Framework of Sustainability and Adaptive Management. 6th ICARD Conference, Cairns, QLD, 12–18 July 2003. Ptroceedings 1048–1052.
- Leblanc, M, Morales, JA, Borrego, J, and Elbaz-Pouchilet, F (2000). 4,500 Year-Old Mining Pollution in Southwest Spain: Long-Term Implications for Modern Mining Pollution. Economic Geology 95, 655–661
- Logsdon, MJ (2011) Questa Weathering and Stability Study: Geological, Hydrogeological, and Geochem-

ical Framework. Tailings and Mine Waste '11, November 5–9, Vancouver BC. estore.informine.com Mitchell, JK (2008) Performance of Engineered Waste Containment Barriers. GeoCongress 2008: Geotechnics of Waste Management and Remediation (M.V. Khire, A.N. Alshawabke, and K.R. Reddy, Eds.). Amer-

ican Society of Civil Engineers, Geotechnical Special Publication No. 177, 1–15.

National Research Council 2007. Assessment of the performance of engineered waste containment barriers. National Academy Press, Washington, D.C., 119 p.

Spatial and Temporal Assessment of Ecological Risks at a Gold Mine Pit Lake

Andrew NICHOLSON¹, Deborah RUDNICK², Les WILLIAMS¹, Jennifer Ortega³.

¹Integral Consulting,²Independent Consultant; ³Newmont Gold Corporation

Abstract An ecological risk assessment (ERA) was conducted to evaluate a proposed expansion of the Twin Creeks Mine in the arid Great Basin ecosystem of northern Nevada. This ERA incorporated a detailed spatial analysis of the mine activities, mine geochemistry, habitat formation, habitat access, and contributions of the pit lake water quality, sediment quality, and wall rock concentrations in evaluating ecological risk. The results of this risk assessment showed that consideration of temporal variations at the mine provided more realistic assessments of wildlife exposure and allowed for targeted mitigation of this exposure.

Keywords Pit lake, ecological risk assessment, Nevada, arid environment

Introduction

Typically, ecological risk assessments use toxicological, ecological, and geochemical information to evaluate risk of impacts to wildlife and habitats from human activities such as chemical spills, resource extraction, and land conversion. If ecological risks are unavoidable, the ERA process can help identify opportunities to minimize or mitigate these risks.

State and federal permitting requires an evaluation of ecological risk associated with mining activities. In the case of proposed pit mine expansion, several spatial and temporal issues complicate the ERA approach. The assessment must be conducted for an ecosystem (a pit lake) that does not yet exist, using predictions of what hydrologic, chemical, and biological conditions are likely to be present several decades into the future as the lake infills The ecological risk assessment needs to account for spatial heterogeneity of chemicals to evaluate chemicals that animals will be exposed to once the pit lake exists. The risk assessment also needs to incorporate site geochemistry, which influences the bioavailability of metals and other chemicals to which wildlife may be exposed (Flynn et al. 2003, Suedel et al. 2006). These issues call for spatially and temporally explicit approaches in

order to accurately predict risk and, if risks of adverse effects are found, inform the approach to reduce or mitigate these risks.

Methods

A screening-level ecological risk assessment was conducted, consistent with regulatory guidance (USEPA 1997, 1999, and 2001), which uses maximum concentrations of chemicals in the proposed pit vicinity, assumes complete bioavailability, and compares chemical data to conservative toxicological criteria. Unsurprisingly, the conservatism of this approach resulted in a long list of metals that may cause risk, with substantial uncertainty about the realism of these risks under future conditions.

To address these uncertainties, a spatially explicit ecological risk assessment was conducted. This approach incorporated an expanded set of modeled and empirical data over multiple time scenarios to evaluate expected future sediment and surface water conditions, including:

• Spatially explicit data sets were used to evaluate what concentrations of metals might be expected at the pit wall surface to which the ecological community could be exposed (Figures1). This effort included

detailed characterization of the vertical extent of concentrations throughout the geologic section (Fig. 2).

- Estimates of pit lake surface water elevation and water quality was modeled over the complete 200 years of lake infill by other workers (Itasca 2010, Geomega 2010)
- A conceptual site model was designed to look at how ecological communities of the lake might be expected to develop after pit closure and infill (Fig. 3).

These data sets and conceptual models were used to inform a site-specific wildlife exposure model. The model creates estimates of exposure to local wildlife that might be expected to colonize or forage in the habitats that develop as the pit lake is created and habitat is formed (Fig. 3). These estimates of exposure were evaluated relative to toxicological criteria for concentrations of metals that have been shown in the scientific literature to cause no or low levels of adverse effects to wildlife exposed to these metals.

Results and Discussion

Results of the wildlife exposure model included:

• No risks were predicted to modeled granivorous birds or ducks from exposure

to chemicals at the site (Table 1).

- Low risks were predicted to ungulates, which could be redressed by considering pit wall mitigation. Exposures to antimony and arsenic were greater than the no-effect criteria for these metals if mule deer were conservatively assumed to spend all their time at the site. This risk could be eliminated if overburden (surficial materials removed prior to mining) is applied to the areas of the pit most likely to be frequented by grazing ungulates (Fig. 2).
- A handful of metals were retained as chemicals of potential concern that exceeded low-effect criteria for one or more taxa of invertivorous mammals and birds (Table 1). However, there are important aspects of the model and the site conditions that are likely to reduce these risks:
- Predictions of risk were largely related to necessarily simplifying assumptions in the model of uptake factors from foods to consumers. From what we know of other metal bioaccumulation patterns, these factors overestimate uptake, particularly at higher concentrations.
- The model assumes complete bioavailability of these metals; however, geochemical modeling indicates that at this site, several metals are likely to be in valence states or composite forms that re-



duce their bioavailability. For example, surface water pH greater than 5 is likely for this site, which would maintain aluminum in insoluble form, substantially limiting bioavailability of this chemical.

The availability of littoral habitat is likely to play a major role in shaping the ecological community of the site. Rapid infill rates over the first 20 years or so (Fig. 4) is likely to preclude the development of littoral habitat and will lead to the formation of a deep, mesotrophic pit lake. As lake infill slows, littoral habitat development will be regulated by the spatial proximity of shallow lake waters to horizontal pit wall benches that could allow for the development of a shallow vegetated photic zone. Low organic matter content in this arid ecosystem is likely to slow and limit shoreline soil capable of supporting substantial vegetation, further limiting habitat development.

Conclusions

The use of spatially and temporally explicit geochemical and ecological modeling to inform risk assessment has substantively im-



Fig. 2.Arsenic concentrations as a function of depth in the proposed Vista Pit.

proved our understanding of the ecological trajectory and potential for risk at the future Vista Pit lake. Following closure and infill from groundwater, Vista Pit is likely to function as a deep, mesotrophic pit lake. The development of shallow littoral habitat capable of supporting wildlife will depend on the intersection of pit geometry and final surface level equilib-

Receptor:	Chukar	Mule Deer	Myotis	Barn Swallow	Mallard	Spotted Sandpiper
Feeding guild:	Granivore	Browsing Ungulate	Aerial Invertivore	Aerial Invertivore	Omnivore	Shoreline Invertivore
Aluminum			Х	X ^b		Х
Antimony	—	X^b	X ^c	No criteria	No criteria	No criteria
Arsenic	_	\mathbf{X}^{b}	b,c	— X		X^{c}
Barium	_	_	_	_		_
Beryllium			—	No criteria	No criteria	No criteria
Cadmium	_	_	_	_	_	_
Chromium	_	_	$X^{b,c}$	X ^{b,c}	_	$X^{b,c}$
Copper	_	_	$X^{b,c}$	X^b	_	X ^b
Iron	_	_	_	_	_	_
Lead	_		_	$X^{b,c}$		X ^b
Manganese	—		—	_		—
Mercury	_	_	_	Х	_	Х
Nickel	_	_	_	_	_	_
Selenium	_	_	X^{b}	X^b	_	$X^{b,c}$
Silver	_		_	_		
Zinc	_	_	_	_	_	_

Notes:

--- = Criteria not exceeded.

X = Criterion exceeded

^aExposures at three time scenarios: 50 years of lake infill, 100, and 200 years were run and all results are summarized here.

^b Criterion for lowest observed adverse effect is not exceeded, indicating risk is low

^cFor one or more time scenarios, concentration does not exceed criterion.

Table 1. Summary of toxicological criteria exceedences^a using the wildlife ingestion model.



*Fig. 3.*Ecological conceptual model of pit infilling and habitat development.

rium, is likely to be prevented during initial rapid infill rates, and will be limited in the long term by low rates of organic matter accumulation in this arid ecosystem. Most chemicals that were evaluated were not found to be present at concentrations that suggest the potential for adverse effects on wildlife. A handful of metals were retained as chemicals of concern, though these risks may be mitigated by considering the conservatism of the exposure model and the likely reductions of bioavailability given predicted site geochemistry. Steps such as the use of overburden to cover pit wall surfaces that present a high likelihood of exposure may also be helpful in mitigating risk.

Acknowledgements

This work was funded and sponsored by Newmont Mining Corporation through subcontract to Enviroscientists, Inc.

References

- Flynn, H.C., A.A. Meharg, P.K. Bowyer, G.I. Paton. Antimony bioavailability in mine soils. Environmental Pollution, Vol.124 No.1, 2003
- Geomega.2010. Vista VII Pit Lake Chemogenesis.Final Draft. Prepared for Newmont Mining Corporation, Carlin, NV. September 9, 2010.

- Itasca. 2010. Appendix D: Predictions of Vista Phase 7 lake infilling. 2010 Update of Twin Creeks numerical groundwater flow model and simulations for Vista Phase 7 Pit. Memorandum submitted to Newmont Mining Corporation. Lakewood, CO. Itasca Denver Inc. August 5, 2010.
- Suedel, B., A. Nicholson, C. Day, and J. Spicer. 2006. The value of metals bioavailability and speciation information for ecological risk assessment in arid soils. IEAM 4(2):355-364.
- USEPA. 1997. Ecological risk assessment guidance for Superfund: Process for designing and conducting ecological risk assessments. EPA 540-R-97-006.Interim final.U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Washington D.C.
- USEPA. 1999. Screening Level Ecological Risk Assessment Protocol for Hazardous Waste Combustion Facilities Peer Review Draft. Appendix C: Media-toreceptor bioconcentration factors (BCFs).August 1999.
- USEPA. 2001. The role of screening-level risk assessments and refining contaminants of concern in baseline ecological risk assessments. ECO Update Intermittent Bulletin. EPA 540/F-01/014. U.S. Environmental Protection Agency.

Managing Water Permits with GIS at Questa Mine

Jeff Schoenbacher¹

¹Chevron Mining – Questa Mine, Questa, New Mexico, USA, jschoenbacher@chevron.com

Abstract The Chevron Questa Mine site (formerly known as the Molycorp, Inc.), situated in northeastern New Mexico includes an operational underground mine, mill and tailing disposal facility. Questa Mine has a rich mining legacy that dates back to the mid 1800s and has been a cornerstone of Taos County and two small local municipalities (Red River and Questa). Due to that legacy, Questa Mine has numerous regulatory benchmarks; therefore the facility implemented a comprehensive Environmental Geographic Information System (GIS) to assist in managing these obligations. This paper will provide insight into how the system was implemented as well as the working components of the system.

Keywords GIS, water quality permits, regulatory, USEPA, NMED, mining

Introduction

Due to Questa Mine's legacy mining impacts, on March 7, 2012, the United States Environmental Protection Agency (USEPA) Superfund Division Director and Chevron Mining Inc. (CMI) President, jointly signed an Administrative Order on Consent that set in motion removal actions to address the historic environmental impacts. As a result, the site was listed on the National Priorities List and the facility is currently engaged in the active remediation of the site.

However, while the remediation is occurring, the mine also complies with five prescriptive New Mexico Environmental Department (NMED) and USEPA water quality permits that have over 180 compliance benchmarks that are monitored and reported to both agencies. Specifically, the mine has four (4) NMED groundwater discharge permits and one (1) USEPA National Pollutant Discharge Elimination System (NPDES) permit. Within these permits, there are daily, weekly, monthly, quarterly, semi-annual and annual compliance benchmarks that are reported to state and federal agencies in accordance with the respective permit. To assist in managing the numerous regulatory benchmarks, Questa Mine focused on implementing a GIS system, that was specific to the mine's environmental themes.

As a result, in June of 2011, Questa Mine conducted a comprehensive compliance inventory of all water quality permit requirements, in an effort to categorize and convert this information to a collection of geographic datasets. The compliance monitoring categories that were developed during the assessment consisted of compiling the following:

- Groundwater Monitoring Wells
- Surface Water Monitoring Sites
- Spring and Seep Monitoring Sites
- Storm Water Monitoring Sites
- Outfall Monitoring Sites
- Domestic Waste Water Monitoring Sites
- Spill and Release Monitoring
- Physical Inspections and Monitoring Sites

In addition, efforts were made to acquire historical datasets that were developed from various Questa Mine departments as well as consultants. The datasets that were discovered internally consisted of numerous hard copy maps; AutoCAD files and individual GIS shape files developed by consultants.

Methods

At the completion of compiling the historical data, the datasets were indexed and a "needs assessment" was compiled to determine the Environmental Department's needs and prioritize the most important datasets. The assessment included identifying datasets that were not discovered in the historic research, but could be acquired from outside agencies and services, such as ArcGIS online, United States Forest Service, Taos County GIS Department, and the New Mexico Resource Geographic Information System. At the completion of the needs assessment, the following dataset were identified as being essential to the system:

- Township Parcels
- Carson National Forest Boundary
- Road and Highway Overlay
- Jurisdictional Waters and Wetlands Boundaries
- County Boundaries
- Section, Township, Range

It should be emphasized; that the needs assessment was a very important component to the development of Questa Mine's Environmental GIS, since it identified essential datasets and also created the frame work for the geodatabase that was created in ArcCatalog. Fig. 1 represents the geodatabase structure and the individual feature classes, within the database that were created after the assessment.

While framing the database structure, priority was given to setting up the datasets that would make up the administrative data within the geodatabase. The "administrative" feature class consisted of property boundaries, roads, buildings, township parcels, municipal boundaries, utilities, and pipelines. The datasets came from active AutoCAD DWG files and were based on local Questa Mine survey coordinates and not the North American Datum of 1983 (NAD83). Therefore, the datasets did not align when adding DWG files to the ArcGIS online aerial. To correct this issue, a custom projection (prj) file was created and saved with the

BASEGDB.mdb

- 🗉 🖶 Administrative
 - AirMonitoringStations
 - E CADOverlay
 - E Consultants
 - 🗉 📴 DGPS
 - EmergencyResponse
- 🗄 🖶 GroundWater
- 🗄 🖶 GroundWaterMonitoring_DP1055
- 🗄 🖶 GroundWaterMonitoring_DP1539
- 🗄 🖶 GroundWaterMonitoring_DP933
- 🗉 🖶 GroundWaterMonitoringDP132
- GWDP933_Pipeline_Inspections
- 🗉 📴 Hydrology
- 🗉 🖶 HydroScar
- 🗉 🖶 MineSitePropertyBoundary09
- 🗄 🖶 MiscSampling
- Image: Book of the second s
- 🕀 📴 Pipeline
- 🗄 🖶 Reclaim
- 🗉 🗗 SDWA
- Image: SnowLysimeterMet Stations
- 🗄 🖶 SPCCProgram
- 🗉 🖶 Stormwater
- 🗄 🖶 TopoMaps
- 🗉 🖶 Underground Footprint
- 🗉 🖶 UnderGroundWaterManagementSystem

Fig. 1 Geodatabase Structure and Feature Datasets

DWG files, which facilitated in the aligning files to the base aerial and assisted with creating the GIS datasets. Fig. 2 represents the Administrative Dataset display.

Another method that was used was the georeferencing tool that is available in ESRI ArcMap toolbox suite. Since the research discovered many hard copy maps that contained historical information, these documents were scanned and indexed. Afterwards, the georeference tool was employed to reference the scanned image file, by selecting control points on the actual image that corresponded with the aerial, which then assigned real-world coordinates for those selected points. An added advantage to this method is once the image is rectified, the same coordinates as the base aerial are assigned to the scanned image. This is done by the image being assigned a world file, which allows the file to be brought into other



Fig. 2 Administrative Dataset display.

GIS projects with the same coordinate system, thereby allowing the image to align for digitizing.

During the production phase of creating the datasets, the first datasets created within the geodatabase were the permit monitoring points. To accomplish this, each permit has its own feature class which represents the individual compliance datasets within that class of the geodatabase. Fig. 3 represents the individual monitoring points for one of the NMED groundwater discharge permits.

Additionally, each monitoring feature was populated along with the specifications related to that particular well. For instance, all of the monitoring well fields were given the permit identifier (*i.e.* well number) and subsequently well design information was entered. Therefore each monitoring well table included (Fig. 4):

- Permit Sampling Schedule
- Permit Sampling Constituents

- □ WATER PERMITS
 - 🖃 🗹 Monitoring_DP-933
 - Quarterly Report Sampling Obligations
 - DP933 Extraction Wells
 - DP933 Ground Water Monitoring
 - DP933 Seeps and Seepage Barriers
 - DP933 Springs
 - 🗄 🔲 DP933 Surface Water Sample (Decant)
 - 🗄 🔲 DP933 Tailings Analysis
 - \pm 🔲 DP933 Upper/Lower Dump Sump MW
 - 🗄 🗌 DP933 Piezometers
 - 🗄 🔲 DP933 Seepage Barrier

Fig. 3 Groundwater Discharge Permit

- Well Installation Date
- Well Completion Zone
- Casing Diameter
- Well Depth
- Well Screen Specifics
- Depth to Water

Other compliance datasets were populated with the sampling frequency as well as the required analytical suite for each site.

At the same time the Environmental GIS system was being configured, a MS Access database (DBMS) was created, as a repository for holding all sample results and compliance inspections. The structure of the DBMS tables was tailored in a manner that allowed the tables to easily join within the GIS tables. This allowed a seamless interaction between the field monitoring DBMS and the GIS datasets; therefore the data is dynamic since it feeds from the

DP933 - Ground	a water Monitoring													
Feature_id	FirstQ	SecondQ	ThirdQ	FourthQ	DateInstalled	CasingDiameter	CompletionZone	WellDepth	TopOfScreen	BottomOfScreen	ScreenLength	DepthToWater	ScreenLngth	SampleAnalysisType
MW-1	Group 1, 2, 3 Table 1	1/1/1979	6	Basal Bedrock (Volc.) Aquifer	117	65	100	35	49	35	All Analytes			
MW-10	Group 1, 2, 3 Table 1	Group 1 Table 1	Group 1, 2, 3 Table 1	Group 1 Table 1	7/1/1993	6	Basal Alluvial Aquifer	124	94	124	30	26	30	All Analytes
MW-11	Group 1, 2, 3 Table 1	7/1/1993	8	Basal Bedrock (Volc.) Aquifer	247	207	247	40	195	40	All Analytes			
MW-12	Water Level Only	Water Level Only	Water Level Only	Water Level Only	2/15/1995	4	Basal Alluvial Aquifer	230	214	230	18	129	16	Water Level Only
MW-13	Group 1, 2, 3 Table 1	9/5/1997	4	Basal Bedrock (Volc.) Aquifer	227	212	222	10	203	10	All Analytes			
MW-14	Group 1, 2, 3 Table 1	Group 1 Table 1	Group 1, 2, 3 Table 1	Group 1 Table 1	8/22/1997	4	Upper Alluvial Aquifer	64	39	59	20	47	12	All Analytes
MW-15	Group 1 Table 1	1/30/2001	2	Upper Alluvial Aquifer	75	64	74	10	32	10	Water Level and Field Parameters			
MW-17	Group 1, 2, 3 Table 1	10/19/2002	2	Upper Alluvial Aquifer	155	135	155	20	130	20	All Analytes			
MW-2	Group 1, 2, 3 Table 1	1/1/1979	6	Upper Alluvial Aquifer	80	28	78	50	66	12	All Analytes			
MW-20	Group 1 Table 1	Group 1 Table 1	Group 1, 2, 3 Table 1	Group 1 Table 1	10/4/2002	2	Basal Alluvial Aquifer	289	269	289	20	101	20	Water Level and Field Parameters
MW-22	Group 1 Table 1	Group 1 Table 1	Group 1, 2, 3 Table 1	Group 1 Table 1	5/12/2003	4	Basal Bedrock (Volc.) Aquifer	430	419	429	10	417	10	Water Level and Field Parameters
MW-23	Group 1, 2, 3 Table 1	4/1/2003	4	Basal Bedrock (Volc.) Aquifer	400	370	400	30	388	12	All Analytes			
MW-24	Group 1, 2, 3 Table 1	Group 1 Table 1	Group 1, 2, 3 Table 1	Group 1 Table 1	10/11/2002	2	Basal Alluvial Aquifer	255	235	255	20	74	20	All Analytes
MW-25	Group 1, 2, 3 Table 1	5/22/2003	2	Basal Bedrock (Volc.) Aquifer	180	160	180	20	110	20	All Analytes			
MW-26	Group 1, 2, 3 Table 1	6/22/2003	2	Upper Alluvial Aquifer	45	25	45	20	26	19	All Analytes			
MW-27	Group 1, 2, 3 Table 1	5/30/2003	2	Basal Bedrock (Volc.) Aquifer	184	103	183	20	45	20	All Analytes			
MW-29	Group 1, 2, 3 Table 1	6/1/2003	2	Upper Alluvial Aquifer	40	35	40	5	23	5	All Analytes			
MW-30	Group 1, 2, 3 Table 1	12/16/2005	2	Upper Alluvial Aquifer	81	60	80	20	18	20	All Analytes			
MW-31	Group 1, 2, 3 Table 1	12/14/2005	2	Upper Alluvial Aquifer	80	60	80	20	38	20	All Analytes			
MW-32	Group 1, 2, 3 Table 1	12/11/2005	2	Upper Alluvial Aquifer	141	121	141	20	83	20	All Analytes			
MW-33	<nul></nul>	<null></null>	<null></null>	<null></null>	12/9/2005	2	Upper Alluvial Aquifer	161	140	160	20	140	20	All Analytes
MW-34	Group 1, 2, 3 Table 1	12/17/2005	2	Upper Alluvial Aquifer	100	80	100	20	82	18	All Analytes			
MW-35	<null></null>	<null></null>	<null></null>	<null></null>	4/1/2008	4	Basal Alluvial Aquifer	288	265	285	20	78	20	All Analytes
MW-36	<nul></nul>	<null></null>	<null></null>	<null></null>	3/29/2008	4	Basal Alluvial Aquifer	281	260	280	20	146	20	All Analytes
MW-4	Group 1, 2, 3 Table 1	Group 1 Table 1	Group 1, 2, 3 Table 1	Group 1 Table 1	1/1/1979	0	Upper Alluvial Aquifer	102	60	95	35	42	35	All Analytes
MW-7A	Group 1 Table 1	7/1/1993	2	Upper Alluvial Aquifer	88	78	88	10	68	10	Water Level and Field Parameters			
MW-9A	Group 1, 2, 3 Table 1	7/1/1993	2	Upper Alluvial Aquifer	43	33	43	10	28	10	All Analytes			
MW-9B	Group 1 Table 1	7/1/1993	2	Basal Alluvial Aquifer	144	115	144	29	NM		Water Level and Field Parameters			
MW-A	Water Level Only	Water Level Only	Water Level Only	Water Level Only	<null></null>	<null></null>	<null></null>	<null></null>	<null></null>	<null></null>	<null></null>	<null></null>	<null></null>	<null></null>
MW-8	Water Level Only	Water Level Only	Water Level Only	Water Level Only	<null></null>	<null></null>	<null></null>	<null></null>	<null></null>	<null></null>	<null></null>	<null></null>	<null></null>	<null></null>
MWCH	Group 1 2 3 Table 1	Group 1 Table 1	Group 1, 2, 3 Table 1	Group 1 Table 1	8/12/1987		Basal Allunial Aquifer	250	149	250	101	NM		All Analytes

Fig. 4 Monitoring Well Table

backend DBMS tables. For example, Questa Mine monitors all active surface water seep flows, which are reported on an annual basis to USEPA as part of a NPDES condition. To comply with this requirement, an environmental staff member conducts the seep inspections on a monthly basis on-site. In turn, that staff member then enters that data into the field monitoring DBMS.

The NPDES permit condition requires that Questa Mine report any changes in seepage flow from the previous year. To conduct this analysis a date range query is created in the DBMS, which updates a "results table" that is joined with the Environmental GIS system. This allows staff to analyze the flow results in a spatial environment and subsequently a GIS exhibit is produced for the regulatory stakeholders, which fulfills that regulatory condition. Fig. 5 represents the "Annual Seep Flow" exhibit that is reviewed on a monthly basis and is produced annually as a permit condition. The product is intended to depict the current annual water flow, which is compared to the previous year in order to gauge whether the flow has increased or decreased.

By creating the DBMS system, which holds the environmental data, the user can retrieve

data and depict any monitored environmental theme in a geospatial platform within the Environmental GIS program. Additionally, the DBMS has built into the system, data integrity rules and queries that allow staff to evaluate compliance trends such as the pH readings for the NPDES requirements. The NPDES permit has a maximum and minimum compliance threshold that cannot be exceeded. Since the DBMS is available to all of the mine staff, a simple date range query can be entered, in order to evaluate the pH results and any other noncompliance trend. Fig. 6 is an example of the DBMS ph query that is used to evaluate compliance with the NPDES permit.

Value Added Products

Since the inception of implementing the Environmental GIS program at Questa Mine, additional environmental datasets have been created, which has added even more value to the system. Essentially it has been expanded to encompass all environmental regulatory obligations and the following are the datasets that reside within the geodatabase.

• Air Monitoring Identifies the location of all monitoring equipment and areas of



Fig. 5 Annual Seep Flows GIS Exhibit

Wolkersdorfer, Brown & Figueroa (Editors)



Fig. 6 Date Range pH DBMS Query

observation in accordance with the air permit.

- **Emergency Response** Location of incident, corrective actions, engineering controls, and history.
- **Sampling** Inventories all miscellaneous sampling conducted at the mine not related to the water permits.
- **Reclamation** Surface disturbance, treatment plots and history.
- Safe Drinking Water Raw water wells, monitoring locations, results.
- **Spill Prevention** SPCC Plan locations, tank locations, tank specifications.
- **Stormwater Inventory** of all engineering controls and as-builts.
- **Surface Drilling** Locations, permitting, footprint specifications.
- Transects Location and specifications.

In addition, the Environmental GIS datasets are provided to the entire mine staff, since the datasets have been published into an ArcReader.pmf format. The ArcReader software is part of the ESRI ArcGIS suite and works with maps authored within ArcMap. ArcReader is an easy-to-use desktop mapping application that allows users to view datasets and print their own maps. This allows anyone with an ArcReader license to view high-quality interactive maps authored in ArcMap which have been published with the ArcGIS Publisher extension. The following benefits have been recognized from implementing ArcReader licenses:

- Allows datasets to be deployed to mine staff, which are new to GIS and only have the interest in viewing Questa Mine's environmental datasets (*i.e.* aerials, well locations, and engineering controls).
- The distribution of the datasets has allowed mine staff to communicate more effectively and while also providing flexibility for graphically marking up maps and distribute internally via email.
- The application increases the knowledge of Questa Mine's regulatory obligations and the locations, requirements and specifics of each monitoring location.
- Lastly, the PMF file preserves a live connection to the datasets within the geodatabase, so the users have up to date views of the environmental themes.

Fig. 7 represents that ArcReader appearance that allows mine staff to become more familiar with Questa Mine's footprint and the associated themes.

Conclusions

At a time when mines are experiencing unprecedented regulatory scrutiny and oversight, Questa Mine's Environmental GIS has been found to be an essential tool in managing the numerous regulatory compliance obligations. Both the field monitoring DBMS and the GIS are dynamic systems, which frequently provide new deliverables at the mine site. Furthermore, the systems that are in place have greatly improved the organization of the envi-



Fig. 7 ArcReader Default Appearance

ronmental datasets since they are now located in one geodatabase. Before, many of the datasets were on hard copy maps or in Auto-Cad files. Adding to that benefit, is that all of mine staff has access to a database resource that can be used for disseminating and analyzing environmental themes in a very prescriptive regulatory environment. This has resulted in the staff becoming more aware of environmental monitoring locations, monitoring requirements, as well as providing a spatial product via the ArcReader application.

Nonetheless, this author believes that the success of the system was due to the pre-planning stage of developing both systems. Specifically, the step to develop a comprehensive needs assessment streamlined the process by flushing out priorities, and resources while providing a framework for constructing both systems. However, as with any data management system the challenge will be in maintaining the data integrity and the numerous datasets in an ever expanding mining regulatory environment.

Acknowledgements

The author wants to thank Chevron Energy Technology Company, specifically Muneer Majid and Tina Althea Morris for their assistance in developing the Environmental GIS program and an additional thanks for their comments on the first draft of this paper. Lastly, to all other authors who submitted one or more abstracts for IMWA 2013.

References

- Hughes Robert, Hewitt Michael, Using GIS to Remedy Coal Mining's Aftermath, ArcNews [Fall 2008], www.esri.com/news/arcnews/fallo8articles/usinggis.html
- Huang Shawn, Alvarado Anthony, Zevenbergen Lyle, Cochran John, Assessing the Success of Surface Coal Mine Reclamation, ArcNews [Winter 2011/2012], www.esri.com/news/arcnews/winter1112articles/assessing-the-success-of-surface-coal-mine-reclamation.html

Mine site water information disclosures in the context of watersheds and reporting frameworks, Eastern Australia

Wendy TIMMS¹, Shane LEONG², Ros TAPLIN¹, James HAZELTON², David LAURENCE¹

¹Australian Centre for Sustainable Mining Practices, University of New South Wales, Sydney, Australia. w.timms@unsw.edu.au

²Department of Accounting and Corporate Governance, Macquarie University, Australia

Abstract Information disclosures by mining companies regarding site water usage and discharge were evaluated within a watershed context, and compared with two sustainability reporting standards. Mining activity often impacts on water in the natural environment and its effects, which include pollution and water reserve depletion, can last for millennia. Communities may be concerned about whether the mining industry's use of water will have impacts on their livelihoods and lifestyle. In many parts of Australia for example, water levels and water quality are increasingly important issues, particularly because water licenses are fully allocated.

This paper reports on research examining disclosures from mining companies regarding their water usage in the Macquarie and Lachlan catchment areas, both parts of the Murray-Darling Basin in New South Wales, Australia. These requirements are then compared to the water reporting requirements of the Global Reporting Initiative (GRI) and Water Accounting Framework for the Minerals Industry (WAFMI). In addition, new ratio analyses for mine water in a watershed context are introduced.

It was found that of the nine mine sites identified, only four had substantial environmental reporting, including a coal and gold mining operation. Reported water use and discharge were a small proportion of average watershed values and compliant with development conditions, although information on water quality and flow variation over time was typically limited. Introduction of a dozen different ratios enable comparison of mine water data in a watershed context, for example: Fresh water take/Watershed storage; Fresh water take/Watershed surface flow, and Groundwater allocation/Watershed groundwater use. Based on these findings, the implications of the size of the local watershed around the mine site for which data was available was considered. The study also found that the development consent conditions for new projects and extensions to existing projects are quite significant, although local state legislation places few reporting requirements on mining companies. Reporting is required on all GRI indicators, although not necessarily to the same level of detail specified by the GRI. The reporting conditions also require some, but not all, of the information required by WAFMI.

A significant implication of this study is that even if the law does not mandate the preparation of social and environmental reports, it does not mean that this type of information is unavailable. Even though Australia does not have a mandatory corporate sustainability reporting regime, a significant amount of reporting resembling GRI requirements was nevertheless made publically available to local communities.

Regulating mine water releases using water quality trading

Sue VINK¹, David HOEY², Sarah ROBBINS¹, Estelle ROUX¹

¹Centre for Water in the Minerals Industry, The University of Queensland, s.vink@uq.edu.au ²NSW Office of Water

Abstract Management of saline water release from coal mines in the Fitzroy Basin Queensland, Australia, is challenged by extreme climate variability and by the ephemeral nature of the receiving river systems. In the past decade, extended periods of drought and the floods of 2007/08 and 2010/11 have tested both strategic and operational mine water management practices, infrastructure and regulation of mine water release. Mine water release is currently regulated by the Fitzroy Model Conditions, a licence-based system which allows for increasing release rates with increasing flow in the receiving waters. The purpose of this study was to evaluate the technical feasibility of implementing a market-based cap-and-trade mechanism for managing saline mine water release into rivers of the Fitzroy basin.

Keywords mine water release regulation, environment, salinity, trading

Introduction

Water quality trading is a market-based approach to water quality regulation, intended to increase flexibility in meeting regulatory requirements with the potential to lower abatement costs. A review in 2009 identified 26 active water quality trading programs world-wide, two of which are currently operational in Australia: the Hunter River Salinity Trading Scheme (HRSTS; Fig. 1) and the South Creek Bubble Licencing Scheme (Selman *et al.* 2009). Types of water quality trading schemes include exchange markets, bilateral trades and sole-source offsets, amongst others (Selman *et al.* 2009).

The HRSTS is one of two water quality exchange markets operational worldwide and

has been attributed as one of the water quality trading programs that comes closest to commoditising water quality credits (Selman *et al.* 2009). The success of the market is attributed in part to having a large number of regulated entities able to participate, creating depth and fluidity in the market space (Selman *et al.* 2009). It is also enhanced by real-time knowledge of market conditions, transparency of data and rules used to operate the system, and involvement of all stakeholders in developing operating rules.

There has been increasing interest in the potential to implement a salinity trading scheme in the Fitzroy catchment (Fig. 1) over recent years. Since 2008 Bowen Basin coal



Fig. 1. a. Hunter River catchment NSW; and b. Fitzroy Catchment (Queensland).

mines have experienced consecutive wet seasons with higher than average rainfall. Excessive rainfall and tighter regulation of mine discharge in the basin has resulted in the accumulation of large volumes of water on most mine sites. It is estimated that most of this water has salinity approximately 6000 mS/cm, around 4 times higher than the end of pipe discharge criteria set in the 2009 Fitzroy Model Conditions. To assist in alleviating concerns with storages reaching their capacity and the compromise to coal production, the Department of Environment and Resource Management (DERM; now EHP) has been granting Transitional Environmental Programs (TEP) to enable discharge of excess mine water. These licences are issued in emergency or other extreme situations in order to ensure safe operation of the mines. While the conditions for release set in the TEP's is reducing the volume of water currently held on sites, there remain significant questions regarding how best to regulate and manage mine water discharge in the basin on an ongoing basis.

Overview of Hunter River Salinity Trading Scheme

In the Hunter catchment in NSW, the Hunter River Salinity Trading Scheme (HRSTS) has successfully managed saline mine release for over a decade. The scheme has been credited for the effective management of cumulative impacts of saline water release in the Hunter River, resulting in water quality objectives being achieved more frequently, whilst providing flexibility to industry. Point source saline discharges in the Hunter Valley were historically regulated by traditional 'trickle discharge' licensing strategies. The primary reason that this system was unsuccessful was that small volumes of saline water could be released at all times, irrespective of river flow or ambient salinity conditions (DoP 2005). A further criticism was that the system was unworkable for operators, being non-flexible and not allowing for licence holders to take advantages of the assimilative capacity of high flow periods.

In general the Hunter River can have naturally elevated salinity (Cameron 2010) especially where tributaries cross Permian geology. Records indicate that creeks within the upper catchment can have salinity between 4000 – 6000 μ S/cm (DoP 2005). In periods of low flow, base flow of the Hunter River is fed by groundwater which typically has elevated salinity between 1000 – 3000 μ S/cm (NSW OEH 2010). Conversely, in periods of high rainfall and runoff, salinity is substantially reduced , to as low as 350 μ S/cm (DoP 2005). Sources of salinity to the river system include both natural, due to the marine origin of the sediments in the region, and anthropogenic sources.

Whilst it was accepted that the majority of salinity in the Hunter River system is derived from natural sources, diffuse and point discharges of saline water from agriculture and industry were recognised as significant environmental management issues in the region. These problems were particularly critical during periods of low river flow when consequences for aquatic ecosystems and other users were the most acute.

The HRSTS was developed as an alternate system for multiple point source saline discharge regulation. The scheme is a market-based cap and trade system, which uses a system of tradable salinity discharge credits to limit the total amount of salt discharged in the Hunter River system from point-source industrial activity. The scheme was developed in consultation between the NSW State Government, mining industry, electricity generators, agricultural interests and environmental groups (DoP 2005). A pilot salinity trading scheme commenced in the Hunter Catchment on 1 January 1995. Fig. 2 shows the mean monthly Electrical Conductivity at Singleton from 1980 and 2000. Prior to introduction of the pilot scheme, the 900 µS/cm target was exceeded 35 % of months. This was reduced to 4 % of months in the 5 year period of the pilot scheme (EPA 2001). In 2002, the Protection of the Environment Operations (Hunter River


Fig. 2 Mean monthly Electrical Conductivity at Singleton 1993 – 2013. Red line is the salinity target.

Salinity Trading Scheme) Regulation 2002 (NSW; the Regulation) was passed which formally implemented the trading scheme.

Under the Hunter River Salinity Trading Scheme, discharges of saline water into the Hunter River are permitted only during periods when the Hunter River is considered to be in high flow or flood flow, and only by parties that hold a discharge licence and discharge credits. Allowable maximum salinity in the river during discharge events is set as 900 µS/cm at Singleton (the most downstream monitoring point of the scheme). Currently 13 mines and 3 power stations participate in the scheme. A credit entitles a discharge licence holder to discharge 0.1 % of the total allowable discharge of salt, determined on a daily (or more frequent basis) dependant on the ambient environmental river flow and salinity conditions.

The scheme involves real-time river monitoring to detect stream flow and ambient salinity conditions and load-based calculations to determine a Total Allowable Discharge (TAD) of salt, noted as the window of opportunity (Fig. 3). This method is similar to the USEPA method for calculating total daily maximum loads.

Under the scheme, mines and industry can discharge according to the number of salt discharge credits they hold. These credits are sold at auction and also traded between users to allow for the market to determine the price of credits. The HRSTS has allowed for better regulation of cumulative impacts of discharge in the Hunter River and has provided increased flexible to mines and industry.



Regulation of Mine Water Discharge in the Fitzroy Catchment

Current discharge license conditions for mines in the Fitzroy catchment are specified in the Fitzroy Model Conditions. These conditions regulate end-of-pipe flow and salinity of mine water released to streams. These relatively conservative conditions were based on the best available data and designed to minimise impacts of mine discharge by ensuring that only water with a relatively low conductivity was discharged into streams with sufficient flow for dilution to achieve background stream salinities, typically around 300 µS cm⁻¹.

TEP's granted to individual mines to alleviate excess water accumulation, allowed water with higher salinity (up to $6,500 \mu$ S/cm) to be released with less dilution from upstream flow. While the granting of the TEP's is providing relief for the current situation, limited periods of stream flow, due to the ephemeral nature of the majority of streams, continues to restrict the volume of water able to be discharged. In addition there has been a considerable impost on the regulator considering TEP applications and anxiety on the part of the mines in terms of lost production and increasingly hazardous conditions of storages.

The overall objective of the work was to explore whether an alternative framework, similar to the salinity trading scheme currently used in the Hunter Valley, might be a more effective model to manage mine water release in the Fitzroy Catchment. Two sub-catchments (Isaac River and Mackenzie River) will be used as representative examples of the characteristics of streams in the Fitzroy catchment.

Comparison of hydrology and salinity relationships

Stream flow in the Fitzroy catchment is generally much larger and more variable than in the Hunter River (Fig. 4). Sub-catchment flows in the Isaac River are of similar magnitude as the Hunter River. Fig. 1b shows the ephemeral nature of the streams reflective of natural flows in the catchment. The Isaac River sub-catchment has approximately the same area as the Hunter River catchment. The ephemeral nature of stream flow in many catchments severely reduces the number of opportunities for mine discharge.

Fig. 5 shows the relationship between salinity and stream flow in the Mackenzie River. Similar relationships are found in the Isaac River. It can be seen that the largest decrease in salinity occurs during the first flow events in the system at the beginning of the wet season. Later in the season there is very little decrease in salinity with flow. In fact the largest flow events exhibited a minimal corresponding decrease in salinity. Although characterising flow/salinity patterns in the Fitzroy was challenged by data availability & mine water discharge, the reduction in salinity during flow events was more moderate and variable in the Fitzroy compared to the Hunter River resulting in an overall lower assimilative capacity.



Fig. 4 Comparison of streamflow characteristics of the Isaac and Mackenzie River sub-catchments with the Hunter River.



In the HRSTS, 12 hours advance notification time of an opportunity to discharge is considered the minimum degree of notice to allow sufficient time for salinity credit trading and preparation for discharge on sites. Often 24-48 hours notification can be given, particularly for the middle and lower sectors of the Hunter. Travel times for peak flows are much faster in the Fitzrov catchment. Fig. 6 shows typical travel times for flows in the Isaac River. It can be seen that mines located upstream of Goonyella would be required to prepare and trade credits within 10 hours of a stream flow event. Downstream of this point travel times increase but are still within 24 hours to Deverill. The majority of mines in this catchment are located upstream of Deverill. The implications of this is that both the mines and regulator will be required to invest in significant automated monitoring and infrastructure associated with releases. The risk is that if the monitoring/release system malfunctions the likelihood of noncompliant discharge would be increased. In addition, the current model used to predict river flow would require significant upgrades to better predict salinity- flow relationships in order to allow calculation of total allowable discharge reliably and faster. One method to achieve this is to use real time rainfall measurements to drive the model, noting that in these catchments rainfall and rainfall intensity are highly spatially variable. This would represent not only a significant advancement of catchment models generally, but increases the level of risk if it is used solely as the means of authorising discharges. However, it could be used as a 'be prepared' warning for discharges

There are also significant implications associated with the location of the control monitoring points where total allowable salt load is calculated in the upper Isaac River. To maintain water quality objectives within the upper Isaac River, control points should be set upstream of the confluence with the Connors River, i.e. upstream of Yatton (Fig. 6). Flows from the Connors River provide considerable dilution of flows in the Isaac River. Thus if the control point is located below this confluence salinity in the upper Isaac River is likely to be much greater than the water quality objective. In addition, there are some instances where the Isaac River has relatively low flow compared to the Connors River. Thus, a monitoring point located downstream of the Connors river confluence may indicate suitable flows and salinity for mine discharge to occur, when conditions in the upper Isaac River may not be suitable

Conclusions

Balancing mine water management and regulated discharge in ephemeral streams is challenging. Opportunities for mine water releases are limited and the lack of flow and a predictable flow salinity relationship complicates planning arrangements. From the analysis given above it can be seen that the stream flow and salinity characteristics of rivers in the Fitzroy catchment have a lower assimilative capacity and significantly faster travel times than the Hunter River. The ephemeral streams, such as the Isaac River, also provide far fewer opportunities for mine water release due simply to the lack of stream flow throughout most of the dry season. In addition, careful consideration must also be given to the location of control monitoring points to ensure that sufficient flow and



Fig. 6 Travel times of peak flows in the Isaac River.

salinity conditions exist in the river for mine discharge to occur.

The flow and salinity relationships in the Fitzroy catchment are not likely to allow direct translation of the Hunter River Salinity Trading Scheme as a mechanism for regulating mine water discharge management in the Fitzroy. Significantly more monitoring stations would be required to link to an automated network. In addition significant investment would be required to enhance the predictive capability of catchment models, particularly where stream flow is highly dependent on spatial rainfall characteristics. Perennial flowing streams with more predictable flow-salinity relationships may be more suited to this type of regulatory regime.

References

- Cameron, K (2010) Technical Feasibility of a Salinity Trading Scheme for the Licensing of Coal Mine Releases in the Fitzroy Basin. Research dissertation (Environmental Engineering), The University of Southern Queensland.
- DOP (2005) Coal mining potential in the Upper Hunter Valley – Strategic assessment, NSW Government Department of Planning.
- EPA (2001) Draft Proposed Protection of the Environment Operations (Hunter River Salinity Trading Scheme) Regulation 2001. NSW Government Environment Protection Authority.
- Selman, M., Greenhalgh, S., Branosky, E., Jones, C. & Guiling, J. (2009) Water Quality Trading Programs: An International Overview. World Resources Institute, Washington DC.

Development and application of water quality criteria for reliable management of off-site risk

Phillip L. Whittle¹, Ross E. W. Smith¹

¹Hydrobiology, 7 Forrest Avenue, East Perth, W.A., Australia, phil.whittle@hydrobiology.biz

Abstract The development and application of water quality criteria (guidelines) for mine water discharges and downstream receiving waters is critical to the management life-of-mine off-site risk for mining operations. While regulatory requirements may cover compliance risk, they may not protect all receiving environment values and may be under or over protective in different regulatory and climatic circumstances. International sets of water quality guidelines and management approaches are reviewed including those of the US, Canada, Australia, Europe (EC) and southeast Asia. The authors provide recommendations with respect to understanding the risks managed by industry best practice approaches to water quality criteria development.

Keywords guidelines, water quality, criteria, management, discharge.

Introduction

Setting quantitative water quality targets or criteria for mine discharges is a common requirement for proposed, active and closed mining operations. These criteria are required for both regulatory and engineering purposes, the former to establish a level of acceptable impact and the latter for feasibility, design and cost calculations. While "motherhood" statements about the intended level of impacts to social and environmental values may provide social and political acceptance for a project, quantitative targets will need to be established to put these statements into practice. Typically the targets will be set in terms of measurable parameters which are monitored over time to establish compliance with the level of impact agreed to by the project stakeholders.

In most developed nations the regulatory requirements for the quality of mine water discharges are clearly defined, if often complicated. The requirements in many developing nations can be less well defined as well as not protective of stakeholder values either locally to the project or internationally. In any case project proponents or operators should recognize the difference between regulatory compliance and risk mitigation. It is important to understand the level of risk mitigation achieved through implementing regulatory water quality criteria and to have considered the adoption of more stringent project specific criteria where residual risk would be unacceptable to the project.

Methods

This paper was developed through years of consulting experience in the field of mine water quality management and impact assessment by the authors as well as a literature review. Literature was sought outlining the philosophy behind the setting of water quality criteria in a suite of developed nations/regions (Australia, Canada, European Union and the US) and developing nations (China, Indonesia, Papua New Guinea and the Philippines). In order to restrict the scope to a manageable size, only criteria/guidelines for aquatic ecosystem protection have been formally referenced. There are many other water quality values that are often protected within the same or parallel frameworks in any given national guidance (e.g. recreational, drinking water, stock water, industrial supply).

Discussion Backaround

The developed nations reviewed displayed a common approach with respect to setting numerical water quality criteria for the protection of aquatic ecosystems in that all placed ecotoxicity tests as a corner-stone in the process (ANZECC/ARMCANZ 2000, Environment Canada 1987, EU 2008, USEPA 1985). However, there were distinct differences in the level of standardization and scientific method used. Despite default criteria being largely derived from assessment of ecotoxicity testing data, almost universally there were alternate methods established in the guidance to allow regional, catchment wide and site specific criteria to be developed (e.g. ANZECC/ARMCANZ 2000, USEPA 1985, CCME 2007, MacDonald Environmental Services Ltd 1997). A common alternative to default guidelines is to allow an acceptable variance from the baseline conditions in the receiving waters as well as conducting ecotoxicity testing on local organisms for the substance of concern. In contrast, the EU has adopted a set of Environmental Quality Standards (EQS) that are common to all member states and which do not allow for regional variation (EU 2008).

There are variations around how substance toxicity data is applied to real-world management, which mirrors the complexity of transposing largely laboratory derived results to diverse aquatic ecosystems. In addition there are mitigating factors (e.g. water hardness, complexing molecules and organism adaptation) and antagonistic factors (e.g. stress from multiple toxic substances as well as pathogens) which are partially incorporated into criteria application in some national guidance (e.g. ANZECC/ARMCANZ 2000, CCME 2003) and not in others (e.g. EU 2008). It is common for guidance on criteria selection to be directed at water use (objective/value) with ecological protection being one of a number of categories of "use", each of which has its own set of numerical water quality criteria. Further, within the category of environmental protection most guidance has incorporated two or more levels of protection based around either the length of time exposed to pollutants (chronic or acute; CCME 1999, CCME 2012, USEPA 2012) or the sensitivity of the ecosystem (ANZECC/ARMCANZ 2000).

The fact that most guidances on setting of water quality criteria are based on scientific testing of the toxicity of specific substances indicates that this is a best practice mechanism for assessing the risk from these substances in the environment. However, there are complications in applying these test data to managing aquatic ecosystems which have diversified the guidelines in this regard. While the more mature and resourced environmental regulatory bodies in developed nations have attempted to address this complexity to some degree, many if not most developing nations do not. The developing nations reviewed all had water quality criteria that was relative to the designated use of a water body (e.g. drinking, recreation, irrigation) though were universally less sophisticated in addressing acute/chronic toxicity ismitigating/antagonistic sues. factors. ecosystem sensitivity or other issues with setting static numerical criteria (DENR 1990a and 1990b, ROI 2001, ROI 2003, ROI 2010, PRC 1984, PNG 2000 and 2002).

A common issue with the developing nation water quality criteria reviewed was that it was either not specific to ecosystem protection (e.g. ROI 2001 and DENR 1990) as well as it contained values that were well above what is considered protective by "best practice" ecotoxicity risk based guidelines (e.g. DENR 1990, ROI 2006, PNG 2002). Older style guidelines often set water quality criteria based on the ability to detect the substance of concern using available standard methods and instrumentation at the time of development and in general usage in laboratories within each country. As the instrumentation improved to be able to detect orders of magnitude lower concentrations the guideline criteria were not similarly amended. This may be a reflection of the often basic and aged instrumentation available in developing nation government labs in the past and the slow pace of adoption of new technologies where funds are insufficient for environmental laboratories to purchase as well as operate them. The authors are aware of instances of donations of new analytical instruments to developing nation environmental laboratories by overseas aid agencies only for the instrumentation to sit unused due to the lack of funding for supplies, maintenance or training of staff in their operation.

There are numerous issues with the application of numerical water quality criteria to specific aquatic environments which have recently been highlighted by the attempts of the United Nations to derive "international" guidelines (UN-Water 2011, UNEP/IWAG-TU 2012). In Australia and Canada the indigenous (first nations) cultural and spiritual values around water have been acknowledged if not smoothly integrated with the scientific management approach (CAGS 2013, DSEWPC 2012, CCME 1999). This is in nations with the financial and institutional resources to attempt to address these issues. In many developing nations the use of water has strong cultural links and perception of impact is as important to stakeholders as any scientific attempt to quantify it. These developing nations have, in general, fewer resources to manage water quality which in turn leads to less certainty on the level of risk to all water related values including cultural, ecosystem protection and economic uses.

Implications for managing mine water discharges

While in developed nations it may be acceptable for mining projects to meet the local criteria for water discharge quality as being arguably "best practice", this is often not the case for projects in developing nations. Multinational mining companies operating in developing countries have to respond to shareholder and international stakeholder expectation for management of environmental risks as espoused in the International Council on Mining and Metals Sustainable Development Framework, which may push them towards implementing water quality objectives that are more stringent than the national regulations require. National companies may also follow this path due to ethical as well as moral considerations, external stakeholder pressure, a desire to work to international best practice or the need to satisfy the requirements of funders and other stakeholders. In order to satisfy international funding (e.g. IFC 2012) risk management requirements, as well as corporate image/governance policy, mining companies are drawn to meet international best practice for projects in developing nations where regulatory requirements may not. Putting aside the moral implications of spending project funding on meeting standards that the developing nation may not have asked you to meet (and thereby reducing tax revenue), the issue then becomes what criteria should the project apply? As noted above, developing water quality criteria is complicated but choosing a set of criteria that are more stringent than those of the local legislation and then applying them is even more so.

Once a mining project starts down the path of setting its own water quality criteria it can choose to adopt default values from a "best practice" developed nation (IFC 2007), develop a table of criteria from a range of different but scientifically defensible sources as well as establish the baseline conditions for the receiving waters to propose an acceptable change over natural variability. This process may or may not involve establishing the values requiring protection within the receiving waters, based on stakeholder engagement as well as expert review. A critical point is that compliance with the local regulatory requirements in developing nations may not remove the risk to the project of being liable for unforeseen impacts. The same may well be true in developed nations, but the greater rigor of the regulatory framework shifts more of the burden of responsibility for the risk to the government as agency for the wider stakeholders.

It is typically hard to justify combining water quality criteria from multiple sets of national guidelines unless the required parameter suite is not available from a single guidance document. The Australian, Canadian and USEPA guidelines all have standardized approaches to setting numerical criteria which are slightly different from each other. In addition, using criteria meant to be protective of one use to manage a different receiving body water use objective is unlikely to be acceptable. An example of this would be using the drinking water criteria for metals where ecological criteria are not available. The human health risk from many metals is much lower than the aquatic ecological risk due to the different pathways of uptake and detoxification for humans, particularly the lack of gill and general body surface uptake pathways.

The Australian guidelines allow the setting of numerical water quality criteria based on an allowed variance from the existing of baseline conditions for the substance of concern. In its default form this approach requires the median concentrations of the impacted (post mine discharge) waters to be below the 80th percentile of the baseline or non-impacted waters (ANZECC/ARMCANZ 2000). This approach uses existing conditions as a guide though has timing issues where the baseline is highly variable and the mine discharge more constant. It also assumes that all substances of concern have the same linear risk increase with respect to increases over baseline concentrations, which is not always the case. Using a combination of the default numerical criteria (which are ecotoxicity based) and acceptable variance from baseline, lowers the risk that existing system will not be unacceptably impacted.

The highest cost, though potentially lowest residual risk approach is to conduct whole effluent or direct toxicity assessment (WET or DTA in the different guidances) where various concentrations of the mine water discharge is mixed with the receiving water under laboratory conditions to assess the toxicity to specific aquatic organisms. This approach covers several of the issues with default trigger values including assessing the mitigating and antagonistic effects of constituents of both the discharge and receiving waters. It also informs potential cumulative impacts as a range of dilutions are tested allowing for assessment of changes in the relative ratios of discharge and receiving waters. The results from WET/DTA testing still require expert ecotoxicological interpretation as the laboratory conditions can never fully replicate the receiving environment, including complex food webs, chronic bioaccumulation/sediment storage and biotransformation geochemical processes (ANZECC/ARMCANZ 2000, USEPA 1985).

A multiple-lines-of-evidence approach is likely to provide the best assessment of the risk from any given mine water discharge. Having an understanding of the hydrology, ecology and physico-chemical characteristics of the receiving environment, including the variability of each aspect, allows for the identification of higher risk conditions. An example would be a river system that has periods of very low flow, anoxia and high water temperatures which could be improved in terms of physiological stress to aquatic organisms by a constant mine discharge of high water quality or the naturally stressed ecosystem could be catastrophically impacted by a water quality discharge that would be considered of minor water quality implications under other circumstances.

Understanding factors such as the sensitivity of the aquatic flora and fauna to any substance of concern can promote adaptive management approaches including lowering or avoiding discharge during critical life-stages. Mining projects can collect valuable information during baseline studies, suitable for ecotoxicity assessment of planned discharges, with relatively minor additional cost. Parameters such as water hardness, major ion concentrations, dissolved organic carbon (mitigates some metal toxicity), sediment particle size and organic carbon content, periphyton coverage (algae that grows on submerged rocks) and flow volume variability can be added to existing water quality monitoring programs for relatively minor additional cost over those of the parameters of potential concern.

Conclusions

The development and application of water quality criteria for the reliable management of off-site risk requires going beyond default guidelines, regardless of the international standing of those guidelines. While the major international guidelines are typically risk assessment based, they also contain considerable guidance and recommendations on going beyond the default criteria they provide. This is the reason that even within Australia. Canada, the EU and the US there are regional and even water body specific guidelines developed under the national frameworks. If different aquatic ecosystems within the same region require their own numerical water quality criteria to be protective (i.e. mitigate the risk of adverse impacts) then it is reasonable to assume that the same may be true of the receiving waters for any mine discharge. This is particularly true when the mine is in a different country and even bio-climatic region. In developing countries with less protective water quality regulation frameworks, simple compliance may not adequately manage environmental risk, and international funding requirements and stakeholder expectations will often drive the need to take a more risk-based approach to water quality management and assessment.

Mining operations can significantly reduce the risk of unacceptable impacts to receiving water ecological values by implementing a set of risk based criteria systematically derived from ecotoxicity data such as those from Australia, Canada or the US. However, the degree of residual risk should be at least assessed as acceptable through understanding of the limitations of the chosen default criteria in the context of the local receiving ecological system.

References

- ANZECC/ARMCANZ (2000) National Water Quality Management Strategy (NWQMS) Guideline 4 – Australian and New Zealand Guidelines for Fresh and Marine Water Quality, Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand.
- CAGS (2013) The Revision of the Australian and New Zealand Guidelines for Fresh and Marine Water Quality (2000) – Joint Steering Committee: Revision Update – April 2013. Council of Australian Governments (CAGS) Standing Council of Environment and Water National Water Reform Thematic Oversight Group.
- DSEWPC (2012) Indigenous cultural and spiritual values in water quality planning. Report prepared by Neva Collings for the Department of Sustainability, Environment, Water, Population and Communities (DSEWPC), Government of Australia. 21 May 2012.
- CCME (1999) Canadian Water Quality Guidelines for the Protection of Aquatic Life. Canadian Council of Ministers of the Environment 1999.
- CCME (2003) Guidance on the Site-Specific Application of Water Quality Guidelines in Canada: Procedures for Deriving Numerical Water Quality Objectives. Canadian Water Quality Guidelines for the Protection of Aquatic Life – Site-Specific Guidance. Canadian Council of Ministers of the Environment 2003.
- CCME (2007) A Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Life 2007. Canadian Water Quality Guidelines for the Protection of Aquatic Life – Protocol. Canadian Council of Ministers of the Environment 2007.
- CCME (2012) Scientific Criteria Document for the Development of the Canadian Water Quality Guidelines for the Protection of Aquatic Life – Trichlorfon. Canadian Council of Ministers of the Environment, November 2012.
- DENR (1990) DENR Administrative Order No. 34 (Series of 1990) – Revised water usage and classification Water Quality Criteria Amending Section Nos: 68 and 69, Chapter III of the 1978 NPCC Rules and Regulations (corrected version). Department of Environment and Natural Resources, Government of the Philippines.

- DENR (1990) DENR Administrative Order No. 35 (Series of 1990) – Revised Effluent Regulations of 1990. Revising and Amending The Effluent Regulations of 1982 (corrected version). Department of Environment and Natural Resources, Government of the Philippines.
- Environment Canada (1987) Federal Water Policy. Government of Canada. www.ec.gc.ca/eau-water/ D11549FA-9FA9-443D-80A8-5ADCE35A3EFF/e_fedpol.pdf
- EU (2008) Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy. European Union.
- IFC (2007) Environmental, Health, and Safety General Guidelines. April 30, 2007. International Finance Corporation – World Bank Group.
- IFC (2012) Performance Standard 6 Biodiversity Conservation and Sustainable Management of Living Natural Resources. January 1, 2012. International Finance Corporation – World Bank Group.
- ROI (2001) Government Regulation 82/2001 Management of Water Quality and Control Over Water Pollution. Dated 14th December 2001. The President of the Republic of Indonesia.
- ROI (2003) Decree of State Minister for Environmental Affairs (Regulation) No. 110/2003 – Guidelines on Stipulation of Accommodating Capacity of Load of Water Pollution in Water Sources. Republic of Indonesia.
- ROI (2006) Regulation of the State Minister of Environment No. 09/2006 – Standard of Quality of Waste Water for Nickel Ore Mining Business as well as Activity. Republic of Indonesia.
- ROI (2010) Regulation of the State Minister of Living Environment Number 01 Year 2010 – Water Pollution Control System. Republic of Indonesia.
- PRC (1984) Law of the People's Republic of China on the Prevention and Control of Water Pollution. Adopted at the Fifth Meeting of the Standing Committee of

the Sixth National People's Congress and promulgated by Order No. 12 of the President of the People's Republic of China on May 11, 1984, and effective as of November 1, 1984.

- MacDonald Environmental Services Ltd (1997) Water Quality – Methods for Deriving Site-Specific Water Quality Objectives in British Columbia and Yukon. November 1997.
- PNG (2000) Environmental Code of Practice Mining Industry. Office of Environment and Conservation, Government of Papua New Guinea.
- PNG (2002) Environmental (Water Quality Criteria) Regulations 2002. Independent State of Papua New Guinea. No. 28 of 2002. Regulation established under the Environment Act 2000.
- USEPA (1985) Guidelines for Deriving Numerical National Water Quality Criteria for the Protection Of Aquatic Organisms and Their Uses. Report by by C.E. Stephen, D. I. Mount, D. J. Hansen, J. R. Gentile, G.A. Chapman, and W. A. Brungs. Report No. PB85-227049.
- USEPA (2012) Aquatic Life Ambient Water Quality Criteria for Carbaryl – 2012. United States Environmental Protection Agency (USEPA), Office of Water, Report EPA-820-R-12-007.
- UNEP/IWAG-TU (2012) Scoping Study International Water Quality Guidelines for Aquatic Ecosystems. Project No. 2011-CPL-5060-3B41-1131-2201. Principal author Dr. Paul T. Yillia, Vienna University of Technology – Institute for Water Quality, Resources and Waste Management (IWAG-TU) for the United Nations Environment Program (UNEP). 25th January 2012.
- UN-Water (2011) Policy Brief Water Quality. United Nations. www.unwater.org/downloads/waterquality_ policybrief.pdf

Management of Mine Water Quality Data from Permitting to Compliance to Closure

Susan WYMAN¹, Makinsey HARMON²

Whetstone Associates, 104 W. Ruby Avenue, Gunnison, Colorado 81230, USA; ¹*swyman@whetstone-associates.com;* ²*mharmon@whetstone-associates.com*

Abstract Data management is a critical link between effective mine water monitoring efforts and informed data analysis and decision making. Developing efficient systems for sample tracking, data validation, storage, retrieval, presentation, and analysis are increasingly important in organizations with limited time and resources. Mine permitting in the United States requires ever-increasing standards for verification and validation of laboratory water quality data. Routine compliance reporting, evaluation of Best Management Practices (BMP) effectiveness, monitoring plan modification, and closure decision-making also rely on accurate and accessible water quality data. Today's technical professionals expect that water quality data be understandable, usable, sharable, secure, and transferable among interested parties.

Keywords environmental database, data validation, statistical analysis, mine permitting, compliance monitoring

Introduction

Large quantities of environmental data are generated during mine permitting, operation, and closure. Successful projects require efficient, accurate, and cost-effective management of environmental data. Gone are the days of dozens of spreadsheet files as the central repository for environmental data. Mining companies, regulators, and consultants have made great strides over the last 20 years toward robust water quality and environmental database systems. Centralized storage of environmental data provides an "official" version of the data, which serves as a valuable resource for project consistency and accuracy. Data management is a critical link between effective mine water monitoring efforts and informed data analysis and decision making.

The purpose of this paper is to describe the relational database structure, list some of the software currently available for managing environmental data, provide general requirements for environmental databases at various phases of the mining project, and provide specific tips and tricks unique to databases for mining projects.

Alternatives to Relational Databases

Several alternatives exist for managing environmental data, depending on the size of the project, scope of the investigation, budget, and user capabilities.

Spreadsheets –Spreadsheets such as Excel are convenient ways to chart and analyze data. Environmental data is typically presented in crosstab format, with samples listed across the top and parameters down the side, or viceversa. However, spreadsheets are limited in size (1,048,576 rows by 16,384 columns in Excel 2010), are easily editable, and standards are typically not enforceable. Users can delete data within a spreadsheet, and most spreadsheets are not set up to require values or enforce restrictions on the data being entered. While useful for data presentation and transfer, spreadsheets are not recommended as a secure, archival repository for large environmental datasets.

Flat files – The laboratory electronic data deliverable (EDD) is typically provided as a flat file, consisting of one analytical result per row. Flat files take up a lot of file space due to duplication (each record contains information for the site, station, date, time, and sample ID). Although a spreadsheet flat file may be sorted and filtered, flat files are generally difficult to read and interpret. The flat file is a useful mechanism for transferring environmental data, but not for using the data.

Laboratory Information Management System (LIMS) – Some laboratories provide online access to their LIMS, which allows for downloading flat-file data or exporting crosstab queries to Excel spreadsheets. Laboratories typically limit the length of time that data is available, and users are limited to software features developed by the lab's IT team. Queries are limited to laboratory results (not lithology, depth, sub-basin, or other spatial qualities) and are therefore less robust than with a fully developed environmental relational database.

Environmental Relational Databases

Relational databases organize the data into tables, and link those tables based on defined relationships. These relationships enable the retrieval and combination of data from one or more tables with a single query. At the most fundamental level, an environmental relational database will consist of Stations, Samples, and Results in a one-to-many $(1 \rightarrow \infty)$ relationship (Fig. 1). Lab parameters are listed in a lookup table (LUT), also known as a valid value list (VVL), which forces the database to use consistent parameter names (*e.g.* "Mercury, dissolved" and not "Hg, diss" or "Mercury, diss."). If a lab is reporting parameters using non-standard names, the Parameter_Aliases table is used to generate consistent parameter IDs.

A more complex relational database structure for a mine site is shown in Fig. 2.Although the relationships may seem complicated at first, the fundamental database structure is the same (Stations $1 \rightarrow \infty$ Samples $1 \rightarrow \infty$ Results). Relationships are set up to investigate correlations between borehole geology, lithology, and water chemistry (Fig. 2). Samples can be grouped by station type (monitoring well, domestic well, seep, spring, pond, exploration borehole), sub-basin, site, lithologic unit, or nearly any common criteria. Data validation can be automated by tracking cooler receiving temperatures, sample holding times, blind field duplicate samples, and laboratory QC batches (Fig. 2).



Fig. 1 A simplified Environmental Relational Database contains tables for Stations, Samples, and Results.



Fig. 2 Relationships in a standard Environmental Relational Database.

"Bulk data" refers to data that doesn't easily fit into the samples/analyses data model, such as time sequence data such as from level loggers and multi-parameter probes, downhole sensor data sensor, shaft or well water quality profiles, and two- and three-dimensional survey data. These datasets often contain large numbers of sample points that are best organized differently than typical laboratory results. While such datasets were typically stored outside of an environmental relational database, some databases have the ability to efficiently handle, store, and retrieve bulk data.

Relational Database Software

Numerous environmental database software packages are available commercially, including EIM, ChemPoint/ChemStat, Enviro Data/EnviroSpase, EQWin, Visual Site Manager (VSM), DataSight, HydroGeo Analyst, EQuIS, ESdat, and others. Historically, custom environmental databases were developed for specific projects using Oracle, Access, SQL Server, or other common database platforms. However, many projects are moving toward standardized, supported, off-the-shelf software. Several factors may be considered in selecting the environmental relational database software for a mining project:

- Initial and ongoing costs and number of user licenses
- Ease of use
- Portability, transferability, and shareability between users
- Ability to import and export between applications (*e.g.* Surfer, RockWare, EVS, EnviroInsite. EPA's ProUCL, Air Force ERPIMS)
- Regulatory requirements (some agencies require a specific software package, for example Colorado Division of Public Health and Environment formerly required EQulSand has now adopted EnviroData[®]. Some agencies simply require that the data be exportable between different databases).
- Support, flexibility

Our firm has standardized most of our mine water quality and geochemistry databases on the Enviro Data® software based on technical support, flexibility, and price (US\$1,000 Viewer, US\$4,000 Single Use Full, US\$5,000 Concurrent Use Full). Enviro Data® operates on the Microsoft Access® platform (for up to about 200,000 records on a network or 500,000 records on a standalone PC) and on Oracle or SQL Server platforms for larger database applications. We also maintain databases in MS Access and ChemPoint/ChemStat. The concepts presented below are applicable to most environmental relational databases, and are not unique to a specific software package.

Numerous water quality relational databases have been developed for mine sites using a user interface that runs on the Microsoft Access platform because this software is inexpensive and the databases are easily shared. Customization of the default database lookup tables is essential for managing data sets generated by routine mine water quality monitoring and unique geochemical studies related to waste rock leachates and whole rock analyses. Standard tools within the database software are combined with customized procedures to meet today's stringent requirements for data validation and verification. Practical databases accommodate an infinite number of problem flags (reason codes) which map to a finite number of validation flags for data presentation and reporting.

Relational Databases for Mine Permitting

One purpose of a relational database for mine permitting is to manage data from groundwater, surface water, soil, whole rock, geochemical leachates, and less often, from air and tissue samples for use in establishing baseline and estimating potential impacts from the proposed project. The care that goes in to developing study plans, logging boreholes, collecting samples, and analyzing samples must continue with the environmental database. Database considerations for mine permitting include the following:

- The framework for the long-lived project database is typically developed during the mine permitting phase. Effort spent in setting up the database correctly will pay off in the long-term.
- Accurate lists of parameters and parameter aliases are set up early in the process. This is not the time to have the summer intern mix all of the phosphate (PO₄) and phosphorus (P) results.

- Use the database to quickly check that the detection limits are well below the regulatory limits. If regulatory limits differ in specific media (*i.e.* surface water or groundwater), the Sampling and Analysis Plan should set the detection limits below the lower of the two regulatory limits for potential impact analysis.
- The initial project analytical suite typically contains a comprehensive list of parameters to be analyzed. The database should provide an efficient and trusted means for paring down the analytical suite to specific constituents of concern, using statistically accepted methodology.
- The database may be used to determine baseline levels of constituents of concern (COCs) using commonly approved statistical methods. The definitions of "baseline concentrations", "upper protection limits", or "background levels" may vary based on state regulations. A simple calculation of mean plus two standard deviations may be appropriate for establishing background of major ions. Statistical analysis of censored (non-detected) results is more complicated and must typically follow established statistical protocols. Internal calculations can be coded in the database, or most databases can export to *.csv for import to EPA's ProUCL for determination of baseline concentrations.
- Legacy datasets often exist where a historical mine is being permitted in the present day. These datasets may lack the laboratory QC packages, reporting units, or portions of the hard copy data may be illegible. Project-specific flags may be added to any questionable data, while well-documented historical data may be used without flagging.

The baseline data is used for decisionmaking by project proponents and regulators. As such, the database must provide robust and accurate datasets for defensible evaluation of potential project impacts.

Relational Databases for Mine Operations and Compliance Monitoring

During operations, most mining projects are required to meet general or site-specific water quality standards at designated points of compliance (POCs). Database considerations for compliance monitoring include the following:

- A relational database is useful for rapid comparison of laboratory results against the site regulatory limits.
- The comparison must be made using validated results. Laboratory analytic flags are generated by the lab and relate to laboratory instrument precision, comparability, accuracy, and bias based on laboratory control samples, laboratory control duplicates, calibration verification samples, matrix spike, matrix spike duplicates, laboratory duplicates, method blanks, and equipment blank samples in accordance with the laboratory Quality Assurance Plan. Validation flags are assigned by the independent data valida-

tion officer based on receiving temperatures, blind duplicate RPDs, cation-anion balance, TDS ratio, and a number of other factors (Table 1). The data validation officer may identify information for a particular sample that is retained in detail in the database but does not result in a specific validation flag code.

An exceedence of a specific parameter • during one sampling event does not necessarily indicate that the site is out of compliance. The database may provide statistical evidence that the result was an outlier, particularly if no other changes in trace metal or major ion chemistry are seen. If the exceedence is recognized early, the lab can re-run the sample either within or out of holding times. (Depending on the lab, samples may be held for three to six months after analysis.) The mine permit will often specify a matrix for confirmation sampling and accelerated monitoring, leading up to mitigation and monitoring to verify the effectiveness of the mitigation measures.

Problem Code	Analytic Problem Description	Maps to Validation Code ⁽¹⁾	Tahle 1	
D1	Dilution due to matrix interference	V ⁽²⁾		
DL	Dilution, no validation flag required	v	Coaes	
D+	Dilution introduced high bias	J+	Val	
D-	Dilution introduced low bias	J-	-	
DT	Dissolved or total not indicated (legacy data)	Q	¹ Validatio	
EA	Estim., <-MDL due to matrix interference	J	rived fro	
EB	Est. based on equip blank detection	FB	- nveu jro	
EQ	Extended qualifer, no ValidFlag required	v	Guidelin	
FB	Est. based on field blank detection	FB	Re	
FD	Field duplicate %RPD criteria not met	J	² Data va	
Н	Exceeds holding time	J	validatio	
H1	Sample rec'd & analyzed past hold time	J	- vanaatie	
H2	Rec'd in time, analyzed past hold time	J	suits oj	
H3	Orig in hold time, re-analyzed past hold	J	may m	
J	Estimated value	J	code if t	
R	Rejected value	R	-	
Rt	Rejected on basis of TDS ratio	R	³ Only s	
TO	Cooler <0 deg C	T ⁽³⁾	. Only s	
T10	Cooler >10 deg C	T ⁽³⁾	tempera	
T2	Cooler <2 deg C	v	preserve	
Т6	Cooler >6 deg C	T ⁽³⁾	require	
Z	unknown	Z	of rece	

Table 1 Example Problem Codes and Associated Validation Flags.

Validation codes U, J, R are derived from the EPA Functional Guidelines for Inorganic Data Review (EPA 2004) ²Data validator may override validation codes based on results of QC process (e.g. D1 may map to J in validation code if warranted by the QC findings) ³Only specific analytes are temperature sensitive; metals preserved with HNO₃ do not require flagging on the basis of receiving temperature

Relational Databases for Mine Closure

Mining projects may be required to meet water quality standards at designated POCs for a fixed time (the post-mining monitoring period). Database considerations for mine closure include the following:

- After mining ceases, bonding is in place for post-mining monitoring and mitigation.
- The relational database often contains decades of monitoring data which may be useful for reducing the list of parameters, to save on analytical costs.
- Automation of data collection, data capture, and reporting are important to save costs in the post-production phase of mining operations.
- The database should facilitate statistical trend analysis (such as Mann-Kendall analysis or quantitative linear trend analysis) to identify whether any trends exist in post-mining water quality.
- The database should have the ability to plot data "on the fly" to visually identify trends and potential outliers.

Mine closure monitoring may be tied to a fixed period of time, or may be linked to demonstrated performance or benchmarks. In either case, efficient evaluation and presentation of monitoring data is critical for mine closure and bond release.

Conclusions

Data management is a critical link between effective mine water monitoring efforts and informed data analysis and decision making. Developing efficient systems for sample tracking, data validation, storage, retrieval, presentation, and analysis are increasingly important in organizations with limited time and resources. Environmental relational databases can be developed using a number of readily available software packages. A well formulated and properly implemented database will serve as a robust tool for mine permitting, compliance monitoring, and mine closure.

Timely data management is required to provide information for compliance monitoring programs that require reporting of water quality results that exceed established permit reporting levels (PRLs). Statistics can be analyzed from within the database, or results can be exported to a variety of formats, including EPA's ProUCL, for rigorous statistical analysis. Given the current agency trend of requiring third party validation of datasets, robust database management is necessary for meeting data quality requirements in-house or for "farming out" the development (input) side of relational databases. Once a database is correctly developed and populated, complete or limited datasets can be extracted as necessary. Mining companies, agencies, and consulting firms can easily utilize these datasets using the UI viewer software.

This approach to managing water quality, whole rock, and geochemical data at mine sites provides a cost effective method for meeting today's increasingly complex requirements for data capture, storage, analysis, and reporting.

References

- GeoTech Computer Systems 2013.Enviro Data software. http://www.geotech.com/envirodata.htm
- Rich, David 2002. Relational Management and Display of Site Environmental Data, Lewis Publishers, 429 pp.
- United States Environmental Protection Agency (2004) USEPA Contract Laboratory Program Functional Guidelines for Inorganic Data Review Final. EPA 540-R-04-0. October 2004.

RELIABLE MINE WATER HYDROLOGY RELIABLE MINE WATER HYDROLOGY



Underground Mine Site Investigations for Estimating Hydrogeological Properties of Regional Fractured Rock Aquifers

Emmanuelle B. GAGNÉ¹, Alain ROULEAU¹, Romain CHESNAUX¹, Denis W. ROY¹, Vincent Cloutier², Réal DAIGNEAULT¹

¹ Centre d'études sur les ressources minérales – Université du Québec à Chicoutimi, Chicoutimi, Québec, Canada, emmanuelle.b-gagne@uqac.ca ² IRME – Université du Québec en Abitibi-Témiscamingue, Campus d'Amos, Amos, Québec, Canada

Abstract A number of analytical models developed either for mines, tunnels or for collector wells can be used to estimate the hydraulic conductivity of a regional aquifer in fractured rock based on data collected at underground mines, in spite of uncertainties affecting the data and the models. Hydraulic conductivity values obtained for the three mine sites (Beaufor, CANMET and Lac Herbin) are presented as intervals of possible values associated with each method. The most probable values are situated between 1.6×10^{-9} m/s and 4.6×10^{-9} m/s, the lowest estimate being 2.0×10^{-10} m/s and the highest 4.4×10^{-8} m/s.

Keywords Regional aquifer, Fractured rock, Hydraulic properties, Analytical methods, Underground mines

Introduction

The hydraulic properties of fractured rock aquifers are largely controlled by fracture networks as well as by major structures such as faults and shear zones. Underground excavations at a mine site constitute a unique opportunity to characterize a fractured rock aquifer in three dimensions, as they provide multiple access points for collecting data and samples at various depth levels. This is particularly useful in areas where limited natural rock exposures and outcrops are available. Mines allow a three-dimensional characterization of an aquifer, observations at various depths, good sampling windows for aquifer structures, and several sampling points for groundwater (fig. 1). However, underground excavations and their dewatering disturb the groundwater flow system, the hydrochemistry and the geomechanical stress fields around the mine.

This project consists of 1-developing and testing methods to characterize fractured rock aquifers at three underground mines (Beaufor, CANMET and Lac Herbin), in the Abitibi mining district located in the Canadian Precambrian Shield, in Quebec, Canada (fig. 2) and 2assessing the usefulness and effectiveness of using underground mines for characterizing regional aquifers in fractured rock.

Data required for normal mine operation, such as structural survey, mine water inflow and outflow, piezometric data and stress field, can be used to obtain valuable information on the regional hydrogeology of the bedrock. A number of analytical models developed to estimate the hydraulic properties of aquifers are designed for draining conditions similar to those observed at mine workings. Such analytical models that are developed either for mines, collector wells or for tunnel can be used with data collected at underground mines to obtain estimates of the hydraulic conductivity of a regional aquifer in fractured rock.

Regional and local geology

The three mine site under study extract gold; they are located at the border of the Bourla-



Fig. 2 Geological map and location of the mines.

maque pluton (fig. 2) composed of dioritetonalite rock. This pluton cut volcanic intermediate to felsic rocks of the Val-d'Or Formation and mafic to ultramafic rocks of the Lower Malartic Group. At Beaufor mine, a sand unit overlaying the bedrock can reach 20 m in thickness. Generally, 2 m of silt and 0.6 m of silty clay cover the sand unit; this is overlaid in places by 0.6 m of organic deposits, and 1.8 m to 2.4 m of backfill around the mine installations (Paradis et al. 2007). At CANMET mine, a dense till composed of silt and sand covers the bedrock, it is overlaid by organic deposit, and 1.5 m to 3.75 m of backfill. At Lac Herbin mine, surface sediments are constituted of clay and silt, near the Bourlamaque River with silt, sand and gravel over the clay. This river is flowing at less than 500 m from the mine. Some small shallow lakes, including Herbin Lake, are located near the mine workings.

Methodology

The first step consists of collecting available information at the selected mine sites, which may include geological maps (rock and superficial deposits), borehole logs, as well as data on geological discontinuity survey (fault, shear zones, fractures, lithological contacts), stream flow rate, hydrochemical analyses, quantity of water inflow and outflow from the mines, location of the mine pumps, geometry of the mine workings and their extension with past time, meteorological conditions, and geomechanical stress fields. Piezometers located near the mine workings may provide periodic water level data. Local estimates of hydraulic conductivity (*e.g.* from packer tests) and groundwater hydraulic gradient may be available. Recorded number of pumping hours may provide estimates of groundwater inflow at different mine levels.

Secondly, analytical approaches provide first estimates of hydraulic properties, since analytical models are relatively simple to use, and they are usually compatible with the quantity and the quality of available data. However, the proper use of these analytical models requires caution, particularly in regards to the limiting assumptions that they imply.

Analytical models that are developed specifically for mine drainage are based on the assumption of a vertical well. The smallest circle that may fully contain the mine plan is determined and a virtual vertical well is located at its center, entirely penetrating the aquifer. Equations have been developed for estimating the flow rate that is required to lower the water table below the circle around the mine (fig. 3; Fawcett et al. 1984). This method assumes that the rock mass above the excavation is dewatered. The equivalent radius r of a non-circular mine may be determined by the following equation (Mansur and Kaufman 1962), where Y and W are respectively the length and the width of the mine workings:

$$r = \left(\frac{2}{\pi}\right) \sqrt{YW} \tag{1}$$

Parameters that are known at a mine site include water inflow, pumping conditions, the

geometry of mine workings, groundwater level and general characteristics of the aquifer. Under these conditions, equations of the models may be rewritten in order to obtain an estimate of the rock mass hydraulic conductivity. A hydrogeological section through the mine, superimposed on a simplified geometry of the mine workings, is required to determine the characteristics of the aquifer. The model equations (Table 1 & fig. 3) are based on the following assumptions (Singh and Atkins 1985):

- Infinite aquifer, homogeneous, isotropic, of uniform thickness over the area influenced by mining, with an impermeable boundary at its base;
- The well is pumped at a constant discharge rate;
- The aquifer is fully penetrated by the well, and thus the water flows horizontally the well over the entire thickness of the aquifer;
- Variations in the diameter of the wells do not affect the discharge or drawdown.

The geometry of a radial collector well is similar to mine workings, taking into account the length of lateral drains (fig. 3). The well is constituted of a reinforced central box and a number of underground side drains (arms). Water enters through the arms and flows into the well when the pump is activated. Usually a radial collector well is modeled as a vertical well having a large radius, corresponding to a percentage of the length of his arms



Fig. 3 Models developed for a mine, a collector well and a tunnel.

Wolkersdorfer, Brown & Figueroa (Editors)

	Condition	Source	Analytical formulas	Variables	
ased on lations	Confined aquifer	Thiem (1906)	$K = \frac{Qln(R/r)}{2\pi b(H - H_w)}$	a: Radius of tunnel [L]b: Thickness of formation being dewatered [L]	
MINE, ba well equ	Unconfined aquifer	Dupuit (1863)	$K = \frac{Qln(R/r)}{\pi(H^2 - H_w^2)}$	 h: Depth of tunnel center from the water table [L] H: Original water head [L] H_w:Head in the central 	
R WELL equations	Confined aquifer	Thiem (1906)	$K = \frac{Qln(R/r_w)}{2\pi b(H - H_w)}$	collector well [L] Q: Well discharge rate equivalent to inflow rate in mine [L ³ /T]	
COLLECTOR based on well	Unconfined aquifer	Dupuit (1863)	$K = \frac{Qln(R/r_w)}{2\pi b(H - H_w)}$	 K: Hydraulic conductivity [L/T] L: Length of drain [L] R: Effective radius of influence [L] 	
Е	Unconfined aquifer	Goodman <i>et al.</i> (1965)	$K = \frac{Qln(2h/a)}{2\pi h}$	 r: radius at which the drawdown is required [L] r_w: Radius of well: % L [L] 	
TUNN	Unconfined aquifer	Rat (1973), Schleiss (1988), Lei (1999)	$K = \frac{Qln\left(\frac{2h}{a} + \sqrt{\frac{h^2}{a^2}} - 1\right)}{2\pi h}$	s: Drawdown at distance r from the well [L]	Table 1 Analytical formulas

(McWhorter and Sunada 1977) which depends on the number of drains. The relationship between these two elements is difficult to assess.

Galleries of underground mines have geometries similar to a tunnel. Several analytical solutions have been developed to estimate water inflow into tunnels for simple cases. They generally assume a homogenous hydraulic conductivity and a flow following Darcy's Law in two dimensions in a plan perpendicular to the axis of the tunnel, and constant-head boundary conditions at the tunnel wall. The water inflow is estimated per unit of length of a tunnel. The tunnel is dewatered at a steady state in a semi-infinite or infinite matrix which is homogeneous and completely saturated. El Tani (2003) has compiled equations for inflow to a tunnel (Table 1).

Results

The results are presented (fig. 4) as intervals of possible values considering the large uncertainties affecting input parameters (Table 2). Note that the extreme *K* values are very unlikely outcomes as they are obtained using jointly the extreme values of all input parameters. Important assumptions must be made regarding the value of a number of variables and some parameters, such as *Q*, vary through time. The value of H for example, is presumed to be lower than the depth of the mine and the effective radius of influence *R* could be assumed to be equal to the radius of the required drawdown *r* multiplied by a specified factor, such as *R* = 1.6 *r*.

Hydraulic conductivity (*K*) values estimated with analytical formulas (Table 1) are



-Arithmetic mean

Fig. 4 Intervals of hydraulic conductivity estimates at each mine with different analytical models.

			Beaufor			CANMET			Lac Herbin		
			Value for a	Arithmetic	Value for a	Value for a	Arithmetic	Value for a	Value for a	Arithmetic	Value for a
			minimum K	mean	maximum K	minimum K	mean	maximum K	minimum K	mean	maximum K
٢	Q	[m³/s]	0.0055	0.0074	0.0164	0.0017	0.0022	0.003	0.0053	0.0086	0.0104
	b	[m]	1181 = H-2	969 = H-14	753 = H-30				894 = H-1	680 = H-15	465 = H-30
	r _w	[m]	800 = 1r	520 = 0.65r	240 = 0.3r	375 = 1r	244 = 0.65r	113 = 0.3r	350 = 1r	228 = 0.65r	105 = 0.3r
ete	R	[m]	960 = 1.2r	1280 = 1.6r	1600 = 2r	450 = 1.2r	600 = 1.6r	750 = 2r	400 = 1.2r	560 = 1.6r	700 = 2r
am	H _w	[m]	500	300	100	500	300	100	500	300	100
Par	Н	[m]	1183=683+H _w	983 = 683+H _w	783 = 683+H _w	630 = 130+H _w	430 = 130+H _w	230 = 130+H _w	895 = 395+H _w	695 = 395+H _w	495 = 395+H _w
_	L	[m]	10000	8000	6000	6000	5500	5000	10000	7000	4000
	а	[m]	5	3	1	3	2	1	3	2	1
	h	[m]	700	375	50	130	85	40	395	220	45

Table 2 Possible value for each parameter

similar from one model to another (fig. 4). The minimum value of *K* is higher for the tunnel models than for other models. The input parameters that have the greatest influence on the calculated *K* value are *Q* and *r*. The calculated value of *K* increases as *Q* increases and as *r* decreases. For a tunnel, the parameter *h* also has an influence on the results; *K* is higher with a smaller value of *h*.

Discussion

All of the analytical models consider a very simple system geometry, and they do not take into account discontinuities such as faults, as well as variations in hydraulic properties with lithology and with depth. In addition, groundwater is commonly observed flowing along fractures and fault zones, from the roof of mine galleries. The assumption of a completely unsaturated rock mass above the mine workings is therefore not exact, as the rock mass remains at least partly saturated. The unconfined aquifer model considers that the rock mass and the overlaying soft material remain unsaturated. However, piezometers frequently show a groundwater table above mine excavations, indicating that at least part of the rock mass above the mine workings remains saturated. This assumption contributes to underestimate the hydraulic conductivities.

Excavations are not homogeneously distributed at a mine site. Mine levels contain different number of galleries, whose length varies in different directions. Assuming a mine as a disk of a radius containing all of the galleries is an important simplification because it overestimates the volume of the excavation, which decreases the estimated hydraulic conductivities. Mine workings are rather constituted of a collection of several galleries and stopes, sometimes with more than one shaft. However, analytical models can easily be used to estimate parameter values considering a number of field cases, using for instance different values of the radius of mine workings. Resulting estimates of hydraulic properties would provide an assessment of their sensitivity to input parameters. Equations used for collector wells are the same as the one used for mines, except that the radius of the well is equal to a percentage of the length of horizontal drains. Analytical models for drainage consider inflow to a single horizontal tunnel without the influence of other drainage tunnels nearby. However, the geometry of a single tunnel is different from the geometry of a mine which is composed of a vertical shaft, stopes, and several sub horizontal galleries. At tunnel having the same diameter as the mine galleries is considered for the estimation: this has the effect of overestimating the hydraulic conductivity.

Models for tunnels are normally used to calculate the inflow by unit length of a tunnel, assuming a value of the hydraulic conductivity of the rock mass. In our application, the hydraulic conductivity is unknown, but a known parameter is the quantity of water pumped for mine dewatering. Generally, the flow quantities provided by different mine levels are rarely known. The use of a tunnel model to estimate the average hydraulic conductivity of the fractured rock mass may require assuming that the total length of the tunnel is equal to the sum of the lengths of all the galleries of the mine.

Conclusion

Results of this study indicate that a number of the analytical models could provide estimates of the hydraulic conductivity of a regional aquifer using available data on groundwater drainage from a mine. Using more than one model provides a greater level of confidence on the estimated hydraulic property values. The obtained values could then be used as input to groundwater flow models either at a regional or a local scale. Mine excavations also provide unique opportunities to characterize the fracture networks and to collect water samples at various depths, which allow an hydrogeochemical characterization of the regional aquifer.

Acknowledgements

This project is funded by the Fonds de recherche du Québec – Nature et technologies (FRQNT) and the Programme d'acquisition de connaissances sur les eaux souterraines du Québec in Abitibi-Témiscamingue (PACES-AT). The authors thank the staff at mines Beaufor, CANMET and Lac Herbin for their cooperation, Daniel Blanchette for fieldwork support, and students Aïda Dassilva (UQAT) and Marie-Odile Chartier (UQAC) for their field assistance.

References

- Dupuit J (1863). Études théoriques et pratiques sur le mouvement des eaux dans les canaux découverts et à travers les terrains perméables. 2^e édtion, Paris, Dunod, 30 pp
- El Tani M (2003). Circular tunnel in a semi-infinite aquifer. Tunnelling and Underground Space Technology 18(1): 49–55
- Fawcett R, Hibberd S, Singh R (1984). An appraisal of mathematical models to predict water inflows into

underground coal workings. Mine Water and the Environment 3(2): 33–54

- Lei S (1999). An analytical solution for steady flow into a tunnel. Ground Water 37(1): 23–26
- Mansur CI, Kaufman RI (1962). Dewatering. In: Foundation Engineering, G. A. Leonards (Eds), McGraw-Hill, New York: 303.
- McWhorther DB, Sunada DK (1977). Groundwater Hydrology and Hydraulics. WaterRessources Publication, Englewood, Colorado
- Paradis SJ (2007). Géologie des formations en surface et historique, Québec, Lac Blouin. Carte 2017A. Commission géologique du Canada
- Park KH, Owatsiriwong A, Lee, JG (2008). Analytical solution for steady-state groundwater inflow into a drained circular tunnel in a semi-infinite aquifer: A revisit. Tunnelling and Underground Space Technology 23(2): 206–209
- Patel HM, Eldho TI, Rastogi AK (2010). Simulation of radial collector well in shallow alluvial riverbed aquifer using analytic element method. Journal of Irrigation and Drainage Engineering ASCE 136(2): 107–119
- Pilote P, Mueller WU, Moorhead J, Scott CR, Lavoie S (1997). Géologie, volcanologie et lithogéochimie des Formations Val-d'Or et Héva, district de Val-d'Or, Sous-province de l'Abitibi. Séminaire d'information sur la recherche géologique. Programme et résumés Ministère des Ressources Naturelles du Québec (DV 97–03): 36
- Rat M (1973). Écoulement et répartition des pressions interstitielles autour des tunnels. Bull.Liaison du Laboratoire des Ponts et Chaussées 68: 109–124
- Schleiss AJ (1988). Design of reinforced concrete-lined pressure tunnels. Proceedings International Congress of Tunnels and Water, Madrid, Balkema: 1127– 1133
- Singh R, Atkins A (1984). Application of analytical solutions to simulate some mine inflow problems in underground coal mining. Mine Water and the Environment 3(4): 1–27
- Singh R, Atkins A (1985). Analytical techniques for the estimation of mine inflow. International Journal of Mining Engineering 3(1): 65–77

Simulated Mining, Backfilling, and Artificial Recharge of the Corani Open Pit

Fred E. BICKFORD¹, Larry BRECKENRIDGE²

¹Global Resource Engineering Ltd., 7000 South Yosemite, Centennial, Colorado 80112, fbickford@globalresource-eng.com ²Global Resource Engineering Ltd., 7000 South Yosemite, Centennial, Colorado 80112, lbreckenridge@global-resource-eng.com

Abstract The Corani mine will produce 160 million tons of silver-lead-zinc ore from an open pit over 18 years. To prevent formation of an acid pit lake at the end of mining, a decision was made to backfill the pit with Potentially Acid-Generating (PAG) waste. At closure, the backfilled waste will be artificially recharged to saturate it as quickly as possible, then capped with an evapotranspiration cover to limit infiltration and surface water/groundwater interactions. A MOD-FLOW Surfact model was constructed to simulate mine groundwater impacts during a complex operational and closure history.

Keywords Acid rock drainage, MODFLOW Surfact, artificial recharge

Introduction

The Corani epithermal silver-lead-zinc deposit in southeastern Peru will produce 160 Mt of ore from an open pit over a projected mine life of 18 years. The project site is in the High Andes 150 km southeast of Cusco, at an elevation of 5000 m. The deposit's sulfide mineralogy ensures that Acid Rock Drainage (ARD) will be produced where water comes into contact with mineralized pit walls and waste rock.

A MODFLOW-Surfact flow model was constructed to predict mine-related groundwater impacts. Modeling goals included predicting groundwater inflow rates to the pit, estimating impacts in the enclosing watershed, predicting postclosure ARD water volumes requiring treatment, and guiding the design of mine elements to minimize ARD water production.

The mine plan calls for backfilling of the pit with Potentially Acid Generating (PAG) waste rock beginning in the later years of mining. Backfilling of the pit will prevent formation of a pit lake, and modeling suggests that this will reduce the volume of ARD water requiring long-term treatment by about 90 %.

Geology

Mineralization is hosted by Miocene volcanic tuffs, which are sandwiched between underlying Paleozoic mudstone and overlying younger unmineralized tuffs (Prado 2008). Mineralization is closely associated with faults, but the host rocks are otherwise largely flatlying and undeformed.

Glaciation has produced broad-floored valleys blanketed with 20 to 40 m of sand, gravel, clay, and peat. The low-relief valley bottoms are poorly drained, and occupied by expanses of verdant wetlands called bofedals. These consist of islands of grass-covered peat separated by a mesh-like network of streams and ponds. Uplands slopes bordering the valleys extend to the high ridgelines bounding the watershed, and are irregularly mantled with tuff-derived windblown sand.

Mine Project Elements

Mine Parameters Fig. 1 shows the domain of the numerical model and the mine facilities inside the domain. Mineralization is localized in three areas, Corani Este, Minas, and Main. The horseshoe-shaped pit produced after 18



Fig. 1 Mine elements and model domain.

years of mining will occupy 190 ha, and will have maximum relief of 375 m. Ore will be trucked from the pit to a processing plant to the east. Slurried tailings will be pumped from there to an impoundment 5 km to the south.

Waste Rock Dumps Waste rock will be disposed at three sites. Unmineralized tuff, which has been determined to be Non Acid-Generating (NAG), will be trucked to the East Dump. PAG waste rock will be trucked to the Main Dump in the early years of mining. Beginning in Year 13 of mining, PAG waste rock will be used to backfill the pit, starting with the Este portion and proceeding to Minas. After mining has been completed, areas of Minas and Main will be backfilled from PAG waste stockpiles. All three waste rock disposal sites will be completed with engineered evapotranspiration covers (ET covers) that permit negligible infiltration. Because the only hydrogeologic impact of the two rock dumps is to deny recharge

to the area beneath them, they are represented in the numerical model by regions of zero recharge that expand as the dump footprints grow.

Pit Backfill The pit will be backfilled to an elevation approximately even with the adjacent lower bofedal. The top surface of the PAG backfill will be slightly below the predicted lowest stabilized postclosure water table, so that when water levels have rebounded after mining, the PAG material will remain permanently saturated. A layer of unmineralized NAG waste rock will cap the PAG backfill, bringing the final ground surface above the range of postclosure stabilized water levels. The backfilled surface will be contoured so that it merges smoothly into the sloping low-relief plane of the lower bofedal.

Pit Evapotranspiration Cover The backfilled pit surface will be completed with an engineered ET cover that excludes atmospheric oxygen and infiltrating surface water from the underlying waste rock. The ET cover has an organic soil layer to facilitate vegetative growth, soil moisture storage, and evapotranspiration. Beneath the organic layer, it has a capillary break of non-reactive rock to prevent upwicking of ARD water through the cap. After closure, an expanded area of bofedal wetlands environment will develop on the ET cover, encompassing both the original lower bofedal and the backfilled surface. The stream from the upper bofedal will cross the backfilled pit surface in a lined, impermeable channel.

Backfill Artificial Recharge Program After pit backfilling is complete, it would take many years for the backfilled pit to become saturated if the water source were limited to groundwater flow, streambed leakage, and recharge from precipitation falling on the backfill surface. To minimize the time during which the PAG waste rock remains unsaturated and vulnerable to acid-generating reactions with atmospheric oxygen, the backfill will be rapidly saturated. The water source would be surface water diverted from various parts of the project site. **Postclosure ARD Discharge** After the backfill is saturated and a new equilibrium water table has become established reflecting post-mining conditions, most of the groundwater that has entered the backfilled pit through the buried pit walls and flowed through the PAG backfill will be discharged to the surface at drains installed at low points on the south pit rim (Fig. 1). This water will be piped to a water treatment plant near the process plant site, treated to applicable standards, and discharged to the drainage below the plant.

Conceptual Model

Fig. 2 is a series of schematic cross sections illustrating the events simulated by the model (line of section shown on Fig. 1). Under premining conditions recharge from precipitation infiltrates fractures in the tuffs of the uplands hillslopes and the unconsolidated sediments beneath the bofedal-floored valleys (Fig. 2A). Groundwater flows downgradient to



Fig. 2 Conceptual model.

discharge points in the bed of the Supayhuasi Stream.

In Fig. 2B the pit has been mined to its maximum depth. Berms have been constructed at both the north and south rims to buttress the cutbanks of unstable surficial sediments. The water table is depressed by the pit, which is a local groundwater sink. The water table falls below the streambed in the lower bofedal, and a perched water table develops in the upper bofedal. The perched-water zone shown in Figs. 2B and 2C is predicted to develop based on the stratigraphy of the upper bofedal sediments and vertical gradients observed in monitoring wells, and is not a modeled prediction. The Supayhuasi Stream is diverted around the pit.

In Fig. 2C, the pit has been backfilled with PAG waste rock, capped by a layer of NAG waste rock. A drain has been installed at the low point at the inner berm on the south pit rim. Artificial recharge of the backfill is underway, but water table rebound is incomplete.

Fig. 2D shows postclosure equilibrium conditions. The PAG backfill is fully saturated, and the water table in the backfill region is within the layer of NAG waste. The ET cover prevents surface water infiltration and minimizes the volume of water flowing through the waste (the NAG layer and low-permeability cap are not shown in the diagram). Groundwater seeps into the backfill volume through the buried pit walls, flows through the backfill, and is collected at the drain, from which it is piped to the treatment plant.

Groundwater Flow Model

Modeling Application The Corani pit was modeled using MODFLOW-Surfact (HydroGeologic Inc. 2011) and the Groundwater Vistas interface (Environmental Simulations Inc. 2012). Surfact was chosen because its adaptive time-stepping module facilitated convergence, it allowed dry cell re-wetting, and the variable properties module allowed replacement of mined-out bedrock and unconsolidated sediments with backfilled waste rock in mid-simulation. **Data Sources** Data underlying the model was based on field and laboratory testing. Bedrock hydraulic conductivity (*K*) came from packer testing of 24 diamond-drilled boreholes. Pumping tests and slug tests were run in a number of wells, and two multiple-well pumping tests were carried out. Laboratory tests were run on samples representing the waste rock backfill.

The steady-state version of the model was calibrated to water levels in a network of monitoring wells and vibrating wire piezometers widely distributed around the pit. The calibration data set also included dry-season streamflow measurements, and average annual precipitation based on several years of records collected at the on-site automated weather station.

Domain The model domain is a rectangle measuring 4400 m by 5600 m with grid lines evenly spaced at 20-m intervals. The extent of the active cells generally corresponds with the boundaries of the enclosing watershed, and the watershed limit is a no-flow boundary (Fig. 1). The base of the domain is flat, at an elevation of 4700 m. The top surface is the existing pre-mining ground surface, with a maximum elevation of more than 5200 m.

The domain is divided into five layers. The form of the layer surfaces was mainly intended to facilitate representation of the pit's complicated pattern of deepening during mining, followed by a rising ground surface during the years of backfilling. Model layering is not intended to represent bedrock stratigraphy, since observations made during drilling and packer testing suggested that aquifer properties are not substantially controlled by stratigraphy.

Steady State Calibration Pre-mining conditions were simulated with a steady state model that was calibrated to water levels measured in monitoring wells and vibrating wire piezometers, while simultaneously matching observed dry-season streamflow. Streams were represented by MODFLOW drain cells.

The calibrated model showed recharge of

8.76 mm/a for most areas underlain by bedrock and 43.8 mm/a for most areas of bofedal sediments. Bedrock *K* ranged from 1.79×10^{-7} cm/s to 5.56×10^{-5} cm/s in six zones, with no vertical anisotropy. K trends shown by the packer testing generally agreed with the bedrock *K* distribution incorporated in the calibrated model. Field work did not produce evidence of discrete large-scale water-bearing bedrock structures of the sort that might be associated with large inflows of groundwater to the pit.

Bofedal unconsolidated sediments were assigned a single horizontal hydraulic conductivity of 1.50×10^{-4} cm/s, with a 10:1 ratio of horizontal to vertical *K* (Kontis 2004). Lumping this layered sedimentary sequence into a single layer represents a considerable simplification, but is considered appropriate given the model's purpose.

Transient Model The transient model incorporates 20 stress periods. Each of the first 19 is one year long, representing the 18-year life of the mine, plus the first year after the end of mining and backfilling. In that year, artificial recharge of the backfilled pit takes place. The final stress period is 80 years long, and tracks the gradual establishment of a new equilibrium head distribution throughout the domain in response to postclosure conditions.

Mining the Pit The Corani mining plan is a complicated one (M3 2012). Deepening of different parts of the pit follows a complex sequence over time, with the aim of achieving the best net present value for the project and balancing the ore-grade requirements of the process plant.

Pit deepening was represented in the model using drain cells. The pit was divided into 18 zones (Fig. 1). Each zone was assigned its own reach of drain cells, and the head settings of each reach were varied year by year to reflect the average pit floor elevation in that reach, controlling leakage into the pit in the zone. For example, if the deepest average pit floor elevation in Zone 10 was scheduled to be 4790 m in Year 5, simulated heads higher than that elevation would produce leakage of water into the pit.

Backfilling the Pit Backfilling of Este began in Year 13, and continued through Year 17. The model used Surfact's variable properties module (TMP1) to change the aquifer properties of the cells affected by the backfill. Cells representing bedrock or bofedal sediments in Year 12 were given the properties of backfilled waste rock in Year 13. The same drain reaches in which declining head settings had been used to show progressive deepening of the pit floor during mining were used to show the year-byyear rise in the backfilled surface during backfilling. Backfilling of Minas and Main took place entirely in Year 18.

Artificial Recharge of the Backfill The artificial recharge program was modeled by applying higher recharge rates in Year 19 to several independent recharge zones covering the backfill areas. A series of model runs were made, involving Year 19 only, to find the inflow volumes needed to saturate the backfill in a single year.

Tracking Postclosure Aquifer Trends A final 80year stress period beginning in Year 20 was run to follow the adjustment of the aquifer to postclosure conditions. The major change from the prior stress period is that recharge applied to the backfill surface is reduced to zero, reflecting installation of the low-permeability cap. MODPATH runs were made to trace the form of pathlines through the backfilled pit, allowing adjustment of the locations of the drains collecting discharge from the backfill. Runs were made to determine the long-term stabilized volume of ARD contact water discharged from the trench drains, and the volume of water seeping through the pit walls above the elevation of the backfilled pit surface.

Results

Pit Inflow Rates Varying rates of inflow to the pit, as represented by the summed volumes discharged from the drain cells representing the 18 pit zones, vary as shown in Fig. 3. Inflow rates increase to a peak value of about

1800 m³/d after four years of mining, and then stabilize before beginning a gradual decline that persists through the end of Year 12. Inflow rates drop sharply at the start of Year 13, when backfilling of Corani Este begins and water is no longer being pumped from the sumps in that area. Inflow briefly rises as final deepening takes place in Minas and Main, falls with expansion of backfilling to those last-mined areas, and shows a brief rise as some water applied during the artificial recharge program is lost through a few drain cells.

Water Levels Fig. 4 shows how water levels in different parts of the pit change over time in response to mining, backfill, and postclosure adjustments. In Corani Este, water levels fall sharply early in the mine's history, with the stair-step pattern of the decline showing close control by the annual changes in the drain head schedule. A gradual rise in water levels begins in Year 13 with the beginning of Este backfilling, and the trend terminates with a sharp water level rebound marking the artificial recharge program. The steadier stair-step decline of Corani Minas shows the even pace of pit excavation in that area. Corani Minas water levels begin rebounding when Minas is backfilled, continuing with artificial recharge in Year 19. The Corani Main graph represents a late-mined portion of Main. Significant water level declines do not begin until Year 15, and since the deepest-mined pit floor is higher than the postclosure stabilized water table, this area does not receive backfill. It is therefore not influenced by the artificial recharge



Fig. 3 Pit inflow rates over time.



Fig. 4 Water level variations in different parts of the pit.

program, and water levels in this area bordering the Corani Main backfill remain permanently higher than water levels in the backfill itself.

Predicted offsite water level impacts are small, and diminish rapidly with distance from the pit. Maximum water level changes of only a few cm are predicted at a monitoring well 2 km downgradient from the pit.

Artificial Recharge Volumes Modeling indicated that it would be necessary to divert surface water at a rate of about 19,000 m^3/d to produce substantially complete saturation of the pit backfill in a single year of artificial recharge. Although flow rates approaching that value might be achievable during parts of the year, it seems more likely that accelerated saturation of the backfill would be carried out over a period of several years after the end of mining. Postclosure ARD Water Production The model indicates that when the aquifer fully stabilizes after the end of mining, groundwater from the backfilled pit will be discharged at the drains at a rate of approximately 121 m³/d. ARD contact water requiring long-term treatment, including seepage from the pit walls above the backfill, will total about 218 m³/d, or 2.5 L/s.

Conclusions

Although sulfide mining projects typically host a range of potential sources of ARD water

(e.g. waste dumps; exposed pit walls), engineering analysis indicated that the most significant ARD water source at Corani would be a flow-through pit lake, if a lake were allowed to form. The decision to backfill the Corani pit reduces the volume of ARD water that must be treated over the long term by avoiding formation of an acid pit lake. If a lake were allowed to form in the Corani pit, calculations based on standard assumptions suggest that it might produce acid water at an average rate of about 20 L/s. In contrast, the cost of long-term treatment of the predicted flow volume of 2.5 L/s appears much more manageable. Beyond that, installation of an engineered ET cover over the backfill, protected from underlying ARD water by a partially saturated layer of NAG waste rock, will allow establishment of an enlarged bofedal wetlands environment that will advance the project's long-term land use goals.

Acknowledgements

The authors thank Bear Creek Mining Company for permitting the results of the study to be presented at the IMWA 2013 conference.

References

- Environmental Simulations Incorporated (2012) Groundwater Vistas Version 6.
- HydroGeologic Inc. (2011) MODFLOW Surfact Version 3.
- Kontis, AL, Randall, AD, & Mazzaferro, DL (2004) Regional Hydrology and Simulation of Flow in Stratified-Drift Aquifers of the Glaciated Northeastern United States (Professional Paper 1415-C). Reston, Virginia: U. S. Geological Survey.
- M3 (2012) NI 43-101 Report on the Corani Project. Tucson, Arizona: M3 Engineering.
- Prado, EA (2008) Estudio Estructural del Yacimiento Epitermal Ag-Pb-Zn-Au de Corani (Structural Study of the Corani Epithermal Ag-Pb-Zn-Au Deposit). Master's Thesis: Universidad Nacional Mayor de San Marcos, Lima, Peru.

Numeric model calibration against both flux and head targets to determine reliable groundwater inflow predictions

Brendon Bredenkamp

GCS Water and Environmental Consultants (Pty) Ltd, 63 Wessel Road, Woodmead, Johannesburg, Gauteng, RSA, brendon@gcs-sa.biz

Abstract Kinsenda Mine is a defunct underground copper mine in the Democratic Republic of the Congo which will be re-opened with the additional development of new underground mining areas. Groundwater inflows were a large problem while the mine was operational in the past. Management of groundwater inflows formed an integral part of the new mine design and scheduling to reduce production losses caused by the inflows and to ensure a safe mining environment.

The mine is located is a complex hydrogeological setting characterised by folding and faulting. Multiple fractured aquifers are associated with the mining area. Geological and hydrogeological data on a regional scale was scare resulting in certain assumptions been made. Groundwater numerical modelling was used as a management tool to aid in the new mine design and dewatering management. The numerical model was calibrated by using measured data collected from the old mine.

Numerical simulations assisted in estimating average groundwater inflows at certain stages of the proposed mine development. The simulated mine groundwater inflow volumes were used as input into the design and scheduling of the dewatering measures to ensure a safe mining environment.

Keywords dewatering, calibration, flux and head targets, groundwater inflow

A deep, non-potable water supply for the Ochoa Sulphate of Potash (SOP) Mine Project, Lea County, New Mexico, U.S.A.

Peter Castiglia¹, Terre Lane², Randy Foote², William Linderfelt¹, Cheng Cheng¹, David Jordan¹, Daniel Wilson¹, Annelia Tinklenberg¹

¹INTERA Incorporated, 6000 Uptown Blvd. NE, Suite 220, Albuquerque, New Mexico 87110, U.S.A., pcastiglia@intera.com ²Intercontinental Potash Corp. (USA), 30 Johnson Road, Suite 300, Golden, CO 80401, U.S.A., tlane@icpotash.com

Abstract Competing with communities, agriculture, and industry for potable-water resources can pose great challenges for mining companies seeking public and regulatory support for proposed projects. In semi-arid and arid regions of the world where fresh-water resources are limited, using potable resources as a water supply for mining operations often faces opposition from existing water users or is subject to lengthy regulatory reviews. This paper describes how Intercontinental Potash Corp. (USA; "ICP") developed a deep, non-potable water supply for its Ochoa SOP Mine Project (Ochoa Project) in southeastern New Mexico, United States of America, that safeguards the limited fresh-water resources.

Keywords Water supply, desalination, brackish water, saline water, potash.

Introduction

Fundamental to the successful development and operation of most mines is securing a sufficient, long-term supply of process water required for routine functioning. In locations where water supplies are short, clashes between mining companies and competing water users can cause delays in development schedules and, in turn, losses in revenue. Those companies that compete for limited fresh-water resources risk losing public and regulatory agency support for their projects. In contrast, those companies that consider non-potable options can avoid pitting their interests against other water users, thereby increasing the probability that they will secure critical support required to advance development and operational goals. This paper presents the water supply strategy used by ICP to develop the Ochoa Project in southeastern New Mexico, a region that contains the largest potash reserve in the United States of America (Barker and Austin 1993), but is relatively water-short.

ICP's fully owned Ochoa Project is located 100 km east of Carlsbad, New Mexico, and less than 35 km from the New Mexico/Texas state line (Fig. 1). ICP aims to become a global industry leader in the production and distribution of high-quality, low-cost specialty fertilizer. The operations will include a conventional underground polyhalite mine and processing facility that will produce SOP and sulphate of potash magnesia (SOPM). The processing of polyhalite, mining, and administrative needs on site require a total water consumption of about 190 liters per second (L/s).

As part of the Pre-Feasibility Study published by ICP (Gustavson Associates 2011), a variety of water-supply options were considered for the Ochoa Project. These supply options included purchasing or leasing potable water from nearby municipalities, purchasing or leasing existing water rights, purchasing an out-of-state source of water, applying to the State of New Mexico for a new appropriation of water, or developing a deep, non-potable resource. Developing a non-potable resource



Fig. 1 Location of Ochoa Project site near Texas/New Mexico state line, Capitan Reef complex (grey), and the Pecos River in addition to large-scale features delineated from subsurface studies from Ward et al. (1970).

from the Capitan aquifer was selected as the water–supply option for the Ochoa Project because:

- The Capitan aquifer is recognized by the U.S. Geological Survey (Hood and Kister 1962) and state agencies (*e.g.* Texas Water Development Board 2010) as a significant brackish water resource with a proven history of industrial use for oil and gas development during the 1960s and 1970s;
- The New Mexico Office of the State Engineer (NMOSE), the state agency responsible for regulating the use water throughout the state, and the U.S. Bureau of Land Management (BLM), the federal agency regulating the construction and operation of the mine, are both supportive of the use of the Capitan aquifer for mining and industrial purposes;
- No permit is required to pump the deep, non-potable water for mining purposes because the aquifer meets several basic criteria that permits development without requiring a lengthy permitting process;

• Developing the aquifer would not compete with other water users in the area who live in the community of which ICP will be a part.

In the Ochoa Project area, domestic, municipal, and agricultural water supplies are produced from shallow, fresh-water aquifers that are thousands of meters above the Capitan aquifer and hydraulically separated from the deeper water. As a result, ICP will be able to secure essential processing-water resources without competing with the surrounding communities' use of fresh water.

Within Lea County, New Mexico, the Capitan aquifer ranges from 240 to 670 m thickness, and is approximately 20 km wide near the Eddy County and Lea County, New Mexico, boundary, and 10 km wide directly east of the Ochoa Project (Leedshill-Herkenhoff Inc. *et al.* 2000). The aquifer is associated with the Permian-age Capitan Reef Complex (Texas Water Development Board 2010), which crops out in the Guadalupe Mountains in New Mexico and Texas and in the Glass Mountains and Apache Mountains in Texas. The Capitan Reef Complex dips below the ground surface to the east and north from the areas of outcrop in the Guadalupe and Glass mountains, and in some areas, the bottom of the aquifer is more than 1,525 m below ground surface (Hiss 1975). Submarine canyons that were incised into the limestone reef and then filled in with sandstone, siltstone, and clay, are present along the northern and northeastern portions of the Capitan Reef complex (Hiss 1975). The most prominent of the submarine canyons occur near the Eddy County/Lea County boundary in New Mexico and create a groundwater divide (Hiss 1975) between the eastern portion of the aquifer in the Ochoa Project area and the western portion of the aquifer near the City of Carlshad and the Pecos River

Methods

ICP drilled two exploratory wells spaced 457 m from one another that fully penetrated the Capitan Reef to provide sufficient data for modeling and water-treatment testing. The wells, each drilled to approximately 1,615 m below ground surface using conventional oilfield drilling technology, were completed in June 2012. Step-drawdown tests were completed to characterize the specific capacity of the wells in support of engineering and design of the well field.

Following well construction and testing, an aquifer test was completed to characterize bulk aquifer properties in support of developing a numerical groundwater flow model for the permitting process. The pumping well was pumped at a constant rate of 31 L/s for 7 days, followed by a recovery period of 23 days. Water levels were monitored in the pumping and observation wells before commencing the test, during the pumping phase, and during the recovery phase. The data were analyzed to define transmissivity, hydraulic conductivity, and storativity.

In support of the permitting effort for the Ochoa Project, conceptual and numerical groundwater models were developed in cooperation with the NMOSE and BLM. The conceptual groundwater model provided the basis for development of a numerical groundwater flow model of the Capitan aquifer. The numerical groundwater flow model provided quantification of potential impacts of pumping deep,



Fig. 2 Model domain with zones of hydraulic conductivity and method of linking CAGWsup model and Capitan aquifer model

saline groundwater from the ICP wells on existing wells and springs producing from, and surface water bodies in contact with, the aquifer in New Mexico and Texas. The aquifer was modeled using the USGS's three-dimensional, finite-difference groundwater flow code, MODFLOW-2000 (Harbaugh *et al.* 2000), which is an updated version of the well-known groundwater flow code MODFLOW (McDonald and Harbaugh 1988).

The portion of the aquifer included in the model domain extends east and south from near Carlsbad, New Mexico, to the Glass Mountains in Texas (Fig. 2). Fortunately, the large number of oil and gas wells in the region provided many well logs with data at the needed depths. A review of available oil and gas well logs, as well as other data sources, and the subsequent development of a database of the formation tops, were key components for delineating the hydrostratigraphic units to be included in the numerical groundwater flow model. In addition to the use of pre-existing data, aquifer test data from the two ICP water wells provided site-specific information on the Capitan aquifer.

Four models were developed: a no-action model, a calibration model, and two predictive models representing the ICP water supply pumping and recovery scenarios. Predictive models were run for 50-year scenarios to cover the period included in the Ochoa Mine Plan of Operations submitted to the BLM using a proposed pumping rate of 252 L/s. Lateral flow exchanges between the Capitan aquifer and adjacent back-reef aquifer or Delaware Mountain Group (the aquifer on the Delaware Basin side of the Capitan aquifer, or basin aquifer) were determined using one-dimensional MOD-FLOW models linked to different sections of the Capitan aquifer boundary. Initial conditions for the one-dimensional models were a uniform, static water level. The thickness of all one-dimensional models was estimated at 304 m based on information from Hiss (1975) on the basin and back-reef aquifers. A standard model domain of 153 km was used for all onedimensional models

Potential impacts to groundwater in the vicinity of the Pecos River near Carlsbad, New Mexico, were based on reduced groundwater discharge to the Pecos River. An extensive and detailed evaluation of the groundwater flow system was conducted by the NMOSE (Barroll et al. 2004). As a result of that work, the numerical model of the flow system in that area, the Carlsbad Area Groundwater (CAGW) model, was developed to assess potential impacts. A superposition model of the CAGW model (CAGWsup) was further developed as a tool for evaluating impacts on river flows due to additional withdrawals from the aquifer in that area (Papadopulos 2008). The CAGWsup model was used to evaluate impacts due to pumping of ICP wells (Fig. 2). The impact evaluated was induced leakage from the Pecos River. This leakage was compared to the overall groundwater discharge to the river estimated using the CAGW model, which averaged 1,625 L/s for the period from 1965 through 2001.

Results

Pump testing indicated that the supply wells can sustain pumping rates of 31 L/s or greater for extended periods of time. The specific capacity of the well is summarized in Table 1. Rapid rebound was observed upon cessation of pumping in the pumping well during the step test, where the water level returned to

Step No.	Flow Rate (L/s)	Water Level Drawdown (m)	Specific Capacity (L/s/m)
1	20	56.1	0.36
2	28	90.5	0.31
3	37	140.8	0.26

Table 1 Results of specific capacity testing at three pumping rates (steps) used for well testing.


Fig. 3 Drawdown in the Capitan aquifer after 50 years of pumping 252 L/s. Area enlarged shows Eddy-Lea County line in vicinity of submarine canyons that restrict flow.

100 % of the pre-test level within one hour. As expected, the specific capacity decreases with an increase in flow rate.

The estimated storativity value from the 7-day pumping test is 5.0×10^{-5} . Transmissivity of the Capitan aquifer was estimated to be 650 m²/d, yielding an estimated horizontal hydraulic conductivity of 2.1 m/d, applying a 304 m thickness for the open-hole producing zone.

Results of the numerical groundwater flow model indicate that drawdown will be greater east of the groundwater divide that is created by the submarine canyons (Fig. 3), far from the Pecos River, springs, and other water users. There will be a limited impact to groundwater discharging to the Pecos River near Carlsbad, New Mexico, after 50 years of pumping. Reduction in groundwater discharging to the Pecos River due to pumping of ICP wells was estimated at 0.07 %. A sensitivity analysis conducted on the Capitan aquifer model established that the parameter estimates used in the model were reasonable and that the model was representative of the groundwater flow system. Impacts on the back-reef aquifer were estimated to be up to 0.007 % of the total amount of water in the back-reef aquifer, and impacts on the basin aquifer were estimated

to be up to 0.002 % of the total amount of water in the basin aquifer.

Conclusions

The exploratory drilling, testing, and modeling work completed by ICP in support of the permitting process significantly reduced the risk to the water supply for the Ochoa Project and provided valuable data for final design and engineering. Well testing confirmed the desired capacity of the deep wells. Aquifer testing confirmed the aquifer is suitable to provide the Ochoa Project with a long-term supply of deep, non-potable water that will not compete with the surrounding community for use of fresh water. Evaluating the effects of pumping with the numerical groundwater flow model shows insignificant impacts to other water uses and surface water connected to the aquifer.

By supplying the mine with deep, nonpotable water from the Capitan aquifer, ICP has avoided a relatively complicated process for developing freshwater, and has instead safeguarded its use for other purposes that are essential to the surrounding community. Though developing deep, non-potable water requires deeper wells and desalination treatment, making the commitment to safeguard limited freshwater resources can add value to a project through public and regulatory support received when proposals do not include a new and competing use of fresh water. As freshwater resources become more limited, those companies that choose to adopt conventional drilling and treatment technologies to develop non-potable resources may also realize value in the support received for such proposals.

Acknowledgements

We thank the shareholders of IC Potash Corp. (TSX:ICP, OTCQX:ICPTF) for their support in developing the Ochoa Project and the men and women who participated in the drilling, construction and testing of the deep groundwater wells. In addition, we are grateful for the support for the proposed Ochoa Project that ICP has received from the communities of Lea County and Eddy County, New Mexico, and for the constructive criticism we have received through this process from the NMOSE and U.S. Department of Interior BLM Carlsbad Field Office.

References

- Barker JM, Austin GS (1993) Economic geology of the Carlsbad Potash District, New Mexico. New Mexico Geological Society Guidebook, 44th Field Conference, Carlsbad Region, New Mexico and West Texas, p 283–291
- Barroll P, Jordan D, Ruskauff G (2004) The Carlsbad Area Groundwater Flow Model. Consultant's Report prepared by INTERA Incorporated and submitted to the New Mexico Interstate Stream Commission
- Gustavson Associates (2011) National Instrument 43-101 Technical Report, Prefeasibility Study for the Ochoa Project: Lea County, New Mexico, December 30, 2011

- Harbaugh AW, Banta ER, Hill MC, Mcdonald MG (2000) MODFLOW-2000, The U.S. Geological Survey Modular Ground-Water Model – User Guide to Modularization Concepts and the Ground-Water Flow Process. U.S. Geological Survey Open-File Report 00-92, 130 p
- Hiss WL (1975) Stratigraphy and Groundwater Hydrology of the Capitan Aquifer, Southeastern New Mexico and Western Texas. Unpublished Ph.D. dissertation, University of Colorado, Boulder, 396 p
- Hood JW, Kister LR (1962) Saline-water resources of New Mexico, U.S. Geological Survey Water-Supply Paper 1601, 76 p
- Leedshill-Herkenhoff, Inc., John Shomaker & Associates, Inc., Montgomery & Andrews, P.A. (2000) Final Report, Lea County Regional Water Plan. Prepared for Lea County Water Users Association. December 7, 2000, 128 p
- McDonald MG, Harbaugh AW (1988) A Modular Three-Dimensional Finite-Difference Ground-Water Flow Model. In Techniques of Water-Resources Investigations, Book 6. Washington, DC: U.S. Geological Survey/U.S. Government Printing Office
- S.S. Papadopulos and Associates, Inc. (Papadopulos) (2008) Carlsbad Area Groundwater Model, Superposition Version GUI. Prepared for the State of New Mexico/Interstate Stream Commission. June 5
- Texas Water Development Board (2010) Aquifers of West Texas. In: Mace RE, Mullican WF, Angle ES, (Eds), Texas Water Development Board Report No. 356, 281 p
- Ward RF, Kendall CG, Harris PM (1970) Upper Permian (Guadalupian) Facies and Their Associations with Hydrocarbons – Permian Basin, West Texas and New Mexico, The American Association of Petroleum Geologists Bulletin 70(3): 239-262

Using Fiber Optics and Vibrating Wire Piezometers to Characterize an Aquifer in Preparation for Ground and Aquifer Freezing

Chris Cottingham¹, Matt Vitale², John Selker⁴, Frank Selker³, Sarah Lupton¹

¹Newmont Mining Corporation, 1655 Mountain City Highway, Elko, NV 89801 ²Meridian Geoscience, 10580 North McCarran Blvd, Reno, NV 89503 ³Selker Metrics, 4225 SW Agate Ln, Portland, Oregon, 97239 ⁴rm 116 Gilmore Hall, Department of Biological and Ecological Engineering, Oregon State University, Corvallis, Oregon 97331

Abstract The frozen ground shaft construction at the Leeville underground mine in northern Nevada provides a unique opportunity for aquifer characterization. Geotechnical borehole HGT-1 was located 15 m north of the shaft collar. The borehole was instrumented with seven vibrating wire piezometers (VWP's) and a fiber optic cable assembly. The instrumentation was mounted to a fiberglass resin epoxy (FRE) rod that minimizes heat transfer. The piezometer and fiber optics were grouted in place to a depth of 591 m. Pressure data from VWP's was used to confirm the fiber optic cable temperature measurements. Initial data shows temperature propagating preferentially along structures.

Keywords fiber optics, ground freezing, aquifer characterization, hydrogeology, temperature

Introduction

The underground Leeville mine is located 33 km northwest of Carlin, NV. The hydrogeology consists of a two-aquifer system, referred to as the Upper Plate (UP) and Lower Plate (LP) aquifers. These aquifers are separated by the regional Roberts Mountain Thrust Fault (RMTF) in Fig. 1. The mined ore body at Leeville is located in the depressurized LP aquifer that is currently being dewatered. The Leeville mine is expanding operations to the north and a ventilation shaft is being sunk through the entire thickness of the UP. near the current north operations boundary. A ground and water control management system must be implemented in order to sink the shaft through the UP Aquifer.

The UP consists of the Ordovician Vinini formation, which is made up of sandstone, siltstone, and chert. The Vinini was classified as gravel (GW) to clay (SC) in the initial boring drilled for a geotechnical and hydrological study (Call and Nicholas 2011). Ground freezing was chosen as the preferred engineering control because of the poor ground conditions. A frozen ground engineering project offers a unique opportunity to investigate geologic structure by monitoring temperature and pressure during the freeze process. The fiber optic cables were used to measure temperature and vibrating wire piezometers (VWP's) were used to monitor pressure. This case study reports the initial construction of the piezometer, ambient aquifer temperature data, and data collected during freeze well drilling.

Hydrogeologic Setting

At Leeville, as with most parts of Nevada, the majority of precipitation accumulates as snow on the mountain ranges, and spring snowmelt is the primary source of groundwater recharge. Precipitation in the area is approximately 25 cm per year (Plume 1996). Recharge occurs primarily along drainages at the valley margins, which feed directly into the alluvial groundwater system. Some recharge also occurs at higher elevations through direct infil-



Figure 1 Hydrogeologic and geologic features are given in both depth and elevation. The ground surface in the area of HGT-1 is 1,845m above mean sea level (amsl). Groundwater is measured in the area at 1,720m amsl. A know regional fault is located from 1,545 to 1,495 m amsl. The beginning of the RMTF is at approximately 1,345 m amsl This RMTF zone extends to a depth beneath the scope of this study. The Lower Plate carbonates are beneath the RMTF zone. The contact between the RMTF and the Lower Plate carbonates in the area of HGT-1 is located beneath the bottom of the fiber optic line and the VWP's.

tration into fractures, eventually recharging the bedrock groundwater systems (Plume 1996). Groundwater flow in bedrock is controlled by fractures and fault boundaries, which compartmentalize the bedrock groundwater system.

The UP and LP groundwater systems are hydrologically distinct. The contact between the UP and LP occurs along the RMTF, as does the transition from the UP aquifer to the LP carbonate aquifer. Regional groundwater generally flows towards major drainages, such as the Humboldt River and Maggie Creek. Localized groundwater within the UP flows both horizontally and vertically towards lower heads within the LP carbonate aquifer. Flow is horizontal within the carbonates with localized vertical gradients caused by dewatering activities.

Groundwater modeling and aquifer testing in the Leeville area indicate that hydraulic conductivity (*K*) ranges from 3.3×10^{-7} to 2.3×10^{-2} cm/s in the UP aquifer and are 4.9×10^{-5} cm/s to 4.3×10^{-2} cm/s in the LP aquifer (Schlumberger 2011). The potentiometric surface is approximately 1,700 m elevation in the UP and approximately 1,150 m elevation in the LP. The current dewatering rate at Leeville is approximately 1,325 L/s. Dewatering occurs in the LP aquifer where groundwater flows radially towards the mine, with steeper hydraulic gradients at the dewatering well network. Site piezometric data indicate a prevalent downward hydraulic gradient in the UP aquifer.

Methods

Boring HGT-1 was converted to a piezometer by installing seven VWP's, one fiber optic cable, and two heating elements. The piezometer collar is located at 1,834 m elevation. The fiber optic cable assembly was constructed as follows:

- A fiber optic cable with four bend-tolerant, multi-mode fibers was packaged in a 3.8 mm steel-reinforced cable. The cable extended from the collar to the bottom of HGT-1 and back to the collar. Approximately 1,220 m of cable was used to reach a depth of about 590 m.
- Three copper direct-burial cables (6, 10, and 14 ga) were joined to the fiber optic cable so that with the application of 220 VAC two heating regimes could be obtained.
- Black electrical-tape binding was applied every 45 to 60 cm to hold the cable assembly together prior to installation.

• The near mid-point (655 m) of the fiber optic cable, at the location of the bottom of the assembly, the optical turn-around and electrical junctions were cast in polyurethane in a 5 cm diameter PVC protective housing.

The field installation occurred as follows:

- A reverse circulation drill rig reamed the boring to 20 cm in diameter and to a depth of 591 m below ground surface (bgs).
- VWP sensors with communication cables, fiber optic cable assembly, and heating elements were attached to the FRE rod using high strength adhesive tape.
- VWP sensors were installed at depths of 275 m, 320 m, 368 m, 417 m, 450 m, 501 m, and 569 m.
- Cement-bentonite grout was used to backfill the instrumentation borehole below 6 m from ground surface. The top 6 m was then sealed with neat cement.

Distributed Temperature Sensing (DTS) Machine

A DTS estimated the temperature along the fiber optic cable by measuring the spectrum of backscattered light (Selker *et al.* 2006). For the preliminary data shown in this paper, this device measured temperature every second at 12.5 cm intervals along the cable for 4.25 h. At each interval temperature was measure on each leg of the cable loop (down and back, thus two measurements per location). This temperature was averaged to obtain a single value. The temperature resolution was 0.01 °C between intervals.

A continuous calibration of the DTS was required to obtain consistent 0.02 °C absolute accuracy with 0.01 °C resolution along the cable. Two insulated baths were used for the temperature calibration; one filled with ice water and the other filled with continuously agitated salt water (allowed to come to ambient, sub-zero, temperature).

Implied Local Thermal Conductivity

Thermal conductivity was calculated from temperature data for comparison to identified geologic structures as well as aquifer characteristics. Saturated soil and rock typically have thermal conductivities between 0.5 and 4.0 W/m/K and sandstone, used to represent UP, typically has values from about 1.5 to 3 W/m/K (Alter 1969). The average observed temperature gradient in HGT-1 is about 0.020 K/m. Multiplying the observed temperature gradient by an average thermal conductivity of 2.25 W/m/K implies a vertical geothermal energy flux of 0.045 W/m². Using this value with the assumption that the geological system was at near steady state, the relative thermal conductivities of the vertical profile could be computed as the inverse of the observed thermal gradient (see Freifeld et al. 2008).

Freeze Well Drilling

Wells installed for ground freezing were drilled 15 m south of the piezometer during temperature and pressure data collection. Fluid lost during well drilling was expected based on past drilling experience in the Vinini formation. Drilling fluids lost to the formation during freeze well drilling acted as a tracer that could be detected by the fiber optic and VWP's.

Results

Temperature data obtained with the fiber optic cable were plotted against depth and compared to a visually fit straight line (Fig. 2). Four distinct variations from the visually fit straight line were detected: (1) the spike from 0 m to 25 m depth; (2) the temperature increase from 100 m to 150 m depth; (3) the spike from 300 m to 350 m depth; and (4) the increased slope at 500 m depth.

The first temperature spike from the 0 to 25 m depth represents ambient warming of the ground. The data expressed by the horizontal tail at 0 m is the portion of the fiber optic cable laying on the surface from the piezometer head to the DTS machine.



Figure 2 Average temperature in HGT-1 from 19:47, 12 December 2012 to 00:02, 13 December 2013. The red line is measured average temperature. The blue line is a visually fit straight line, for comparison.

The temperature profile from 25 m to 100 m represents the unsaturated zone. The temperature increase at 100 m is the first indication of the potentiometric surface. This elevation corresponds to historically observed UP heads.

The temperature spike from 300 m to 350 m reflects a transient source of heat. The shape of the anomalous temperature spike appears more consistent with a varied flow system than with thermal conduction, since a spreading thermal conduction signal would typically show a smooth Gaussian-shaped disturbance.

The 300 m to 350 m spike exhibits one major peak, with a large shoulder immediately below the peak. In the absence of cooling, the temperature in this area would gradually move to a value between the deep temperature and this elevated spike. Eventually, the temperature profile would "fill in" the cool valley between the anomalies, changing the anomaly from a spike to a change in slope of the profile. Since heat propagates slowly in the ground without moving fluids, it could take hundreds of years for this to occur. The fact that this thermal "valley" has not filled in indicates a recent injection of heat, such as adjacent drilling fluid loss from the freeze wells. The location of this spike corresponds to a known local structure.



Figure 3 Implied thermal conductivity of substrate in HGT-1 based on temperature profile of 12 December 2012 (W/m/K).

The increased slope at 500 m depth indicates a long-term temperature change. This slope is interpreted as the location of the RMTF, which is expected to be at this approximate depth. The temperature data show the RMTF starting at 500 m and extending to a depth beyond the bottom of the boring. The LP, located beneath the RMTF, has not been instrumented with fiber optics, so the top elevation of the LP cannot be determined.

Fig. 3 shows thermal conductivity calculated from the temperature profile in Fig. 2. Heat flux is the vertical energy conducted through the formation from the earth's core and is typically expressed in watts per square meter. Heat flux is equal to the coefficient of thermal conductivity, k, multiplied by the temperature gradient. In the absence of transient temperature changes, the heat flux is constant with depth. If flux is constant, the temperature gradient is inversely related to the conductivity. Thus, in the absence of heat sources or sinks, deviations from a uniform temperature gradient (blue line in Fig. 2) arise due to variations in thermal conductivity (Fig. 3). Steeper gradients reflect less conductive material and shallow gradients reflect more conductive material. Values outside the range expected for ground materials likely reflect water movement. Moving water can also transport heat, and where that is the case the gradient is not necessarily an indication of material conductivity.

Steady state conditions are assumed in Fig. 3 with no heat sources or sinks between the bottom of the piezometer and ground surface. Values outside of the range of 1-5 (indicated by red-filled arrows), and negative computed values (green-filled arrows) are interpreted to reflect conditions that are not controlled by steady state thermal conduction but rather heat advection from natural flowing water or injected drilling fluids. The white arrow indicates a location where the computed thermal properties could be conceivably explained by thermal conduction, but we believe this is better explained by local water movement.

The temperature profile in the top 100 m in Fig. 2 corresponds to the three peaks in the first 100 m of Fig. 3. This represents the area above the aquifer in HGT-1. The local water movement interpreted in Fig. 3 at the 100 m depth corresponds to the potentiometric surface observed in Fig. 2. The area from 300 m to 350 m of injected drilling fluids corresponds to the spike at the same depth in Figure2.

VWP Pressure Data Compared to Temperature Data

Pressure data from sensor "G" appear to be the most stabile and is the best representation of

the potentiometric surface at 1,700 m elevation. This elevation corresponds to the observed temperature increase from 100 m to 150 m depth. The erratic pressure in sensors "F" through "B" can be attributed to fluid losses from adjacent freeze well drilling.

Drilling activity creates pulses of pressure that are strongest at 320 m, and affects all but the deepest sensor. Sensor "F" shows pressure fluctuations and pressure dampening effects corresponding to the depth of the sensor.

Observed pressure anomalies are attributed to the adjacent freeze well drilling and the subsequent drilling fluids transported along preferential flow zones intersecting both the freeze wells and HGT-1 (Fig. 4). These pressure anomalies are specifically prevalent in sensor F installed at 1,514 m (320 m bgs). This anomaly corresponds to the temperature spike from 300 m to 350 m. Pressure data were compared to fluid volume losses with depth from driller reports, but the fluid data from drilling reports are difficult to correlate.

There is a consistent reduction in pressure with depth, with the exception of sensor "A". The dramatic reduction of pressure at sensor "A" reflects depressurization and resulting transient conditions within the RMTF from mine dewatering. The pressures observed in



Figure 4 Potentiometric surface pressure represented as total elevation head in HGT-

1. Symbols shown on the right side of the graph correspond with VWP sensor installation depths in HGT-1. The average total depth of the freeze wells drilled for construction of the shaft 15 m south of HGT-1 is indicated by "freeze drill TD." The final drilled depth of HGT-1 is indicated by "total boring depth". sensors "G" through "B" show a prevalent downward hydraulic gradient in the UP. Water flow in the UP is not absolutely vertical, because there is a horizontal flow vector that cannot be established using a single piezometer. Pressure gradients show the direction of flow, but not the volume or existence of movement.

There is a distinction between propagation of pressure and propagation of temperature changes: pressure can propagate either with or without any flow. Any hydraulic connection can transmit pressure, even if low connecting permeability prevents significant flows. However, pressure propagation is attenuated with resistance to flow and distance. Changing temperatures, indicate significant flows that deliver fluids with different temperatures.

Conclusions

Fiber optics and VWP's were successfully installed in the UP adjacent to the planned frozen ground shaft construction collar. Temperature measurements from the fiber optic cable identified four major aquifer characteristics as well as geologic structures: (1) the unsaturated zone from 25 m to 100 m; (2) the potentiometric surface at 100m; (3) a major regional fault from 300 m to 350 m; (4) the RMTF at 500m. These locations were verified with the VWP pressure data. Both the fiber optic data and the VWP pressure data show the expression of lost drilling fluid in the formation. Lost drilling fluid movement through the aquifer was confirmed with implied hydraulic conductivity data. VWP data also confirmed the downward vertical hydraulic gradient in the UP aquifer.

Future studies will involve use of the heating wires. The correspondence between geologic structure and thermal conductivities implied by the temperature profile may be enhanced by the results of heat-pulse experiments. Pressure data will continue to be collected with VWP's, and will be used to correlate fiber optic temperature data. During ground freezing for shaft construction, the fiber optic cable will also be used to measure temperature as the temperature gradient propagates from the shaft location outward. Observation of these aquifer stresses will provide more accurate estimates of aquifer characteristics.

Acknowledgements

The authors would like to acknowledge Clem Hartery and Newmont Mining Corporation for their support of this project. The authors would like to thank Bob St. Louis for insights and editorial comments on the initial version of this text.

References

- Alter AJ (1969) Water Supply in Cold Regions. U.S. Army. Cold Regions Research and Engineering Laboratory. Monograph III-C5a.
- Call and Nicholas, Inc (2011) Data Report for Geotechnical Logging of HGT-00001 – Leeville. Unpublished report.
- Freifeld BM, Finsterle S, Onstott TC, Toole P, Pratt LM (2008), Ground surface temperature reconstructions: Using *in situ* estimates for thermal conductivity acquired with a fiber-optic distributed thermalperturbation sensor, Geophys. Res. Lett., 35, L14309, DOI:10.1029/2008GL034762.
- Plume R (1996) Hydrogeologic framework of the Great Basin Region of Nevada, Utah, and adjacent states. US Geological Survey Professional Paper 1409-B.
- Schlumberger Water Services (2011) Hydrologic Characterization of Geotechnical Hole HGT-00001. Unpublished report.
- Selker JS, Thévenaz L, Huwald H, Mallet A, Luxemburg W, Van de Geisen N, Stejskal M, Zeman J, Westoff M, Parlange MB (2006), Distributed fiber-optic temperature sensing for hydrologic systems, Water Resour. Res., 42, W12202, DOI:10.1029/2006WR005326.

The application of ecohydrology to mine water impact assessment

Gareth DIGGES LA TOUCHE, Nina SRAJ, Grace YUNGWIRTH

Golder Associates, Attenborough House, Browns Lane Business Park, NG12 5BL, Stanton-on-the-Wolds, Nottinghamshire, UK, gdiggeslatouche@golder.com

Abstract The assessment of the impact of proposed, and in some situations existing, mining operations on groundwater is, on occasion, hampered, particularly during the early stages of project development, by a lack of groundwater information beyond the immediate footprint of the proposed mine. This paper will review the use of ecohydrology or ecohydrogeology to derive hydrogeological information that can facilitate the development of groundwater conceptual models for environmental impact assessment, in the absence of conventional groundwater data.

The use of ecohydrological methods for groundwater characterisation and conceptual model development is not routine. This paper will present a synopsis of ecohydrological indicators of groundwater in a range of climatic regimes and their application to the assessment of the environmental impact of mining operations. Additional supporting information requirements, such as an understanding of the meteorological conditions and underlying geology, to maximize the benefits of the ecohydrological method will be highlighted and discussed.

The use of ecohydrology provides a valuable tool for groundwater investigations particularly when other data is not available. In addition the limitations of the ecohydrological approach will be discussed and potential areas for future research outlined.

The application of ecohydrology/ecohydrogeology to groundwater investigations for mine impact assessments in areas with limited or no existing data provides a valuable addition to conventional hydrogeological approaches. The use of ecohydrology has the potential to allow the development of better constrained hydrogeological conceptual models at an earlier stage of study in the absence of more conventional hydrogeological data and to allow additional refinement when combined with conventional hydrogeological data.

Keywords Ecohydrology, ecohydrogeology, groundwater, ecology

Designing a Large Scale Pit Slope Depressurization System at Bingham Canyon

Jeremy Dowling¹, Geoff Beale², Jack Bloom³

¹Schlumberger Water Services 1875 Lawrence St., Suite 500, Denver, Colorado, USA, JDowling@slb.com ²Schlumberger Water Services, Schlumberger Water Services (UK) Ltd, The Pump House, Coton Hill, Shrewsbury, UK, gbeale@slb.com ³Rio Tinto, Kennecott Utah Copper, 4700 Daybreak Parkway,South Jordan, UT 84095

Abstract In 2008, Rio Tinto commissioned a Feasibility Study for major expansion of the South wall of the Bingham Canyon open pit mine. As with any large open pit mine, the economic viability of pit expansion is sensitive to achievable overall slope angles. A constraint on slope design angles at Bingham Canyon is the ability to significantly reduce groundwater pressure present in the pit slope. This paper overviews the hydrogeology of the mine and work involved with implementing a pit slope depressurization evaluation as part the overall slope design process.

Keywords Depressurization, Hydrogeology, Drainage Tunnel, Numerical Modeling, Mining

Introduction

The Bingham Canyon open pit copper mine is located approximately 30 mi (48 km) south of Salt Lake City, Utah. It is owned and operated by Rio Tinto. The ore deposit has been mined via open pit since 1906. In the current day, the open pit is approximately 10,000 ft (305 m)wide at the crest and approximately 3,000 ft (914 m) deep (Robotham 2011). Skarn deposits surrounding the open pit were also mined in the past via underground methods. Underground mining is currently ceased.

During the mid 2000s, Rio Tinto evaluated a number of options for expanding the mine to exploit additional resources beyond the existing life of mine (LOM) plan. One of the options considered was a major expansion of the south wall of the mine through implementation of a major pushback. Through long term operating experience at Bingham Canyon it was realized from the onset of Pre-Feasibility level evaluation that a South wall pushback would require a significant program of pit slope depressurization to support preferred overall slope angles. On this basis, a hydrogeologic and pit slope depressurization study was initiated and fully integrated with the geotechnical and slope design program. The workflow adopted for the study is shown in Fig. 1 and selected aspects are reviewed in the remainder of the paper.

Mine Wide Empirical Hydrogeologic Model

The open pit hydrogeologic conceptual model is built from empirical experience gained during many years of general dewatering and pit slope depressurization effort at the site. Key data sets and operating experience that help to build the mine hydrogeology picture include:

- Routine surface horizontal drain drilling in multiple slope sectors, with flows that can be reconciled with rock type, structural domain and relative permeability ranges.
- Depressurization drilling from within the Highland Boy Drainage Gallery (HBDG), an underground tunnel driven behind the Q-Cut expansion of the west corner of the mine. Approximately 200,000 ft (61 km) of drain holes were drilled into the West wall from tunnel in the 2005 to 2007 window, with flows and pressure responses



Fig. 1 Pit Slope Depressurization Workflow with Linkage to the Geotechnical Study

reconciled to rock type, major structure and relative permeability ranges.

- Flow and pressure response observed during implementation of low-flow toe area depressurization pumping wells, in prior phases of South wall mining.
- Flow and water level data from maintenance pumping of the historic underground mine workings including Niagara, Lark, Carr Fork and NOSS.
- A network of over 100 vibrating wire piezometer strings located in multiple slope sectors, allowing definition of vertical head gradients in the slopes and hydraulic response to the operational depressurization efforts.

South Wall Hydrogeologic Conceptual Model

A detailed account of the South wall hydrogeologic system is not possible within this paper, but a brief overview is described. The south half of the mine includes intrusive Monzonite and Quartz Monzonite Porphyry (QMP) occupying the pit floor, middle, and lower interramp sectors. Sedimentary bedrock comprised of Quartzite and Limestone beds sit behind the intrusive units and is exposed in the upper slope sectors. In the west sector, the sedimentary beds are sub-vertically inclined but to the east have a more shallow dip. Illustrative geologic cross sections of the west and central sectors are show in Figs. 2 and 3.

The intrusive Monzonite and QMP have low permeability. The Quartzite is moderately permeable, but the limestone beds also have low permeability. Table 1 summarizes typical values. Within the sedimentary bedrock, the contrast in properties between the beds in combination with the variable dip, creates hydraulic anisotropy, with permeability and groundwater flow favored in the direction of bedding. For the intrusive rock, the major structure and contact between the intrusive

Geologic Unit	South Wall (ft/day)	Entire Mine (ft/day)	
Monzonite	4×10^{-3}	1×10^{-2}	Teble 1 Maan normaalailitu
QMP	1×10^{-2}	2×10^{-2}	Table T Mean permeability
Quartzite	5×10^{-2}	4×10^{-2}	for the main rock types
Limestone	8×10^{-4}	8×10^{-4}	



Fig. 2 Hydrogeologic Section Through the West Sector of the South Wall

units imparts discrete zones of increased fracture permeability and anisotropy that mirrors the structural fabric.

Current-day groundwater levels in the south wall are controlled by a combination of a) district scale groundwater levels surrounding the mine, b) partially-flooded historic underground workings including Niagara behind the west sector and Lark behind the extreme east corner, c) local seasonal recharge near the slope crest. The district driving head behind the slope is in the 5,300 ft (1615 m) above sea level (asl) to 5,700 ft (1737 m) asl range. There is perched or 'de-coupled' groundwater higher in the slope associated with local seasonal recharge and encountered on bedding or within the fractured blast damage zone. During the study, geotechnical data sets were utilized to enhance the hydrogeologic model, specifically:

• The geotechnical model identified a zone of generally degraded rock mass in the skin of the pit slope to a depth range of 200 to 400 ft (61 to 122 m), characterized by a lower RQD, and attributed to a combination of blast damage, geomechanical unloading and historic rock mass displacement. A zone of increased permeabil-



Fig. 3 Hydrogeologic Section Through the Central Sector of the South Wall

ity was inferred from this data, and was reconciled with shallow piezometer data.

- Zones of high clay altered Monzonite in the south wall, were identified as distinct geotechnical materials and were reconciled with reduced permeability in the hydrogeologic model, based on observation of high clay Monzonite behavior in the HBDG.
- The fissure fault system, present in the west sector Monzonite, were reconciled as having discrete fracture permeability, based on reconciliation of the structural mapping with historic horizontal drain flow in the same sector.

Definition of Slope Depressurization Priorities

The proposed South Wall Expansion, would involve a 1,000 ft wide cut and deepening of the pit floor by 100 to 300 ft (30 to 90 m) beyond the existing LOM, to a final elevation of approximately 3,750 ft (1143 m). The pushback would be implemented over a 14-year mine plan and result in ultimate overall slope heights in excess of 3,000 ft (914 m).

The geotechnical and mine design group established criteria from the outset of the study that involved designing the steepest

achievable overall slope angles, while remaining within acceptable Factor of Safety and Probability of Failure criteria, established from a combination of published industry standards (Stacey and Read 2009) and internal Rio Tinto risk acceptance criteria (Robotham 2011). It was indentified from prior experience that aggressive depressurization of the intrusive rock in the lower inter-ramp sectors and final slope toe, would be necessary to support acceptable geotechnical performance for preferred overall slope angles. This general deobjective pressurization presented а significant challenge given the existing hydrogeologic environment, with key issues as follows:

- The majority of the current and proposed lower slope and toe area was occupied by low permeability intrusive rock that would not readily depressurize.
- The groundwater pressure regime in the critical geotechnical areas was already significant.
- Vertical pore pressure dissipation in the intrusive rock would likely be slow when compared to the proposed rate of mining, given the low permeability of the rock, although not necessarily applicable in the more fractured over-break zone
- Groundwater levels in the district system, the Niagara and Lark workings, would create a source of recharge and driving head to the intrusive rock in the lower slope, with district groundwater levels in the range of 1,500 to 2,000 ft (457 to 610 m) more elevated than the proposed final pit floor.

Given the above challenges, an aggressive conceptual pit slope depressurization was developed, consisting of the following components:

• Installation of a drainage tunnel, (South Wall Drainage Gallery "SWDG") driven behind the final toe of the proposed push-

back, with a dense array of drill bays and fan drains installed to depressurize the Monzonite occupying the lower slope and pit floor, and following similar design to the previously successful HBDG,

- Gradual dewatering of the Niagara underground workings over a period of 7 years to a) reduce the potential for recharge and groundwater pressure in the mid slope inter-ramp sectors, and b) reduce driving head acting upon the lower inter-ramp sectors in the west and central areas.
- Gradual dewatering of the Lark underground workings over a period of 5 years, to reduce the amount of driving head feeding towards the lower inter-ramp sectors in the east corner of the pushback.
- Surface Horizontal Drains, placed systematically on all benches beneath currentday pit slope groundwater levels, as a secondary means to depressurize the outer skin of the slope and intercept transient groundwater that may seasonally locally recharge into the over-break zone of the pit slope.

Depressurization System Design Evaluation.

Pit slope pore pressures models and geotechnical models were constructed and used interactively to assess the potential benefit of the proposed active pit slope depressurization measures. Five models were constructed to represent the main slope design sectors. In each case, the pore pressure model and geotechnical model contained the same geology, pit profile and future mine plan. This allowed predicted pit slope pore pressure profiles to be exported and one-way coupled into the associated geotechnical model, thereby allowing the rock mass behavior and pit slope stability to factor the impact of pore pressure and slope depressurization. The Finite Element code FE-FLOW was used for pore pressure modeling with results one-way coupled into the Slope/W and FLAC geotechnical codes.

Each pit slope pore pressure model was

run forward in time in transient mode with the annual mine plan implemented. Initially, a 'reference' model was run through LOM, which contained no active depressurization measures. Subsequently, the active pit slope depressurization system components were incorporated into the model based on a conceptual schedule for implementation within the mine plan. The value and benefit of each pit slope depressurization system component was evaluated in annual mine plan increments, by quantified comparison to the reference case, with criteria including:

- Absolute groundwater pressure reduction effected at selected locations within the pit slope, with particular attention to the intrusive rock in the ultimate toe and lower inter-ramp sectors,
- The amount of time required for each depressurization measure to effect ground-water pressure reduction,
- The change in overall slope FoS imparted by active depressurization measures.

Fig. 4 presents an example pit slope pore pressure profile that predicts the impact of an underground drainage tunnel plus the dewatering of Niagara mine workings on the west sector of the pushback.

The main conclusions from integrated hydrogeologic-geotechnical analysis were:-

• The preferred overall ultimate slope de-



Fig. 4 Example pit slope pore pressure prediction with the SWDG and Niagara dewatering included

sign for the west and central sectors of the pushback would be achievable with installation of the SWDG to aggressively depressurize the Monzonite in the toe and lower inter-ramp sectors.

- The critical years when aggressive depressurization of the lower slope and toe area would be required to maintain acceptable design criteria, were indicated to be mining years 11 onwards. The SWDG would therefore need to be constructed and functional before this time.
- Gradual dewatering of the Niagara workings and Lark workings as the stand-alone pit slope depressurization approach would not be adequate to support the overall slope design for the west or central sectors. However, a secondary benefit would be attained in the form of a) general reduction in the groundwater flux feeding towards the mid inter-ramp slope sectors and potentially into the fissure fault system, and, b) a small incremental increase in the overall pit slope factor of safety in the west and central sectors.
- For the east corner of the pushback, the integrated analysis suggested that a combination of the slope design angles and more favorable rock mass properties lower in the slope, may preclude the need for extending the SWDG to this sector, with a combination of gradual Lark dewatering and horizontal drain implementation adequate to attain groundwater pressure distributions that support acceptable slope design criteria.
- Horizontal drains were not effective for supporting overall and lower inter-ramp slope performance, a) because of the late timing of installation within the mine plan, and, b) because they did not penetrate deep enough into the pit slope to depressurize the geotechnical areas critical to overall or lower inter-ramp slope performance. However, based on long term site experience, they are considered an important element of pit slope manage-

ment with secondary or smaller bench or multiple bench scale.

Validation and Confidence Building

A combination of practical operating experience at the mine and predictive modeling were used as the basis to design the pit slope depressurization system for the South Wall Expansion. Since the groundwater pressure regime and depressurization system represented an integral part of the slope design, a high degree of confidence that the proposed depressurization system would accomplish objectives was required. Confidence building was developed via:

- Technical peer review, conducted by impartial industry experts at regular intervals during the study
- Benchmarking of predicted depressurization in the south wall Monzonite against the practical results obtained in a very comparable setting with the HBDG.
- Cross-comparison of hydraulic parameters and conditions in each of the five pit slope pore pressure models.
- Comparison of the pit slope pore pressure models to a coarser scale 3D groundwater flow model of the district groundwater system built on a previous occasion.
- Model sensitivity analysis completed with hydraulic parameters increased and decreased based on the observed variability in the field data.

Based on the combination of all the above factors, a high level of confidence was developed in the ability for the depressurization system design to accomplish the groundwater pressure targets required within the preferred overall slope design. A significant program of piezometer monitoring, targeting the key geotechnical domains, was built into the design, to provide for a continuing process of measurement and verification that the depressurization measures are accomplishing the desired results.

Conclusions

For the Bingham Canyon South wall expansion, hydrogeology and pit slope depressurization was integrated with the slope design and geotechnical program from initiation of the PFS. The integrated study process was highly beneficial because, a) the developed geotechnical and hydrogeologic data sets and conceptual models were mutually enhancing, b) the pit slope depressurization system was designed in a way that addresses the geotechnical priorities and ensures that value is gained from active depressurization when implemented, and, c) the depressurization assessment contributed to the development of a viable and economic slope design.

References

- Read, J., Stacey, P. (2009). Guideline For Open Pit Slope Design. CSIRO Publishing, Collingwood.
- Robotham, M.E. (2011). Slope Design in Large Open Pit Mines. In: Slope Stability 2011: International Symposium on Rock Slope Stability in Open Pit Mining and Civil Engineering, Vancouver, Canada.

An Integrated Model for Mine Dewatering at the Bagdad Mine

Jeremy Dowling¹, Benjamin Zimmerlund², Jamie Kennealy³, Elmer van den Burg⁴

¹Schlumberger Water Services, 1875 Lawrence St., Suite 500, Denver, Colorado, USA, JDowling@slb.com
²Schlumberger Water Services, 2525 Gambell St., Anchorage, Alaska, USA, BZimmerlund@slb.com
³Schlumberger Water Services, 2045 N. Forbes Blvd., Suite 103, Tucson, Arizona, USA, JKennealy@slb.com
⁴Schlumberger Water Services, 2045 N. Forbes Blvd., Suite 103, Tucson, Arizona, USA, EBerg@slb.com

Abstract The ore deposit hydrogeology of large open pit porphyry copper mines in the southwestern U.S. typically involves large spatial variability in rock hydraulics. An integrated conceptual hydrogeologic model and validated predictive groundwater model are key to assessing dewatering and pit slope depressurization. In the case of the Bagdad mine, in Arizona, a 3D empirical model of the hydrogeology was developed using Petrel software. Three-dimensional hydrogeologic properties were exported to the MODFLOW-SURFACT groundwater modeling code providing a tool to target geologic zones for dewatering and pit slope depressurization. The resulting simulation accurately represents pit conditions and enhances mine planning.

Keywords Groundwater modeling, Petrel, Arizona, Groundwater Vistas, MODFLOW-SURFACT, dewatering, open-pit, mining, copper, MineSight, pit slope depressurization

Introduction

The ore deposit hydrogeology of large open pit porphyry copper mines in the southwestern U.S. typically involves large, spatial variability in rock mass hydraulics. The occurrence of groundwater flow and the distribution of groundwater pressure within the rock mass is influenced by many geologic factors including: structure, lithology, alteration, mining practices, and past and present mine dewatering efforts. Many of the Southwest mines require a program of pit slope depressurization to support geotechnical performance or a general dewatering program to maintain dry working conditions. An integrated conceptual hydrogeologic model and validated predictive groundwater model are key to decision making associated with dewatering and pit slope depressurization design and operation. In the case of the Bagdad mine, located in west-central Arizona, a sophisticated 3D empirical model of the mine hydrogeology was developed using the Petrel Seismic to Simulation software tool (Schlumberger 2011). Petrel allows for the storage, visualization, and interpretation of a wide variety of geo-scientific data types, the construction of geological models which include complex structures and the preparation of the input for and analyzing the output of numerical flow models.

A fully integrated analysis was completed in Petrel to examine relationships between rock mass properties, fault properties, and the distribution of observed flows and heads in pit slope horizontal drains, wells, and boreholes. The analysis allowed for improved understanding of the influence of lithology and structural sets/orientations on rock mass hydraulics. Three-dimensionally distributed hydrogeologic properties developed in Petrel were subsequently exported to the 3D MOD-FLOW-SURFACT (HydroGeoLogic, Inc. 2011) groundwater modeling code. The groundwater flow model was well calibrated to observed mine area groundwater levels and flows and has subsequently been used as a tool to target prospective geologic zones areas for dewatering production pumping and to guide the strategy for horizontal drain drilling in the less conductive slope sectors.

This paper describes the hydrogeology of the Bagdad mine and the process of constructing the Petrel and groundwater flow models to support the mine dewatering and pit slope depressurization program. The evaluation is relevant to any large open pit mine operation and represents an advancement in mine hydrogeology by integrating hydrogeologic information in the empirical model and accurately translating this into the conceptual hydrogeologic model. The result is a simulation that more accurately represents the pit conditions and enhances mine planning.

Site overview

The Bagdad mine, owned and operated by Freeport-McMoRan Copper & Gold; Inc., is a porphyry copper deposit containing both sulfide and oxide mineralization. Bagdad area covers approximately 38 mi² (98 km²) and lies within a mountainous region located 100 mi (160 km) northwest of Phoenix, Arizona. The Bagdad mine consists of open pit mining of copper and molybdenum. The ore processing facilities include a mill/concentrator, several heap leach facilities, and a solvent extraction and electrowinning (SX/EW) plant. The current proposed mine plan includes deepening of the open pit by 1,000 vertical ft (300 m), along with significant lateral expansion over the 40year Life of Mine (LOM).

The regional geology of the Bagdad area was described in detail by Anderson (1955) and consists of a combination of lava mesas and mountains cut by the deep canyons of Boulder and Copper Creeks. Many of the rocks exposed are a metamorphosed Precambrian complex with associated igneous intrusions. Erosion and deposition formed widespread conglomerates capped by regional basalt flows, which create the flat mesas seen today. The largest regional scale faults trend north-south and include the Hawkeye Fault, which bisects the current Bagdad open pit. Regional groundwater occurs within the highly faulted and fractured bedrock. Groundwater flow is generally from the Santa Maria Mountains to the northeast to the lower reaches of the Big Sandy and Santa Maria Rivers to the southwest of the mine. Regional groundwater elevations were based on data from Arizona Department of Water Resources drilling logs (ADWR 2011).

Historical dewatering efforts prior to 2010 were fairly minimal, consisting of 1) dewatering well pumping from less than 10 wells, typically for water supply purposes, 2) drilling of over 400 horizontal drains to depressurize specific pit slopes, and 3) continual pit sump pumping to remove groundwater inflow to the pit. In 2011, two dewatering wells produced a total of 200 gpm (13 L/s), approximately 60 horizontal drains were being drilled annually and pit sump pumping averaged 800 gpm (50 L/s).

Pit Area Hydrogeology

The vast majority of the open pit area consists of Quartz Monzonite (QM) and Porphyritic Quartz Monzonite (PQM) intrusions, which contain most of the ore body. The Precambrian Alaskite Porphyry (AP) intrusion comprises the upper slope of the west pit slope. The Precambrian metamorphic complex (PCM) comprises the upper slope of the south, east and northeast pit slopes. The Precambrian Lawler Peak Granite (LPG) is not exposed in the pit area but exists extensively behind the north and northeast pit slopes. The Copper Creek and Sanders Mesas make up the north and east pit crest, respectively. The mesas are comprised of Gila Conglomerate (Gila), overlain by Sanders Basalt (SanBas). Waste rock surrounds the open pit in the form of construction fill and roads. Historic tailings, waste rock piles, and heap leach dumps have been deposited in historic drainages on the south wall pit crest. Several major northwest-southeast trending faults bisect the pit area, the most significant of which are the Crusher Fault, Hawkeye Fault, Post/Gizmo Fault, and East Fault.

Groundwater Head Distribution

Over twenty, multi-level grouted-in vibrating wire piezometers (VWPs) have been installed

in the pit area since 2010. The VWPs target specific pit slopes, geologic units, and structures, greatly increasing the understanding of the 3D groundwater head distribution. Continuous monitoring of VWPs using dataloggers has provided verification of dewatering and depressurization activities.

Pit area groundwater heads range from 3,400 ft (1,036 m) amsl on the south pit crest to 2,000 ft (610 m) amsl in the pit bottom (approximately land surface). Heads in the east, west, and north sectors are relatively depressurized compared to the south and northeast sectors. The south pit slope has elevated pore pressures due to pit crest facility leakage, while the northeast sector groundwater is fed by the highly fractured and permeable LPG.

Several structures appear to impact groundwater flow in the pit area leading to compartmentalization. Saturated pit slopes can be seen behind the Crusher Fault in the southwest sector, indicating groundwater is backing up behind the fault. The Hawkeye Fault separates the pit bottom into two compartments where dewatering well pumping west of the fault has little impact to the east. The Post/Gizmo Fault has shown increased groundwater production along its axis and has become a target for dewatering infrastructure. The East Fault appears to back up groundwater flowing into the pit from the east which will cause concerns for eastward pit expansions.

Groundwater Production

Bedrock groundwater production in the pit area is highly variable, with measured rates ranging from 0 to over 500 gpm (32 L/s). Along with known dewatering well pumping rates, airlift production rates during drilling were collected for over 20 RC drill holes from 2010 to present. Historic drilling records and logs were examined and groundwater production data was collected. Additionally, drain flow data was available for over 400 horizontal drains drilled within the pit from 2003 to present.

An initial assessment indicated that groundwater production was strongly tied to

geologic units, with structural and sectorbased influences. The QM, located on the south pit slope, tends to produce little or no groundwater, likely due to long-term alteration of the rock from pit crest facility leakage. PCM rocks tend to produce little groundwater except for along major structures such as the Post/Gizmo Fault. The AP, PQM, and QM located in the pit bottom and north wall tend to be moderately productive (25 to 100 gpm, or 1.5 to 6.5 L/s). The LPG, behind the northeast and north pit slopes, has produced over 500 gpm (32 L/s) in dewatering wells and appears to be pervasively productive.

Horizontal drain flow data shows that drains drilled into the east and west walls tend to be more productive than those drilled into the north and south walls, likely due to eastwest drain orientations cross-cutting the northwest-southeast trending structures and fabric.

Hydraulic Testing and Parameters

Hydraulic testing has been performed since 2010 in the form of RC drill hole airlift/injection tests and dewatering well pumping tests. Hydraulic conductivity values are approximately proportional to groundwater production data. Measurements in PCM and south wall QM show bulk conductivities of $1 \cdot 10^{-6}$ to $1 \cdot 10^{-5}$ cm/s. AP and QM in the pit bottom/ north wall show bulk conductivities of $1 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$ cm/s. LPG and PQM in the north and northeast sectors show bulk conductivities of $1 \cdot 10^{-4}$ to $1 \cdot 10^{-3}$ cm/s. Storage parameters have been measured in a few locations from piezometer responses to dewatering well pumping tests. Measured storage values range from 0.0002 in the pit bottom QM to 0.003 in the LPG.

Petrel Model Development

A 3D Petrel model was developed to assemble all of the geologic and hydrogeologic datasets into one model format with the ultimate aim of creating a conceptual model/flow model grid. Petrel has numerous tools for 3D data visualization, spatial analysis and flow model grid creation.

The mine has developed a 3D resource geologic block model, using the MineSight software tool (Mintec 2011), based on considerable mineral exploration drilling. The block model represents the geology as 50 ft cubes within the mine area. The centers from each block were exported from MineSight and imported into Petrel as an exact copy of the MineSight model grid (Fig. 1). Topographic surfaces representing the current and pre-mine land surface were imported into Petrel as 3D lines and interpolated to continuous surfaces. Surface expressions and measured dips for major pit area structures were obtained from the mine and interpreted into 3D faults in Petrel.

Hydrogeologic datasets were imported into the Petrel model, including: surface collars and drilling paths for all dewatering wells, piezometers and RC holes containing hydrogeologic data; depth-specific well logs were imported along well paths, including RC airlift production with depth and interpreted hydraulic conductivity profiles; and water levels from multi-level grouted-in VWPs. In addition, collar locations and drilling paths for all horizontal drains were loaded into Petrel along with their measured flow rate.

Petrel Analysis

Petrel was used to perform analysis and interpretation on the geologic and hydrogeologic data to ultimately support the conceptual model and groundwater flow model. Analysis was done both qualitatively, through visualization of datasets, and quantitatively, through data statistics.

3D visualization of datasets is a key part of understanding the complex hydrogeology of a fracture based groundwater flow system. Petrel was used in conjunction with the resource block model and fault network to interpolate the hydrogeologic data. Analyses of hydrogeological features that could not be explained clearly due to the lack of historic data were evaluated by bringing together various data sources in Petrel. For example, little was known of an existing dewatering well with high groundwater production in the northeast sector of the pit. The path of the well was loaded into the Petrel model and overlaid with the resource block model, showing that the bottom of the well was in the LPG, which was hypothesized as the source of the production and later confirmed with additional drilling. Additionally, Petrel was a key tool in defining a low conductivity area on the southern pit wall, a major component of the conceptual model. Hydraulic conductivity, water produc-



Wolkersdorfer, Brown & Figueroa (Editors)

tion, multi-level VWP and drain data were loaded into Petrel and visualized to define a 3D volume of apparent low conductivity, low water production, and high pore pressure rock.

Extensive analysis was performed on the historic horizontal drain flow dataset. consisting of loading the drain paths and measured drain flow into Petrel, merging the drain flow data with lithologic and fault compartment properties, and performing general statistics on the results. Drain flow magnitudes were upscaled into the resource block model grid and output with geology and fault compartment codes. The analysis indicated that compartment between the Crusher and Hawkeye Fault was not sensitive to drain drilling and produced very little drain flow. It also showed that drains that cross key faults, such as the Hawkeye Fault on the north wall and the Crusher Fault on the west wall, tend to produce more groundwater. This analysis gave key spatial information on pit slope hydrogeology which helped guide future depressurization programs and supported conceptual model development.

Groundwater Flow Model Development

The inputs for a 3D numerical groundwater flow model were constructed in Petrel. The groundwater flow modeling code selected was MODFLOW-SURFACT for its increased performance in low hydraulic conductivity simulations. Groundwater Vistas v6 (Environmental Simulations, Inc., 2011) was used as the MODFLOW-SURFACT interface.

The total model area is approximately 168 mi² (435 km²), with active cells comprising approximately 114 mi² (373 km²). Model domain boundaries were placed at assumed hydrogeologic boundaries located away from the mine area. A tartan flow model grid was developed in the Petrel model, separate from the block model grid, consisting of 111 rows and 101 columns, rotated 37° to align with the primary northeast to southwest flow direction and predominant pit area structures and refined around the LOM pit (Fig. 2). Model layering was developed in Petrel as horizontal layers throughout the model domain, refined in the section covered by the mine block model. Boundary conditions were placed within the model domain, including drain boundaries to represent creeks and major washes, drain boundaries representing the surface of the open pit, and aerial recharge boundaries to represent bedrock groundwater recharge.

Cells within the active model area were grouped together based on geologic unit with the initial assumption that hydrogeologic properties are similar within a geologic unit. The resource geologic block model was upscaled into the flow model grid but only existed in the immediate mine area. USGS surface geology and geologic cross sections (Anderson 1955) were imported into the Petrel



model to guide the cell property population outside of the resource block model area. The focus of the model was the mine area so the regional geology was simplified into basalts, sedimentary (predominantly conglomerates) and intrusives.

Groundwater Flow Model Calibration

Calibration of the groundwater flow model was carried out in two phases. The first phase was a steady-state calibration to mid-2011 hydrogeologic conditions. The second phase consisted of transient calibration to dewatering well pumping records and piezometer responses over a six month period.

The steady-state calibration was achieved through the trial-and-error approach using hydraulic conductivity ranges defined by the conceptual model. The calibration was finetuned through the use of automatic calibration software. During steady-state calibration, several modifications to the hydrogeologic conceptual model were needed: 1) An "overbreak" zone was applied to the uppermost active model cell in the open pit area representing increased hydraulic conductivity due to blasting, 2) pit slope depressurization due to historic horizontal drain drilling was accounted for by applying increased hydraulic conductivities to those model cells intersecting drains in the Petrel model, and 3) the QM unit, compromising the majority of the pit, was divided into two distinct HGU's based on reduced hydraulic conductivity from longterm rock alteration on slopes below pit crest mine facilities.

The overall steady-state calibration resulted in a scaled RMS below 4 % and calibrated values of HGU hydraulic parameters were within ranges of the hydrogeologic conceptual model. Simulated flows in creeks within and at the edges of the model domain ranged from 100 to 500 gpm (6 to 31.5 L/s), which are reasonable given the climate and riparian ET rates for the area. Simulated groundwater inflow closely matched the open pit water balance and pit pumping data. A transient calibration was carried out consisting of simulating pumping records from two pit-dewatering wells and matching measured piezometer responses to those wells. The correspondence between simulated and observed heads was improved by adjusting the storage values for all HGUs. Despite unknown or coarse pumping records, a reasonable transient calibration was obtained. Simulated pressure heads were exported from the groundwater flow model following the transient calibration and displayed on geotechnical cross sections for each pit sector in order to represent current groundwater conditions.

Groundwater Flow Model Predictions

The calibrated groundwater flow model was used to evaluate groundwater levels and pit slope pore pressures through LOM. Future mine plans were loaded into Petrel in order to construct the input files of pit surface drains and "overbreak" zone properties. Short-term mine plans were more detailed (quarterly to yearly stress periods) and long-term mine plans were more coarse (three to nine year stress periods), allowing for detailed analysis of near future depressurization strategy and LOM bulk dewatering strategy. All stress periods were combined into a single model using the Time-Variant Material Property Package (TMP1) of MODFLOW-SURFACT v4.0 to simulate the increase of hydraulic conductivity of the "overbreak" zone as the pit face advances through time.

A "Do Nothing" predictive model was run through LOM to simulate the development of the open pit with no active dewatering or depressurization measures (Fig. 3). The simulation results were provided to the geotechnical consultant and used as input to LOM pit slope stability models. The purpose of the "Do-Nothing" simulation was twofold: 1) provide a benchmark with which to compare active depressurization and dewatering simulations and 2) guide long-term dewatering strategy based on geotechnical slope stability results.



Fig. 3. Simulated LOM "Do-Nothing" (top) and Active Depressurization (bottom) results

Active dewatering simulations were run through LOM based on the results of the "Do-Nothing" simulations and practical knowledge of the site hydrogeology. Dewatering wells and horizontal drains were simulated through LOM for lithologic units and pit slopes requiring active depressurization (Fig. 3). The results from the active dewatering simulations were fed back into the geotechnical slope stability models in an iterative process until an optimized dewatering and depressurization plan was achieved.

Summary

An integrated conceptual hydrogeologic model and validated predictive groundwater model were developed for the Bagdad open pit mine. The mine resource block model was integrated with hydrogeologic datasets in Petrel to develop a hydrogeologic conceptual model, which was exported to a 3D groundwater flow model grid. The flow model was calibrated to pit area flows and heads and subsequently used to predict pit slope pore pressures for future mine plans. Predictive pit slope pore pressures were fed into geotechnical pit slope stability models allowing the LOM dewatering strategy to be optimized.

Petrel Seismic to Simulation software was a key tool for data visualization, spatial hydrogeologic analysis, conceptual model and groundwater flow model development. Petrel is a three-dimensional interpretive modeling environment ideally suited for conceptual model construction and the preparation of inputs for groundwater flow models. Petrel is a standard tool for the oil and gas industry, where it is used for reservoir characterization and engineering.

References

- Anderson, C.A., Scholz, E.A., Strobell, J.D., Jr. (1955) Geology and Ore Deposits of the Bagdad Area, Yavapi County, Arizona: Geological Survey Professional Paper 278, 103pp
- Arizona Department of Water Resources (ADWR) (2011) Well Registry Database (https://gisweb.azwater.gov/ waterresourcedat/WellRegistry.aspx). Downloaded September, 2011
- Environmental Simulations, Inc. (2011) Groundwater Vistas, Version 6.0
- HydroGeoLogic, Inc., 3D (2011) Modflow Surfact, Version 4.0

Mintec, Inc. (2011) MineSight Mining Software Schlumberger (2011) PETREL E&P Platform Network

Hydrogeologic Characterization and Numerical Modeling of Groundwater Inflow to Support Feasibility Studies for Underground Mining – a Case Study in the Southeast Idaho Phosphate District

Brent Everett¹, Scott Effner¹, Jon Kaminsky¹, David Kramer²

¹Whetstone Associates, 104 W. Ruby Avenue, Gunnison, Colorado, USA, beverett@whetstoneassociates.com, seffner@whetstone-associates.com, jkaminsky@whetstone-associates.com, ²Paris Hills Agricom, Inc., 9 N. Main St., Paris, Idaho, USA, dkramer@parishills.com

Abstract Reliable characterization of groundwater inflow and water quality is a critical component of feasibility studies for underground mines. Prediction of inflow volumes, timing, and location are required to support mine design and cost estimates. Water quality and disposal issues often affect mine economics and permitting strategies. The following paper presents an overview of hydrogeologic issues relevant to mine planning and a case study of the hydrogeologic investigation and inflow analysis that was prepared to support the feasibility study for the Paris Hills Underground Phosphate Project.

Keywords mining hydrology, inflow prediction, groundwater modeling, mine planning

Introduction

Preparation of a successful feasibility study is a key milestone in the development of new underground mines. Feasibility studies are often required to obtain financing from outside investors. They also provide mine planning information and analysis of the economic viability of the project. Mine dewatering and environmental issues related to disposal of pumped water can be significant costs. The dewatering approach, volume of discharge, and timing of capitalization for pumping systems are all important considerations for the economic analysis. Environmental concerns such as impacts to water quality or decreases in groundwater levels and availability may also affect the project's ability to obtain required permits.

Given the potential importance of groundwater issues to the viability of a new underground mine, hydrogeologic characterization should start at an early stage in project development. If possible, the investigation should be incorporated into the mineral exploration drilling program to minimize costs. Early data collection allows for a phased approach to the investigation which can be adapted with increased understanding of the groundwater system. The following paper discusses the types of hydrogeologic data required to support feasibility studies and provides recommendations for a phased testing approach. It also presents a case study of the hydrogeologic investigation and numerical groundwater model for the Paris Hills Underground Phosphate Project.

General Approach to Feasibility–Level Hydrogeologic Investigation

The first phase of hydrogeologic investigation to support feasibility studies for new underground mines should begin during the earliest phases of mineral exploration drilling. Data including depth to water, air-lift discharge, losses in circulation, and field water quality parameters for pH, specific conductance, and temperature are easily recorded by exploration crews and provide the first indication of groundwater issues that may become significant cost and regulatory considerations for the future mine. As confidence in the grade and extent of mineralization increases, a formal groundwater investigation should be initiated. The timing of the investigation should coincide with the final phase of delineation drilling to provide access to boreholes that are spatially distributed across the deposit and intersect significant structural or stratigraphic features. The focus of work is to collect hydraulic conductivity and water level data that will be used to support the preliminary mine design and dewatering analysis. Water chemistry data should also be collected to evaluate environmental issues associated with dewatering discharge.

Several practical approaches exist to collect hydraulic conductivity and water level data in uncased exploration boreholes. Packer permeability tests can be used in consolidated formations. There are a number of testing methods, but generally, the tests are performed by pumping water into or out of a section of borehole that has been isolated using an inflatable packer or pair of packers. The flow rate, injection pressure, and water level recovery data are used to calculate the hydraulic conductivity of the isolated interval. Shut-in water levels also provide valuable information that can be used to calculate vertical gradients and pressure heads on hydrologsignificant features ically (e.g. faults, permeable beds, aquitards). Packer tests can be performed in cored or air-rotary boreholes using upstage or downstage testing methods. The downstage method interrupts drilling and uses a single packer to test the bottom of the hole as it is advanced. The upstage method uses two packers to isolate sections of the borehole after it has been drilled to the total depth. Selection of the testing approach depends on consideration of variables such as formation stability, drilling method, depth of testing, and depth to water.

Packer tests typically have short duration (15 to 20 min) and relatively small radii of influence. It is therefore important to perform a statistically significant number of tests to develop adequate confidence to extrapolate the calculated hydraulic conductivity values to the larger rock mass. Packer testing should target competent and fractured rock as well as structural and stratigraphic zones of interest.

Vibrating wire piezometers (VWPs) can also be used to provide targeted groundwater level data during delineation drilling. The instruments measure pore pressure by sensing changes in the vibrational frequency of a wire stretched between a fixed anchor and a diaphragm. Multiple VWPs can be installed in a single borehole to evaluate stratified aquifers or different zones of interest. VWPs are permanent installations that are grouted in place during borehole abandonment. As such, they have the added advantage of being able to monitor dewatering progress as the mine is put into production.

Airlift pumping tests are another method that can be used to evaluate hydraulic conductivity in stable exploration boreholes. The tests may be performed at any point during drilling with an air-rotary rig and favorable water level configuration. Drilling is stopped with the bit near the bottom of the hole and the rig compressor is used to airlift water to the surface. Discharge and water level recovery data are collected and used to estimate hydraulic conductivity. Airlift tests have significant limitations in that the data are often difficult to interpret because of multiple productive zones or lost circulation. The volume of annular space, depth to water, and percent submergence of the air turnaround point are additional variables that affect the efficiency of pumping. Water may not return to the surface in boreholes with deep water levels and low submergence of the turnaround point.

In addition to providing an opportunity for cost-effective measurement of hydraulic conductivity and water levels in open boreholes, mineral exploration drilling programs provide the basic stratigraphic and structural data that are required to develop the conceptual hydrogeologic model (CHM). The CHM is a working understanding of the patterns of groundwater flow, depth of mining submergence, and relative hydraulic conductivity of structural and stratigraphic features that have potential to provide groundwater inflow to the underground workings. The CHM is continually updated as new information becomes available.

A second phase of hydrogeologic investigation may be required near the end of the exploration program if the project is viable and initial data indicate significant potential for groundwater inflow. Indicators of inflow hazard include the depth of mining below the regional groundwater level and proximity of the planned workings to surface water, permeable strata, and water bearing structures. At this point, the mine plan is better defined and areas of potential high inflow can be targeted for additional testing. The second phase of investigation should also include installation of monitoring wells to develop water quality data that can be used to estimate costs associated with treatment and disposal of dewatering discharge. Water disposal issues can trigger permitting requirements that affect the project schedule.

Depending on the importance of groundwater issues, the level of confidence in the CHM, and the available budget, a multi-well aquifer test may be warranted prior to preparation of the feasibility study. Aquifer tests are expensive, but provide high confidence data for large rock masses if designed and performed correctly. Design considerations are site-specific, but at a minimum the tests should provide transmissivity and storage data for the hydrogeologic unit of interest. Aquifer tests can also provide information about compartmentalization of the aquifer, anisotropy of drawdown, hydraulically active structures, and water availability to drive sustained groundwater inflow.

At the end of the second phase of testing, hydrogeologic data should be sufficient to support a feasibility-level dewatering design and estimate of mine discharge. The CHM and dewatering analysis will typically have substantial uncertainty, but should be adequately conservative to ensure that potential dewatering costs do not make the project unviable. A general rule to follow is that feasibility-level cost estimates should have an accuracy of at least \pm 20 % (Lowrie 2002). This level of accuracy usually requires development of a numerical model for all but the simplest of mining plans and hydrogeologic environments.

Case Study-Paris Hills Project

The Paris Hills Underground Phosphate Project is being developed by Paris Hills Agricom, Inc. (PHA) in Bear Lake County, Idaho. The project will recover stratiform phosphate ore from the Meade Peak Member of the Permian-age Phosphoria Formation using room and pillar mining methods followed by retreat mining with an average 60 % pillar extraction and subsidence of the overlying strata. Entry and crosscut dimensions will be 5.25 m wide with a minimum height of 1.65 m (1.5 m with 0.15 m out of seam dilution). The entries are laid out quartering the plunge of the horizontal limb to provide an apparent dip of about 12.5°. Mining will be by continuous miners and the depth of the workings will increase from the surface at the south portal down to about 900 m below ground surface (bgs) at the northern extent of the mine.

The CHM for Paris Hills includes upper and lower flow systems separated by a leaky aquitard. The upper flow system includes the Rex Chert member of the Phosphoria Formation and overlying strata such as the Dinwoody Formation and Thaynes Limestone. It is recharged by infiltration of precipitation, flows to the northwest, and may be semi-confined to confined depending on location. The lower flow system is part of a regional-scale limestone aquifer that occurs in the Wells Formation. Groundwater in the lower flow system is confined and flows northwest roughly parallel to the plunge of the synclinal fold that contains the ore deposit. The Meade Peak is a leaky aquitard that separates the two flow systems. The submergence of the mining horizon increases to the northwest. The elevation of the portal will be 30 to 50 m above the water

table. The northwestern extent of the underground workings will be submerged by more than 700 m.

Groundwater flow is affected by structural features in the mine area. Increased fracturing along the axis of the associated syncline appears to exert controlling influence over the flow direction with groundwater flowing northwest into the hinge. The Consolidated Fault Zone also exerts local control over the direction of groundwater flow with potentiometric surface lines for both the Rex Chert and Wells Formation bending into the structure. Increased hydraulic conductivity is also likely to be associated with other faults in the project area. The Paris Thrust Fault is a large displacement fault located west of the planned mine. It places lower Cambrian-age rocks over younger Paleozoic sedimentary strata and is conceptualized to act as a barrier to groundwater flow.

The hydrogeologic investigation for the feasibility study was developed using a phased approach. Initial exploration was accomplished using air rotary drilling to pre-collar the holes to a point above the Meade Peak Member. Delineation of the ore body was performed using HQ- and PQ-diameter core drilling. Because of issues with lost circulation and the depth to groundwater which typically exceeds 200 m, little hydrogeologic data were available from the initial exploration drilling program.

The first phase of hydrogeologic investigation for the site began in 2011 and consisted of packer testing in cored mineral exploration boreholes and installation of VWPs in known aquifers above and below the mining horizon. The packer tests used a downstage method with a wireline packer assembly. The program experienced significant technical challenges because of the depth of testing which often exceeded 700 to 800 m. The high inflation pressures required to properly seat the packers deformed the rubber elements making retrieval through the core bit at the end of testing difficult. However, a total of 21 packer tests were successfully completed using the USBR step injection method (O'Rourke *et al.* 1977). Calculated hydraulic conductivities ranged from 2.8×10^{-5} m/d to 1.3×10^{-1} m/d. Measured water levels for the shut-in sections indicate that portions of the ore body will be submerged below the regional base level by more than 700 m.

Paired VWPs were also installed in eight boreholes to monitor water levels in aquifer units above and below the mining horizon. The upper flow system is separated from the mining horizon by approximately 60 m of low permeable shale. The lower regional aquifer is located 1 to 3 m below the floor of the mine and is separated from the planned underground workings by a thin mudstone bed at the base of the Meade Peak. VWP data confirmed groundwater depths in the upper and lower aquifers and were used to document a northwest groundwater flow direction.

The second phase of hydrogeologic investigation included installation and testing of eight monitoring wells. Three wells were installed in the lower aquifer and one in the upper aquifer to evaluate the chemical characteristics of the planned dewatering discharge. Two wells were installed in a perched zone near the toe of the planned waste rock dump to provide baseline data for permitting, and two wells were installed to monitor water quality in the area that is being considered for reinjection of the dewatering discharge. Pneumatic slug tests in the monitoring wells returned hydraulic conductivity values between 4.6 m/d and 16.4 m/d for the lower regional aquifer and 3.2 m/d for the upper aquifer.

The results of the hydrogeologic investigation were used with regional data to develop numerical simulation of mine dewatering in MODFLOW-SURFACT version 3.0 (HydroGeologic 2001). The groundwater model was prepared in two parts: an initial steady-state model to simulate the pre-mining groundwater flow system and a transient model to simulate time-dependent dewatering as a funcGolden CO; USA

"Reliable Mine Water Technology"

Zone		Effect	Extent	Characteristics
Caved Zone		Increased Vertical and Horizontal Transmissivity intersected groundwater quickly drained into mine	6 to 10 times the height of the mining horizon	Zone of complete stratigraphic disruption. Extends 6 to 10 times the mining height above the workings. Roof strata collapse into the opening and form rotated blocks with increased volume that limits the upward progression of caving. Groundwater intersected by the caved zone is quickly drained into the mine.
Fractured Z	one	Increased Vertical Transmissivity Potential for increased seepage from overlying units	Top of caved zone to a maximum height of about 24 to 30 times the mining thickness	Zone of vertically transmissive fractures without rotation. Bedding retains original attitude and does not fall or detach. Fracture density and permeability increase downward. The combined height of the fractured and caved zones can be 24 to 30 times the mining height. Increased vertical and horizontal permeability allow for drainage of intersected water into the mine workings.
	Dilated Zone	Increased Storage Potential for temporary local decrease in water levels to fill additional storage volume	Top of fractured zone to a maximum height of about 60 times the mining thickness	Zone of beam deformation in which strata sag but do not form vertically connected fractures. Bed dilation increases groundwater storage but does not allow for vertical transmission of water into underlying zones. Generally extends about 24 to 60 times the mining height above the workings. Wells and surface water intersected by the dilated zone will experience temporary reductions in level/volume as water goes into storage.
Continuous Zone	Constrained Zone	No Change Potential for hydrologic impacts is minimized	Top of the dilated zone to 15 m below ground surface	Zone of no significant effect on transmissivity and storage. Strata are affected by subsidence but are not sufficiently deformed or strained to dilate and significantly increase storage. Overall extensile strains remain less than 0.1 %, the point at which rock masses are not sufficiently disrupted to increase permeability.
	Surface Fracture Zone	Increased Transmissivity Potential for localized, short-duration changes in groundwater levels	0 to 15 m below ground surface	Surface zone with shallow tension fractures caused by subsidence. Fractures generally extend less than 15 m below ground surface and are spatially related to panel/trough edges and areas of local extension. Changes in shallow hydraulic regimes are short lived because fractures are localized and quickly filled by sediment.

Table 1 Hydrologic effects of mining subsidence (Kendorski 1993).



Fig. 1 Three dimensional dia- gram of model domain.

tion of mine development. The model includes representations of the upper and lower aquifers, the leaky aquitard formed by Meade Peak, and structural features such as folds and faults that influence groundwater flow. Hydrogeologic changes from subsidence during retreat mining are simulated according to the conceptual model in Table 1.



Fig. 2 Predicted average annual pumping rates for mine dewatering.

The flow field for the steady-state groundwater model was calibrated using water level data from VWPs. Dewatering of the underground workings was simulated using 17 wells to intercept groundwater before it enters the mine. Some groundwater will bypass the well field and report to the underground workings. Discharge from the mine was simulated using drain cells that start near the portal and move northward with mine development. Subsidence from retreat mining was simulated by increasing vertical and horizontal hydraulic conductivity in the caved zone and vertical hydraulic conductivity in the fractured zone. Hydrologic changes in the continuous zone are not expected to influence mine dewatering and were not modeled. A diagrammatic representation of the numerical model is shown in Fig. 1. The predicted average annual dewatering requirement for the mine is shown in Fig. 2.

Conclusions

Hydrogeologic characterization should start during the initial stages of project development for underground mines. Groundwater issues often affect the viability of new mining projects and reliable hydraulic conductivity, water level, and water quality data are needed to support mine planning. Early data collection allows for a phased hydrogeologic investigation that can be adapted to site-specific conditions as understanding of the groundwater system increases. This approach was used to support the feasibility study for the Paris Hills Underground Phosphate Project. PHA completed a successful feasibility study for the Paris Hills Underground Phosphate Project in December 2012, and is on track to start production in 2014.

Acknowledgements

We thank Paris Hills Agricom, Inc. for their assistance with this paper and for allowing us to present the results of the dewatering analysis for their project.

References

- HydroGeoLogic, Inc. (1998) MODFLOW-SURFACT v. 3.0: A comprehensive MODFLOW-based flow and transport simulator. Code Documentation Report. HydroGeoLogic, Reston, VA
- Kendorski FS (1993) Effect of high-extraction coal mining on surface and ground waters. 12th Conference on Ground Control in Mining, West Virginia University

Lowrie RL (2002) SME Mining Reference Handbook, p. 1

O'Rourke JE, Essex RJ, and Ranson BK (1977) Field permeability test methods with applications to solution mining. U.S. Bureau of Mines Report Bu-Mines °FR, p. 180

Field and Laboratory coupled Fracture Deformation — Pore Pressure-Permeability Experiments that provide Insight for Depressurization of Fractured Rock Slopes

John E. Gale¹, Eunjeong Seok²

Fracflow Consultants Inc., 154 Major's Path, St. John's, NL, Canada, A1A 5A1 ¹john_ffc@nfld.net, ²eunjeong_ffc@nfld.net

Abstract Slope failures in fractured rocks occur along fracture planes and through rock bridges. Pore-water pressures within fracture planes, with a critical orientation relative to the driving and resisting forces, can trigger slope failures. For 500 to 1000 m high mine slopes the need for pore pressure control is extremely important, especially in low-permeability fractured rocks. Predicting the rate and effectiveness of depressurization of slopes requires that models incorporate fracture characteristics and coupled behaviour for the full range of stresses. Model calibration against sparse data without comparison of blind predictions to well controlled experimental data is no substitute for model validation.

Keywords Fracture deformation, slope depressurization, model validation.

Introduction

Most argillaceous and crystalline rock masses consist of rock blocks bounded by discrete fracture planes. The blocks may be porous and permeable rock, such as sandstone, or may have low porosity and very low permeability, such as granite. It is the ratio of the permeability of the rock blocks to the permeability of the fractures that determines the significance of the fractures in a given flow system. In metamorphic and granitic rocks, it is generally accepted that the hydraulic conductivity of rock blocks is <10⁻⁹ cm/s and thus significant flows can occur only through the fracture system. Very little data are available on the effect of fractures on flow in shales and other low-permeability argillaceous rocks. In the more permeable argillaceous rocks, there have been almost no systematic attempts at distinguishing the contributions to flow from the rock blocks and from the fracture system. Groundwater studies in these rocks have assumed that the rock block-fracture system is a porous medium. Thus the most significant data base in fracture hydrology is primarily for metamorphic and crystalline rocks. In addition, extensive literature exists on fluid movement through fractured carbonate rocks in which solution channels are the primary conduits but these systems are generally considered to act as open channel flow systems.

Considerable effort has been and will be devoted to understanding how pore water pressures in fractured and fractured-porous rock slopes can be managed to reduce the risk of slope failures, especially in open pits where the slopes can and will range up to hundreds of metres in height. Fractures open and close due to changes in pore pressure within the fracture planes as well as changes in the applied normal and shear stress. The original fracture permeability is controlled by the properties of the fracture plane and the overall fracture geometry. Fluids moving through a fracture plane over long periods of time create a network of open pore space and contact points or asperities (Fig. 1) that are in meta-stable equilibrium under the applied stresses. (The pore structure map in Fig. 1 was created by resin impregnation under the applied load, followed by sectioning the fracture plane on 5 mm grids and digitizing the images (Seok



Fig. 1 Fracture apertures from resin injection experiments (Seok 2012)

2012)). Decreases in the applied stress and increases in the pore pressures will cause the fractures to open with a corresponding increase in permeability, while increases in the applied stress and decreases in the pore pressures will cause the fractures to close with a resulting decrease in permeability and crushing of the asperities producing a permanent change in the fracture permeability and hence the pore pressure distribution within the fracture planes and within the fractured rock slope.

Clearly, the ratio of the permeability of the fracture plane relative to the permeability and porosity of the bounding rock blocks will determine if fluid pressures that are either induced by mechanical loading, infiltration or thermal loading will dissipate along the fracture plane or into the adjacent rock block. Goren and Aharonov (2008) presented finite difference numerical simulations of a simple block model bounding a shear zone with two types of boundary conditions. One boundary condition shows pore pressure evolution within a shear zone for conditions where the initial velocity of the bounding block is zero but where the non-dimensional pore pressure is greater than zero which corresponds to fluid pressurization within a shear zone by either fluid addition by rain, deformation or thermal loading. The second boundary condition is the case where the bounding block is given an initial velocity while fluid is neither added to the shear zone nor initially pressurized within the shear zone. Fig. 2 represents the second set of boundary conditions and shows how the dissipation of the generated pore water pressure depends on the permeability of the fracture relative to the permeability of the rock that is bounding the shear plane. For the simulations with the lower permeability, the pore pressures cannot dissipate faster than they are generated and the block slides in an uncontrolled fashion. With the higher permeability, the generated pore pressures are dissipated and the movement of the block is arrested.

In-Situ Measurements of Fracture Deformation

Direct evidence of fracture deformation due to changes of fluid pressure in the fracture system is limited. One of the first direct measurements of fracture deformation was performed by Davis and Moore (1965). They placed deformation gauges across a fracture at approximately 25 m below the ground surface in a cave and were able to measure relative movements of the fracture walls of a few microns due to earth tides but with no obvious changes in water pressure. Snow (1968) described a 24 m deep water supply well at the Cecil H. Green Geophysical Observatory, Bergen Park, Colorado. This well, drilled in metamorphic rock, produced radial and tangential surface ground



Fig. 2 Effects of permeability ratios on pore pressure dissipation and shear movements (Goren and Aharonov 2008).

strains of 10⁻⁷ to 10⁻⁸ up to 75 to 95 m from the well for a drawdown of 10 m. In addition, a two hour time lag was observed on the strain records every time the well was pumped. The measuring devices in this case were 24 m long quartz rod strain meters. More indirect evidence of fracture deformation was the difference between pumping into and pumping out of a well (Evans 1966) and the nonlinear relationship between fluid pressure and flow rate during injection tests (Louis and Maini 1970; Louis 1976).

Gale 1975, used a specially designed borehole deformation gauge to measure aperture changes for two different shallow sub-horizontal fractures in granite, one fracture at approximately 6.75 m of depth and a second fracture at approximately 9.75 m of depth. For each fracture, an inflatable packer was placed in the borehole immediately above the borehole fracture deformation gauge and water was injected into the isolated borehole interval. Fluid pressures were measured both in the injection borehole and in a second borehole at a radial distance of approximately 1 m where the test fracture was isolated using a double packer system. In this field experiment, both the changes in fluid pressure (changes in effective stress during injection and withdrawal) and the change in fracture aperture (fracture deformation) were measured in the borehole (Fig. 3), obtaining an *in situ* measure of the fracture normal stiffness. The measured fracture opening and closure are consistent. The three line segments in Fig. 3 demonstrate the non-linear change in the fracture normal stiffness for these shallow fractures. The measured changes in fracture apertures due to changes in fluid pressure represent a significant change in the permeability of this isolated fracture.



Fig 3 Changes in fracture aperture due to changes in borehole packer injection pressures.



Fig. 4 The Coaraze Laboratory site (from Cappa et al. 2005)

Schweisinger et al. (2009) reported on a borehole tool that was used to measure changes in fracture aperture during packer injection tests and these authors demonstrated that significant changes in aperture were produced at moderate increases in pore pressure. On a large block scale, the hydro-mechanical coupled processes in a shallow fractured rock mass were investigated in situ through field experiments at the Coaraze Laboratory Site (France; Cappa et al. 2005). This carbonate rock slope (30 m × 30 m × 15 m; Fig. 4) was extensively instrumented for meso-scale hydraulic and mechanical measurements during waterlevel changes. The slope is naturally drained by a spring that can be closed or opened by a water gate. The experimental approach consists of performing simultaneous and frequent measurements of fluid pressures and displacements at different points on the surface and in boreholes and on different fracture types within this carbonate block. The observed

changes in fracture aperture for a corresponding large increase in pore water pressures were not as large as one would expect. However, the fractures in the rock block at this site have been subjected to a very large number of loading and unloading cycles due to the repeated opening and closing of the gate that controlled the fluid pressures in the rock block. It is reasonable to assume that these repeated loading cycles have crushed the asperities on the fracture plane removing the non-linear stress-displacement that would be characteristic of fractures in more brittle rocks.

Hydro-Mechanical Characteristics from Laboratory Experiments

Laboratory tests on natural and induced fractures collected from the same brittle rock mass show that the permeability versus stress relationship and the overall hysteresis or permanent fracture closure for natural and induced fractures are very different. However, data from a series of coupled hydraulic-mechanical experiments on samples from the same natural fracture plane (Fig. 5) show a similar coupled non-linear response under normal and shear loading with similar dilatant and contractant behavior (Gale *et al.* 2001). Small shear displacements tend to produce large changes in fracture permeability (Fig. 6) in brittle rocks even at high normal stress (Esaki *et al.* 1999).

Validation of Model Predictions of Slope Depressurization

Field and laboratory data show that fracture apertures open and close with increase and decrease in pore water pressures. Depending on the relative permeability of the fracture planes versus the adjacent rock blocks, increases in pore pressures that are generated by mining activities will either dissipate or produce shear movements that will combine to form failure planes in rock slopes. In any fractured rock slope, the fracture system will form a complex pattern of fracture orientations and interconnections in which fracture planes will both open and close under changes in normal and shear stress producing a range of pore pressure changes. Applying numerical models with confidence to such complex systems, requires that the models replicate the coupled hydromechanical characteristics that have been documented for discrete fractures that exist in all



Fig. 5 Measured fracture closure as a function of normal stress showing decrease in hysteresis and permanent deformation with repeated loading cycles (After Gale et al. 2001).

rock slopes. Literature reviews demonstrate that neither large scale laboratory experiments nor large scale field experiments have been conducted that are well suited to both slope depressurization model calibration and model validation. Model validation requires that the characteristics or parameters of the sample or area be used to predict the experimental outcome before the experiment is conducted or the area is stressed. Validation ex-



Fig. 6 Hydraulic conductivity of a granitic joint as a function of shear displacement under a normal stress of (a) 1 MPa and (b) 10MPa, Esaki et al. (1999).

periments need to be completed using either metre scale centrifuge samples or actual fractured rock slopes that are at least 30 to 40 times higher than the average fracture spacing in the slope. Predicting the failure of a well characterized slope within well-defined limits in an inactive mine setting and then failing the slope by increasing the water pressure in the fracture network would constitute a credible validation experiment.

References

- Cappa F, Guglielmi Y, Fénart P, Merrien-Soukatchoff V, Thoraval A (2005) Hydromechanical interactions in a fractured carbonate reservoir inferred from hydraulic and mechanical measurements. International Journal of Rock Mechanics and Mining Sciences 42, 287–306
- Davis SN, Moore GW (1965) Semidiurnal Movement Along a Bedrock Joint in Wool Hollow Cave, California. National Speological Society Bulletin 27(4), 133-142
- Esaki T, Du S, Mitani Y, Ikusada K, Jing L (1999) Development of a shear-flow test apparatus and determination of coupled properties for a single rock joint. International Journal of Rock Mechanics and Mining Sciences 36(5), 641-650
- Evans DM (1966) The Denver Area Earthquakes and the Rocky Mountain Arsenal Well. The Mountain Geologists 3(1)
- Gale JE (1975) A numerical, field and laboratory study of flow in rocks with deformable fractures. Ph.D.

thesis, University of California, Berkeley, CA, 255 pp. Also, Scientific Series No. 72 (1977), Inland Waters Directorate, Environment Canada, Ottawa, Canada

- Gale JE, LeMessurier P, Seok E (2001) Design and Application of a Biaxial, Servo-Controlled, Test Frame to Determine the Coupled H-M-T Properties of Discrete Fractures, DC Rocks 2001, The 38th U.S. Symposium on Rock Mechanics (USRMS), Washington D.C.
- Goren L, Aharonov E (2008) On the stability of landslides: A thermo-poro-elastic approach. Earth and Planetary Science Letters
- Louis C (1976) Introduction a 1 hydraulique des roches. Ph.D. Dissertation: Paris, Universite Pierre et Marie Curie
- Louis C, Maini YN (1970) Determination of In Situ Hydraulic Parameters in Jointed Rock, Imperial College of Science and Technology, Rock Mech. Res. Report No. DIO, 24 pp
- Schweisinger T, Svenson EJ, Murdoch LC (2009) Hydromechanical well test to characterize fractured rock aquifers. Groundwater 47(1), 69-79
- Seok E (2011) Impact of variability in laboratory and field fracture permeability data on simulated flux as a function of scale and spatial structure. Ph.D. Thesis, Memorial University of NL, St. John's, NL
- Snow DT (1968) Fracture Deformation and Changes of Permeability and Storage upon Changes of Fluid Pressure. Quarterly Journal Colorado School of Mines 63(1), 201-244
Airlift Testing In Exploration Coreholes

Roger HOWELL

SRK Consulting, Denver; 7175 W. Jefferson Avenue, Suite 3000, Lakewood, CO 80235 USA

Abstract Hydrogeologic studies at mining exploration sites rely on airlift-pumping tests because it is a relatively fast, simple, and accurate method of obtaining hydraulic conductivity values in deep fractured aquifers. A single data set from a typical packer-isolated airlift test can include falling-and rising-head slug sequences, discharge-rate decay from the constant-head pumping, and long-term recovery data. Slug tests need not be instantaneous to be analyzed by the Hvorslev method. Recovery from constant-head pumping can be analyzed by Theis methods, however, casing-storage effects can limit the use of the Theis analysis when the discharge rate is less than about 0.13 L/s (2 gpm).

Keywords Testing in exploration drillholes, airlifting, Theis analysis, Hvorslev analysis

Introduction

Mining operations, especially in the early exploration, scoping, and pre-feasibility stages, include extensive HQ (78 mm diameter) diamond-core drilling programs. As a consequence, hydrogeological investigations for these early mine development stages are to a large extent based on hydraulic testing in slim holes, and this is best done by airlift pumping. Mine-development programs also drill with reverse-circulation (RC) rigs, which also lend themselves to airlift testing.

Airlifting is a preferred method to "pump" water from small-diameter holes because it employs simple equipment often found at remote sites, and it can produce relatively high discharge rates, especially when static water is at significant depth (as much as 200 m) below surface. Airlift-pumping tests are not as clean, sophisticated, nor easily-interpretable as conventional tests with down-hole pumps. Other differences with conventional tests include:

- Airlifting approximates constant discharge, rather than constant-head pumping;
- A discharge flow meter cannot be used (air and water must be separated);
- Analyses are done on recovery data alone,

and on discharge-rate trends;

- Airlift recovery data are almost always burdened with excessive casing storage; and
- Airlifting is poorly described in hydrogeological literature, and is susceptible to misinterpretation and misunderstanding by reviewers.

Airlifting Procedures

A typical airlift test in an advancing corehole requires a diverter wellhead threaded onto the drill rods, an airline (nominal 1-in threaded PVC or steel pipe, nominal ¾-in polypropylene tubing, or PEX tubing) inserted through the wellhead and down the rods, a connection to an air compressor, and a discharge hose and measuring tank. A transducer may be installed in a packer housing, secured at the end of the airline, or lowered into the well after airlifting stops.

Airlift pumping then proceeds by injecting air at about 70 to 140 L/s (150-300 cfm) down the airline. Air bubbles rise in the water column, entraining and lifting water up the rods and out the discharge hose. Discharge water is measured by timing the flow of air/water discharge into an open-top drum or tank of known volume.



Fig. 1 Airlift Submergence and Test Intervals for Tests in Coreholes and Air-Rotary Boreholes

Dubek and Beale (1992) provide an early description of airlift testing in rotary boreholes in Nevada. When testing in air-rotary boreholes, the dual-wall pipe constitutes both the airline and the eductor pipe. Importantly, it is assumed that the rotary bit and drill rods do not fit tightly in the borehole, so that the entire saturated thickness of the borehole contributes to the pumping discharge and to the recovery (Fig. 1b). Air, generally from the rig compressor, is injected down the rods, and the discharge water is measured as it exits the cyclone. At the end of pumping the air must be turned off and vented as quickly as possible, and the drilling head broken open to allow rapid insertion of a transducer down the inner tube of the dualwall pipe, where water-level recovery is measured. The transducer record (t'=0) must begin the moment the airlift stops, even though the first water level recorded in this way may be as much as 5 minutes into the recovery.

Time and Discharge Rate

Where rig time is at a premium, airlift pumping continues for periods of time typically between one and three hours while the discharge rate is periodically measured; recovery of the groundwater is monitored for approximately equal periods of time. Longer-term pumping tests, of as much as 2 to 5 days, can be conducted in completed wells.

The rate of airlift discharge depends directly upon the dynamic submergence of the airline. Fig. 1 illustrates static submergence; dynamic submergence is always less than static submergence due to drawdown in the casing. In low-transmissivity test intervals where the formation cannot quickly replace the water blown from the casing, dynamic submergence, and the resultant discharge rate, can be quite low. Expected discharge rates from HQ rods using an 860 kPa (125 psi) compressor, and assuming that the airpipe is inserted to the maximum unloading depth, range from 0.1 L/s (1.5 gpm) where static water level is about 140 m btoc, to 2 L/s (31 gpm) where static water is less than 30 m btoc. A larger compressor, e.g. 1,700 kPa, will yield similar discharge rates, but over a greater depth range. Rates are lower in NQ pipe and 51mm (2-in) wells; in 102 mm wells and PQ pipe, discharges can be up to 9.5 L/s (150 gpm).

Well and Aquifer Responses

Fig. 2A shows a complete hydrograph from a transducer housed at the bottom of a water-in-flated packer (IPI SWPS® system) during a packer-isolated airlift test in a moderately deep (228 to 259 m) bedrock interval with a moderately high hydraulic conductivity (0.3 m/d). The hydrograph shows multiple data sequences that can be analyzed to provide estimates of hydraulic conductivity in the test interval. These include:

- The equivalent of an instantaneous falling-head slug test (#3 in Fig. 2A);
- An "instantaneous" rising-head slug test (#5 in Fig. 2A);
- A constant-head pumping test (#6), the discharge values for which must be collected periodically during the airlift; and
- Relatively long-term recovery data (#8 in Fig. 2A).

The nearly flat drawdown curve in Fig. 2A illustrates the constant-head flow characteristic of airlift tests, while the recovery curves of



nearly 100 ft show the large casing-storage effects inherent in the method. Another critical factor is implied in Fig. 2A: the test interval, 228 to 259 m, is only a fraction of the thickness of the saturated aquifer. (In this case, the saturated aquifer extends from 91 m btoc to at least bottom of hole at 259 m).

Analysis of Slug Data

The falling-head and rising-head sequences illustrated in Fig. 2 follow very-large slug stresses of, in the case shown, 60 m and 30 m respectively. These data are generally analyzed by the Hvorslev (1951) method of plotting the logarithm of the ratio of residual stress to total stress, $(H-h)/(H-H_0)$, *vs.* recovery time *t* on an arithmetic scale, as shown in Fig. 2C. Hydraulic conductivity is then derived by:

$$K = \frac{r^2 \cdot \ln\left(\frac{L}{R}\right)}{2 \cdot L \cdot t_o} \tag{1}$$

Where:

r = radius of unscreened portion of well casing

R = radius of screen or open portion of hole

L = length of screen or open interval (test interval), and

 t_0 = time to recover 37 % of initial stress. In most instances, 5 to 15 minutes may pass from airlift initiation until a poor airlift is recognized and the air is shut off to record slug recovery. Although seemingly a violation of a widely-held "rule" of slug testing, Butler (1998) shows that the Hvorslev analysis does not require an instantaneous slug. If the slug is fully introduced before data collection begins, according to Butler, and as long as storage effects do not impact the test, the Hvorslev equation can be applied. The former condition should be considered when identifying the starting point of the slug (pressure release followed by air-water surging can sometimes make this difficult). The latter condition is generally not a concern in fractured-bedrock aquifers.

Analysis of Discharge Rate

The decline in the rate of discharge during a constant-head pumping or flow test also can be used to calculate a transmissivity for the test interval. Reidel and others (2005), for instance, used discharge data as the primary method of analysis of high-volume airlift tests in highly transmissive basalts in Washington, and compared the results to Theis analyses of the airlift recovery data.Discharge-time data are commonly ignored in analyses of airlift

tests because the data can be hard to obtain with precision. More importantly, the discharge data from many airlift tests are rendered invalid as a consequence of ill-advised attempts to maintain constant discharge by varying the air volume during pumping.

Analysis of constant-head discharge is based on Jacob and Lohman's analysis (1951) for a free-flowing well. The analysis requires time, discharge rate, and "shut-in" pressure. Discharge rate should be measured periodically through the entire duration of the airlift (the initial, violent surge at the beginning can be ignored). The shut-in pressure is usually taken as the static head minus the head measured by the transducer during the airlift (*i.e.* the difference between segments 6 and 8 in Fig. 2A). Values of pressure divided by discharge rate are then plotted arithmetically *vs.* time on a logarithmic scale, and transmissivity is found by:

$$KD = \frac{0.183}{\Delta \left(\frac{P}{Q}\right)} \tag{2}$$

Where:

K = hydraulic conductivity of test interval,D = thickness of test interval,

P = shut-in pressure (a constant value),

Q = discharge rate at each time step, and $\Delta(P/Q)$ = the change in the (P/Q) value per log cycle.

Fig. 3 demonstrates the applicability of the discharge-rate data even when it has not been assiduously collected. Fig. 3A shows a Theis analysis of recovery following a 90 min airlift in an RC borehole, during which the discharge rate declined from 0.16 L/s to 0.025 L/s. Because of the low pumping rate, casing-storage effects are large, and the Theis analysis of the recovery data is questionable (see below). But as shown in Fig. 3B, the discharge-decay analysis, based on only a few data points, corroborates the results of the Theis analysis.

Analysis of Long-term Recovery Data

Theis (1935) described a simple and robust method to interpret recovery data from a pumping test. Although the Theis recovery method was originally developed for constantdischarge pumping tests, it can also be applied to airlift recovery tests. Rushton and Rathoud (1988) show that the Theis method can be applied to constant-head tests as long as the discharge value used in the analysis is the discharge measured just before pumping ends, and not an early or average value.

Theis Recovery analyses are preferred over slug analyses because long-term airlift pumping produces a greater stress on the aquifer, which extends beyond the immediate borehole walls, and therefore induces more representative responses. The Theis analysis plots the log of the ratio of total test time to recovery time (T/t') on the *X* axis *vs*. residual drawdown (or change in head) on an arithmetic scale on the *Y* axis. Where time is sufficiently large, Equation 3 yields a transmissivity of the test interval:

$$T = \frac{0.183 \cdot Q}{\Delta s} \tag{3}$$

Where:

 $T = \text{transmissivity of test interval } (m^2/d),$



Wolkersdorfer, Brown & Figueroa (Editors)

 $Q = \text{discharge rate (m^3/d)},$

s = residual drawdown (or convenient measure of recovery) (m),

 Δs = change in residual drawdown over one log cycle of *T*/*t*'.

Fig. 2B shows a recovery curve typical of single-well tests, with some perturbation in early time resulting from surging at the end of the airlift. The useable data fall in the later period of T/t' equal to about 3 to 2. Typical of airlift recoveries, the useable segment represents about 1.5 m of aquifer recovery following about 27 m of casing recovery. Fig. 3A shows another shape common to airlift-recovery curves, which is seen in tests of higher-T intervals where transducers are lowered into wells during the recovery. Again, only latest data are used.

The Theis method does not strictly account for casing storage effects, which occur in the data of all pumping wells (hence, affect all single-well tests). Papadopulous and Cooper (1967) showed that if pumping and recovery time are sufficient, then the Theis method can be applied to drawdown and recovery in pumping wells. They present the following equation to estimate the effect of casing storage on pumping and recovery data:

$$t > \frac{25 \cdot rc^2}{KD} \tag{4}$$

Where:

t = pumping time and/or recovery time,

rc = radius of the non-screened portion of the well,

K = hydraulic conductivity of the formation, and

D = Depth of the well, (thickness of the aquifer)

According to Papadoulos and Cooper, where pumping and recovery times exceed by a factor of 25 or more the square of the casing radius divided by transmissivity, then the casing storage will not affect the outcome of the analysis. Table 1 shows pumping times for 24 airlift tests selected from multiple projects. The table indicates whether or not the recovery data were successfully analyzed using the Theis Recovery method. Unsuccessful tests are so designated because a reliable straight-line segment could not be interpreted in the semilog plot of late-time recovery; primarily, it is judged, because of excessive casing storage.

The Papodapolous-Cooper relationship is rearranged in Table 1, where 9 out of 10 unsuccessful analyses show pumping-time factors of less than 19 (compare to the suggested factor of 25), and 12 of 14 successful tests had time factors greater than 19.

Table 1 was then sorted according to airlift discharge rate (as seen below), from less than 0.003 L/s (0.05 gpm) to 2.2 L/s (about 35 gpm). Again, 9 out of 10 unsuccessful analyses correspond to tests that sustained discharge rates of less than 0.13 L/s (2.0 gpm), whereas 13 of 14 successful tests discharged at rates exceeding 0.13 L/s.

Both the time factor and the discharge rate are functions of transmissivity (T). In both low- and high-T intervals airlifting initially purges the same large volume of water from the casing. However, that casing volume con-

Test Number	Screen Interval	Hydr. Condt.	Pumping Time	Time Factor	Airlift Rate	Successfull
	(m)	(m/day)	(minutes)	t'·KD/rc ²	(m ³ /day)	Theis
pack4 test2	14.3	0.016	471	50	0.3	No
pack5-302	17	0.034	54	14	2.7	No
MW-11a	30.49	0.001	76	2.5	5.5	No
H11HR-04b	54	0.0047	60	7.0	5.5	No
Sask 477	53	0.0018	60	2.6	6.0	No
MW-23-565	25.9	0.003	172	3.6	6.8	No
pack1-382	22.3	0.004	291	12	7.6	No
Sask528	77	0.0023	180	15	8.7	No
Hydro-03	560	0.00064	1431	236	9.81	Yes
pack1-276	13.4	0.002	300	3.7	10.4	No
Ed628-205	80.8	0.0044	70	11	10.9	Yes
MK12-333	45.7	0.001	120	6	12.0	Yes
MW-24-540	36.6	0.006	66	3.9	12.5	No
247 test 6	80	0.003	200	22	14.2	Yes
Sask603	77	0.0174	180	111	18.5	Yes
Ed627-301	274	0.0026	136	45	23.4	Yes
4178 - 1828	30.5	0.3	73	307	25.6	Yes
MW-11b	30.5	0.007	78	19	27.3	Yes
Sask 630	50	0.07	146	235	48.5	Yes
Ed594-706	155	0.018	62	79	51.8	Yes
ED594-396	250	0.008	115	106	60.0	Yes
MK11-196	32	0.42	100	1446	65.4	Yes
246 Test 3	102	0.022	120	124	76.8	Yes
MK-1083	125	0.35	125	1471	190.8	Yes

Table 1. Pumping Time and Discharge Rate vs.Theis Analysis

stitutes a greater percentage of aquifer yield, per time, from a low-T interval. Hence, in low-T intervals, longer pumping is required to sufficiently draw down the aquifer so that aquifer recovery will still be measureable after the casing volume is replaced.

These relationships are useful not only as backward-looking validation of an analysis, but also as a means in the field to determine how to proceed with an airlift pumping and recovery test. In some cases, for instance, if it appears in the first 10 minutes that the long-term airlift rate will be 0.13 L/s (2.0 gpm) or less, then a test might either be stopped early and slugrecovery data recorded, or continued for a much longer period of time in order to overcome the casing storage effect. Conversely, if discharge rates can be easily and accurately measured through time, then the pumping might be continued solely for that purpose.

Conclusions

Airlift pumping is a simple and robust means of stressing aquifers to obtain hydraulic parameters in deep fractured-rock settings. In small-diameter casings and wells, airlift discharge rates can significantly exceed rates from submersible pumps. Discharge data, if carefully collected, should be analyzed to provide reliable K values. Water-level recovery from short term or aborted airlifts can be analyzed by the Hvorslev method, even though the slug is not instantaneous. The Theis method can be applied to the recovery from the long-term constant-head pumping, using the final discharge value in the calculations. Casing storage effects can invalidate the Theis method, especially at low discharge rates or following short pumping times. Empirically, airlifts that produce 0.13 L/s (2.0 gpm) or less should be stopped early, and slug recovery recorded, or be run for much longer periods of time.

References

- Doubek, G.R., Beale, G. (1992) Investigation of groundwater characteristics using dual-tube reverse-circulation drilling: Society for Mining, Metallurgy, and Exploration, annual meeting February: Phoenix.
- Hvorslev, M.J. (1951) Time lag and soil permeability in groundwater observations. U.S.Army Corps of Engineers Waterways Experimentation Station, Bulletin 36.
- Jacob, C.E., Lohman S.W. (1952) Non-steady flow to a well of constant drawdown in an extensive aquifer. Trans, Amer. Geophys. Union, vol. 33, pp 559-569.
- Kruseman, G.P., and DeRidder, N.A. (1970) Analysis and Evaluation of Pumping Test Data, 2nd edition. International Institute for Land Reclamation and Improvement, Publication 47.
- Papadopoulos, I.S. and H.H. Cooper (1967) Drawdown in a well of large diameter, Water Resources Research, vol. 3, no. 1, pp. 241-244.
- Rushton, K. R. and Rathod, K. S. (1980) Overflow Tests Analysed by Theoretical and Numerical Methods. Ground Water, 18: 61–69.
- Theis, C.V., (1935) The relation between the lowering of the piezometric surface and the rate and duration of discharge of a well using groundwater storage. Trans, Amer. Geophys. Union, vol. 16.
- Reidel, S.P, Spane, F.A., Johnson, V.G (2005) Potential for natural gas storage in deep basalt formations at Canoe Ridge, Washington State: a hydrogeologic assessment. Pacific-NW Natl. Lab.: PNNL-15386.

The General Scheme for Hydrogeological and Environment Geological Investigation of Large Scale Coal Bases, in China

Xiangquan LI, Xinwei HOU^{*}, Lingxia LIU, Zhenxing WANG, Ming GAO

Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, Shijiazhuang 050061, China, houxinwei2007@163.com, *corresponding author

Abstract This paper systematically illustrated the overview of the large-scale coal bases. The articles introduced the main coal bearing layers, aquifer types & distribution and the superposition relationship between coal bearing layers and aquifers. Water resources crisis, mine water in-rush, aquifer structures and groundwater resources damage, heavy water pollution and ecological deterioration are the major hydrogeological and environmental-geological issues in the mine areas. Based on the hydrogeological and environmental-geological characteristics, those coal bases can be divided into five major types. The investigation scheme in the next decade has been put forward.

Keywords Hydrogeology; Environmental Geology; Issues; Coal Bases

Introduction

During the 12th "Five-Year Plan", China plans to build 14 key large-scale coal bases: Shendong base, Northern Shanxi base, Huanglong base, Eastern Ningxia base, Northern Jin base, Central Jin base, Eastern Jin base, Central Hebei base, Henan base, Western Shandong base, Huaibei-Huainan base, Eastern Inner Mongolia base, Yunnan-Guizhou-Sichuan base, Xinjiang-Qinghai base.

Currently, the large-scale coal bases in China are universally faced with a series of problems of water shortage, aquifer damages, aggravating mine water in-rush and eco-environmental degradation, which have severely hampered the sustainable development of those coal bases. Therefore, it is of great necessity to thoroughly investigate those aforementioned hydro-geological and environmentalgeological problems and come up with corresponding solutions.

Geologic framework

The main coal bearing layers in those coal bases include late Carboniferous-early Permian layer, late Permian layer, lower-middle Jurassic layer, and lower Cretaceous layer. The late Carboniferous-early Permian layer is mainly distributed around the Erdos basin area, Shanxi base, Hebei-Shandong-Henan-Anhui base. The tectonic element in the area is the main body of North-China Platform, with the coal layers representatives being Taiyuan Formation and lower Permian Shanxi Formation.

The late Permian layer is mainly distributed in the Yunnan-Guizhou-Sichuan base, the tectonic element of which is Yangzi Platform and South-China fold system, with the representatives being upper Permian Longtan Formation.

The lower-middle Jurassic layer is mainly distributed in Erdos basin area and Xinjiang-Qinghai base. Its tectonic elements include Talimu Platform, Tianshan section of western Tianshan-Xingmeng fold system, Qinqi-Kunlun fold belt, Qilian fold belt and western Qinling fold belt.

The lower Cretaceous layer is mainly distributed in eastern Inner Mongolia base, the tectonic element of which is the eastern section of the Xingmeng fold system, north-eastern part of North-China Platform as well as the fold system along the Pacific Ocean.

Hydrogeologic settings

The karst aquifers of carbonate rocks are mainly distributed in the Northern Jin base, Central Jin base, Eastern Jin base, Central Hebei base, Henan base, Huaibei-Huainan base, Huanglong base, Western Shandong base, Eastern Ningxia base, Yunnan-Guizhou-Sichuan base, and Junggar mining area in the Shendong base. The karst aquifers largely belong to the karst fissure aquifer types of the Ordovician upper-lower Majiagou Formation, which boast abundant karst groundwater resources and rich distribution of karst springs. However, the western Henan mining area is lack of Ordovician limestone, the aquifer of which is the Cambrian karst aquifer with weak waterretaining capability, while the aquifer in the Yunnan-Guizhou-Sichuan base is the type of karst aquifer of Triassic Gejiu limestone and Permian Maokou limestone with strong water vield property.

Detrital rock-type fissured aquifers include those aquifers of the Cretaceous, Jurassic, Permian, and Carboniferous Periods, with the sandstone, conglomerate, and sandy conglomerate, which are mainly distributed in the Northern Shanxi base, Shendong base, Huating mining area of Huanglong base, eastern mining area of Greater Khingan Mountains in Eastern Inner Mongolia base and the Xinjiang-Qinghai base. The Northern Shanxi base and Shendong base usually possess fissured aquifers of sandstone and conglomerate in the lower Cretaceous Zhidan Formation with uneven water yield property. The deep fissured aquifers have stronger water yield property with higher pressure-bearing performance. The Huanglong base usually possesses the sandy conglomerate-type aquifers of upper Tertiary and Cretaceous Zhidan Formation with moderate and relatively strong water yield property. The eastern mining area of Greater khingan Mountains in Eastern Inner Mongolia base owns weathering fissured aquifers of early Cretaceous Period, the shallow zones of which are relatively abundant with groundwater resources. The XinjiangQinghai base contains Jurassic fissured aquifers, while the Carboniferous-Permian fissured aquifers are mainly distributed in the North-China region.

Pore aquifers of unconsolidated rocks, consisting of quaternary and unconsolidated tertiary strata with poor diagenesis, can be found in almost each one of those coal bases with the lithology being medium-fine sand and sandy gravel-pebbles. In the Shendong base and Northern Shanxi base, the quaternary unconsolidated pore aquifers are mainly those in the Salawu Formation of the quaternary upper Pleistocene period, which boast strong water yield property and contain a number of separated spring fields. The Western Shandong base, Huaibei-Huainan base, and Central Hebei base all have exceptionally thick Cenozoic coverage, and four aquifer groups can be distinguished from the top to the bottom. The Huaibei-Huainan base, in particular, has unique hydrogeological conditions and possesses unconsolidated Cenozoic pore aquifers, which can be divided into four aquifers and three aquicludes. Besides, the bottom and the third layer of aquifers have great influence on the coal mining. The Huanglong base and Eastern Ningxia base boast quaternary alluvial-proluvial sandy gravel-type aquifers, which are mainly distributed along the river valleys.

The coal-bearing aquifers exist in the fault-subsidence basins of Yimin and Huolin in western Greater Khingan Mountains of the Eastern Inner Mongolia base, where the coalbearing layers themselves are aquifers that belong to the diagenetic fissured and weathering-fissured aquifer types with shallow depth but strong water field property.

Major Hydrogeological and Environmental-Geological issues

1) Water Resources Crisis

Currently, most of the coal bases are confronted with water scarcity. Statistics show that 70 % of coal bases in China are inflicted by



Figure 1 Histogram of Water Scarcity in Major Coal Bases

water shortage and 40 % of the coal bases are facing severe water scarcity. Except for the Huaibei-Huainan base and Yunnan-Guizhou-Sichuan base, 12 of the 14 key large-scale bases suffers different degrees of water scarcity. The water scarcity amount is expected to reach 747 Mm³ in 2020, what' more, the water scarcity of the coal bases in the 4 provinces of Shanxi, Sanxi, Inner Mongolia, and Ningxia will amount to 495 Mm³, accounting for 66 % of the whole amounts (Fig. 1). Water scarcity for the coal bases in plateau areas, e.g. Qinghai Plateau, becomes more acute in winter time. Overall, water scarcity has become a most severe bottleneck that will restrict the development of those coal bases.

2) Mine Water in-rush

With the development of coal mining and increase of mining depth, water-related disasters have frequently occurred, which has badly threatened the safety of coal mining. Among the major mining accidents, water-related disasters have ranked as the second threatening factor for the safety of coal mining following the gas accidents. It's estimated that since the 1980s, about 250 mines have been submerged, leading to a death toll of around 9,000 and an economic loss of more than 35 billion RMB. Specifically speaking, from 1995 to 2011, there have been 1,540 cases of water-related disasters in the coal mines, causing a death toll of around 6,355 and an economic loss of more than 20 billion RMB (Fig. 2).

Major mine water in-rush include floor gushing-out of karst groundwater, gushingout of roof aquifers, inrush of surface water, and inrush of goaf water. In recent years, goaf water inrush accidents have accounted for 80 % of the total, featuring heavy death tolls and economic losses.

3) Aquifer Structures and Groundwater Resources Damage

Owing to mining activities, the groundwater level has drastically dropped (Qiang *et al.* 2002), altering original structures of coal-bearing layers, groundwater systems, and dynamic fields in the overlying unconsolidated rock strata.

Mining activities have severely destroyed aquifers in coal-bearing layers and adjacent aquifers. In the Shendong base and Northern Shanxi base, shallow aquifers in the Salawu Formation have been damaged by mining, leading to ecological deterioration. In the Huaibei-Huainan base, mining has destroyed deep aquifers of quaternary period. In Qinghai base, groundwater resources above the permafrost have been damaged by mining, causing degradation of alpine meadow. In the Eastern Inner Mongolia base, weathering fissured groundwater and quaternary pore groundwater have been destroyed and drained, leading to ecological deterioration of the grassland in this area (Fu et al. 2011).

Mining has aggravated the draining of groundwater, thus causing severe wastes of groundwater resources. In 1989, about 1.3 billion tons of mine water was drained; this Fig. increased to 4 billion tons in 2003; and then it continued to increase to 4.5 billion tons and 5.4 billion tons in 2005 and 2007, respectively, while the utilization rate was as low as 30–40 %. In North-China, more than 80 % of large karst springs have suffered sharp decrease in



Figure 2 Death Tolls Caused by Mine Water in-rush since 1995

the flow amount; moreover, about 30 % have dried up or been on the brink of running dry.

4) Heavy Water Pollution

Long-term mining activities have produced large quantities of waste solids, waste water, and waste gas, resulting in heavy pollution of water environment. Each year, coal mines in China can yield 2.2 billion tons of mine water, 28 Mt of waste water of coal preparation, 30 Mt of industrial waste water, 400 Mt of sewage, and 150–200 Mt of gangue.

5) Ecological Deterioration

Mining-induced subsidence has forced the groundwater level to dramatically drop and exacerbated ecological environment in the mining area. Especially in the Shendong base, Northern Shanxi base, Eastern Ningxia base, and Huanglong base in North-West China with arid climate and poor vegetation covers, the ecological environment is more vulnerable to the problems of desertification, water losses and soil erosion.

Types of Coal Bases

Based on the hydrogeological and environmental-geological features in those coal bases, they can be divided into the following five types: The first type is the coal bases in northwestern ecologically-fragile area, which includes Shendong base, Northern Shanxi base, Eastern Ningxia base in the Erdos basin area as well as Xinjiang-Qinghai base, featuring fragile ecological environment, severe environmental-geological problems and insufficient water resources.

The second type is coal bases in central & eastern large Karst springs area, which are mainly distributed in the central and eastern parts with karst-geological development in North-China, including the Northern Jin base, Central Jin base, Eastern Jin base, Central Hebei base, Western Shandong base, and Henan base, featuring wide distribution of large karst springs, severe threats of karst groundwatergushing disasters and obvious damages of karst aquifers and water resources.

The third type is coal bases in eastern plain area, which are distributed in the plain regions in Eastern China, including Central Hebei base, Western Shandong base, Henan base and Huaibei-Huainan base, which suffer gushing disasters of quaternary pore groundwater and karst groundwater and are confronted with damaged aquifers and groundwater resources as well as severe environmentalgeological problems.

The fourth type is coal bases in northeast-

ern ecologically-fragile area, which mainly include the Eastern Inner Mongolia base, featuring vulnerable grassland ecological- environment and serious environmental-geological problems caused by mining activities.

The fifth type is coal bases in southwestern Karst area, namely, the Yunnan-Guizhou-Sichuan base in Southwestern China, featuring severe mine water in-rush and serious environmental-geological problems.

Overall scheme of hydrogeological survey

1) General Objective

The general objective is to carry out hydrogeological and environmental-geological survey on the scale of 1:50,000 in key coal bases, and investigate aquifer structures, the conditions of groundwater recharge, runoff and discharge as well as major environmental-geological problems, thus providing scientific basis for protecting aquifers and dealing with water scarcity in the coal bases.

2) Main Tasks

Hydrogeological Investigation on the Scale of 1:50,000 in Coal Bases : Hydrogeological survey on the scale of 1:50,000 should be carried out on the basis of groundwater systems, focusing on the investigation of groundwater types, aquifer structures, reservoir structures,



Figure 3 Overall Scheme of Hydrogeological and Environmental-Geological Survey in National Large-Scale Coal Bases

and the characteristics of groundwater recharge, runoff and discharge. Assessment work should be done to evaluate groundwater resources amount and their utilization potential, locate regions with high water-yield property and find out prospective water supply regions. Surveying work needs to be made to probe into the superposition relationship between coal-bearing layers and aquifers in those coal bases, find out distribution of faults, collapse columns and their water transmissibility, inquire into the distribution of goaf and goaf water, and evaluate the risks of mine water inrush.

Environmental-Geological Investigation on the Scale of 1:50,000 in Coal Bases: The environmental-geological survey is required to evaluate the influences and damages brought to the aquifers and groundwater resources by mining activities, and investigate the types, distribution and developmental trends of such problems as water-soil pollution, ecological degradation. Assessment on groundwater environment and ecological environment quality should also be performed to help make aquifer-protection plans.

Thematic Research on Major Hydrogeological issues : Thematic research needs to be made to investigate the hydrogeological features in the coal bases under the extreme environmental conditions (such as in deep depth and arctic & alpine climate), study the groundwater circulation and evolution regularities under the influence of mining activities, evaluate the risks of serious gushing-out disasters (such as floor karst water gushing-out and goaf water gushing-out) and risks of geological-ecological environment during mining activities, as well as explore the technology of integrated utilization of recharge-discharge-ecology-environmental protection of mine groundwater, thus protecting regional aquifers.

Development of Hydrogeological and Environmental-Geological Database and Information System in Key Coal Bases: Efforts should be made to set up the hydrogeological and environmental-geological database and information system in key coal bases to formulate an information platform, thus providing digital and dynamic management on the hydrogeological and environmental-geological information in coal bases.

3) Prospective achievements

Improving investigation Accuracy and understanding of conditions: By virtue of conducting hydrogeological and environmentalgeological survey on the scale of 1:50,000, the surveying accuracy in major mining areas can be improved from the scale of 1:200,000 to the scale of 1:50,000. Besides, thematic research on major problems is expected to improve our understanding on the hydrogeological problems in those coal bases.

Establishing Digital Information Platform: We need to develop the hydrogeological and environmental-geological database and information system in key coal bases to realize dynamic management on digital information.

Compiling Hydrogeological Maps on the Scale of 1:50,000: By carrying out the work of mapping on the scale of 1:50,000, a compilation of hydrogeological maps on the scale of 1:50,000 is expected to be yielded.

Establishing a Comprehensive Technological System of Groundwater Utilization, Aquifer Protection, and Disasters Prediction in Coal Bases: Efforts need to be made to set up a comprehensive technological supporting system by assessing the groundwater resources and their utilization potential, evaluating the integrated utilization of recharge-dischargeecology-environmental protection of mine groundwater and predicting & assessing the risks of mine water in-rush, thus providing scientific basis for aquifer protection.

Determining a number of prospective water-supply regions.

Summary

In brief, this paper has introduced the status quo of those large-scale coal bases, the main coal bearing layers, aquifer types & distribution and the superposition relationship between coal bearing layers and aquifers. Currently, the major hydrogeological and environmental-geological problems those large-scale coal bases are facing consist of water scarcity, mining-induced aquifer damages, aggravating threats from mine water in-rush and deteriorating ecological environment. Based on the hydrogeological and environmental-geological characteristics, those coal bases can be divided into five major types: coal bases in western ecologically-fragile area, coal bases in central large-scale Karst springs area, coal bases in eastern plain area, coal bases in northeastern ecologically-fragile area and coal bases in southwestern Karst area. The investigation scheme in the next decade has been put forward, which requires carrying out hydrogeological and environmental-geological survey on a scale of 1:50,000, identifying aquifer structures and major environmental-geological problems, performing thematic research on major hydrogeological problems, establishing information system, determining a number of prospective water supply regions, as well as setting up a comprehensive technological support system with integration of comprehensive utilization of groundwater, aquifer protection and disasters prediction.

Acknowledgements

This work was supported by grants from the project of China geological survey (1212011140028, 1212011220971) and National Science Funds of China (40672169).

References

- Wu Qiang, Dong Dong-lin, Fu Yao-jun, Bai Xi-qing, Sun Zhan-qi (2002). Research on water pollution induced by coal mining. Journal of China University of Ming Technology, vol. 31, No.1, 19–22
- Fu Yao-jun, Zhai Li-juan, Ma Xiu-fen, Tang Yan-bo, Li qiming, Li Jun-you, Ren hu-jun, Hua Jie-ming (2011). Strategy Research on regional aquifer protection of large scale coal bases, in China. Hydrogeological Exploration Bureau, CNACG. P. 61-65.

Mine Dewatering in a Compartmentalized Hydrogeologic Setting at Sishen Mine in South Africa

Houmao LIU¹, Elaine NEL², Johanita Kotze³, Dong DING⁴

¹Itasca Denver, Inc., 143 Union Boulevard, Suite 525, Lakewood, Colorado, USA, hliu@itascadenver.com ²Anglo American Kumba Iron Ore, Centurion Gate, 124 Akkerboom Road, Centurion, 0157, South Africa, elaine.nel@angloamerican.com

³Anglo American Technical Solutions, Room 602, 45 Main Street, Johannesburg, 2000, South Africa, johanita.kotze@angloamerican.com

⁴Itasca Denver, Inc., 143 Union Boulevard, Suite 525, Lakewood, Colorado, USA, dding@itascadenver.com

Abstract Sishen mine in South Africa is one of the largest open-pit iron mines in the world. It is characterized by a complex, compartmentalized hydrogeologic setting that comprises numerous dykes, regional water-bearing faults, and inter-bedded localized geologic units. The groundwater flow in the vicinity of Sishen mine is mainly controlled by regional dykes and faults in a karst aquifer. A 3-D finite-element groundwater flow model using MINEDW[™] was constructed to simulate the unique geologic setting for effective mine-water management and dewatering planning at the mine.

Keywords compartmentalized, dykes, faults, flow model, rainfall, dewatering, MINEDW

Introduction

Sishen mine's complex, compartmentalized hydrogeologic setting, along with irregular shapes in the open-cast pit configuration, the formation of swallets (similar to sink holes) in the riverbed, and large sporadic torrential rainfall events in South Africa, pose significant challenges for effective mine-water management and dewatering planning at the mine. Dry mining conditions are necessary to ensure stability of slopes, optimize mine production, and minimize costs.

A conceptual model was developed to assess the regional hydrogeologic setting before and during the course of mining. The conceptual model integrated the collected data to produce an accurate representation of the geologic and hydrogeologic setting and is continually being refined as new hydrogeologic information becomes available.

Development of a 3-D finite element groundwater flow model using MINEDW[™] is considered to be one of the key components of the mine-water management strategy. The aim of the model is to accurately predict mine dewatering rates by integrating the conceptual model with site characterization data, the mining development plan, and the mine closure plan. The numerical model is designed to:

- predict dewatering requirements that must be implemented to manage water levels to ensure 'dry' conditions;
- identify data gaps in the conceptual model;
- scope out targeting hydrogeologic investigations to improve the confidence level of the model results;
- expand the groundwater monitoring system;
- assess uncertainties related to future dewatering scenarios;
- predict the areal extent of influence due to dewatering and the impact of mining activities on the water demands of stakeholders. Given that several mines have been operating in the catchment area, a robust groundwater flow model is critical

to simulate the hydrogeologic impacts attributable to different mines; and

• predict post-mining conditions after mining has ceased.

Current Dewatering Status

The pit area is approximately 14 km in length and 4 km wide and consists of a number of individual pits (fig. 1). Currently the deepest mining level is at 270 m below ground surface and by 2030, this level will reach 400 m below ground surface. Numerous diabase dykes and faults are encountered in the mining area. The nature of these regional structures will be discussed in the following sections.

Dewatering at Sishen mine is effectively achieved by pumping continuously from a series of dewatering wells in and around the pit. Surface water from rainfall events is removed by the installation of mobile pumps in sumps on the mine floor and pumping this water to the surface. Currently 19 dewatering wells, with a total abstraction rate of approximately 1500 m³/hr, are in operation to maintain 'dry' working conditions in the different pit areas.

Water exploration wells are continuously being drilled and developed into dewatering wells to lower water levels below mining levels. Due to the pit configuration and mining operations, this practice is becoming more challenging. In the deepest pit, depicted in fig. 2, measured water levels are currently very close to the pit bottom.

Due to the complex hydrogeologic setting and pit configuration of the mine, a high confidence level, calibrated 3-D groundwater model that can incorporate flow through fractures is required to predict future dewatering rates to maintain 'dry' working conditions, which are crucial input to determine engineering and infrastructure requirements to discharge mine water.

Geologic Setting and Conceptual Hydrogeologic Model

The Sishen iron ore deposit is situated on a major domal structure which is defined by a basal carbonate platform sequence termed the Campbellrand Subgroup and the overlying iron-formation of the Asbesheuwels Subgroup. This carbonate sequence, which is the oldest lithostratigraphic unit, forms the basement rock and is considered as having high storage potential for groundwater.

A siliceous, residual breccia (Chert in fig.3) unconformably overlies the carbonates and is thought to have developed on an irregular karst surface as a possible residual solution collapse breccia. Due to the brecciated nature of this Chert formation, it is considered to act



Fig. 1 Sishen Pit Configuration, Dewatering Wells, and Hydraulic Compartments



Fig. 2 Current and Future Pit Bottom Elevations and Current Water Levels Along Section A-A'

as an important pathway for groundwater. A number of high yielding water strikes have been encountered in this formation during drilling.

Folded banded ironstones (BIF in fig. 3) overlie the Chert breccia with laminated hematite ore forming the top part of this unit. This unit is highly fractured and considered as having a high hydraulic conductivity (*K*).

The BIF is overlain by conglomerate and shales (Gamagara and quartzite in fig. 3) that grade upward into a purple hematite rich, finegrained quartzite. This unit generally has low K and low storage coefficient.

Along the western side of the mine area, lava (lava in fig. 3) has been thrust over the shales and quartzite alongside a $9 \text{ to } 11^{\circ}$ thrust

plane. The top part of the lava is highly weathered and is considered as having higher K than the lower parts. Groundwater flow in the lava is generally restricted to faults and dyke zones that are encountered in the unit.

The regional area has been subjected to intensive structural deformation in the form of folding, thrusting and faulting or fracturing. Easterly directed crustal compression led to the development of large-scale regional northsouth trending folds. These prominent northsouth striking, moderately (60° to 70°) westerly dipping, normal faults occur in the area and represent deformation zones. A number of dewatering wells are within the permeable faults and the permeable bands associated with the dykes, and relatively high pumping



Fig. 3 Geologic and Hydrogeologic Settings of Sishen Mine

rates can be sustained from these water-bearing zones.

In the pit area a number of prominent diabase dykes with very low K are present and form impervious barriers that compartmentalize the groundwater (fig. 1).

Tertiary clay, calcrete and Aeolian sand of the Kalahari Formation cover a large part of the area and are on average approximately 50 m thick in the vicinity of Sishen mine. The clay below the calcrete and sand acts as an impermeable zone and a shallow aquifer is present in the Kalahari Formation.

Swallets have been observed in the site area, the largest of which was formed in the channel of the Gamagara River (figs. 1 and 2) to the south of the mine area (Meyer 2009; PHD 2007). A major karstic feature was also encountered in the southern part of the mine (Mc Gavigan 2009). It is unlikely that the swallets in the Gamagara River would have an impact on dewatering during the dry season; but following intense rainfalls, the runoff to the swallets could, over short periods of time, locally affect groundwater conditions. For example, on 2 May 2008, a rainfall of approximately 86 mm/d was recorded in the mine vicinity. Such a large storm event could introduce a large amount of recharge to the groundwater system through the swallets. Swallets will be simulated in the model update to assess the effect they have on the predicted dewatering requirements.

Description of Numerical Groundwater Flow Model

The numerical groundwater flow model constructed for this investigation utilizes the 3-D numerical code, MINEDW[™] (Azrag *et al.* 1998), developed by Itasca, which solves groundwater flow problems with an unconfined (or phreatic) surface and confined aquifers using the finite-element method. MINEDW[™] has several attributes that were specially developed to address conditions often encountered in mine dewatering. This modeling code is internationally recognized and has been used and verified at numerous mine dewatering projects throughout the world.

The model domain shown in figs. 1 and 4 is approximately 45 km along the west-east direction and 60 km along the north-south direction. The area of the model domain is approximately 3,000 km². The numerical model comprises 159,475 nodes and 288,764 elements. The finite-element mesh configuration and the simulated geologic units in the vicinity of pit, which encompasses about one-tenth of the entire model domain, are depicted in fig. 4. The finite-element discretization is finest in the areas where dewatering wells are clustered with horizontal dimensions of less than 10 m (fig. 4). The size of the mesh then gradually increases toward the boundaries of the model with a distance of approximately 3.5 km between adjacent nodes at the edge of the model. The structures as shown in fig. 1 are simulated in the model with a finely-discretized element as indicated in fig. 4.

Ten model layers were used to simulate the pit areas and the detailed geologic units to the west of the pits. To the east, there are seven model layers. This difference in layering, which is made possible with the pinch-out capability of MINEDW[™], represents the absence of some of the geologic units to the east of the pit (and also reduces the computational requirements of the model). The groundwater flow model incorporates all geologic settings as depicted in fig. 3. The total thickness of the model is approximately 1,200 m with the bottom of the model being 800 m below the final pit bottom.

The first two layers of the northern and southern model boundaries were assigned with constant-head boundary conditions. The bottom of the model was assigned with noflow boundary conditions. The variable-flux boundary condition, a special feature of MINEDW[™] that enables an essentially infinite groundwater flow system to be simulated at the model boundaries, was assigned to the western and eastern lateral boundaries of the model. The recharge is simulated with a timevarying value.



Fig. 4 Plan View of Model Grid and Geologic Units of Model Layer 3 in Mine Vicinity

Model Calibration

The groundwater flow model was calibrated to both pre-mining and transient conditions. Prior to simulating the mining activities, a simulation of "pre-mining, steady-state" groundwater flow conditions was conducted to establish initial groundwater conditions. Because there are limited measured water levels prior to mining at Sishen mine, the goal of the steady-state simulation was to obtain reasonable regional groundwater levels and flow directions. The model-simulated groundwater flow direction is from the southeast to the northwest, as observed at the site.

Using the water levels derived from the "pre-mining, steady-state" simulation, a transient model calibration was conducted by simulating the dewatering wells and pit excavation from January 1953 to December 2010. The measured water levels from 60 monitoring wells and piezometers were used in the calibration.

In addition to water levels, residual passive inflow (RPI), which refers to the seepage rate to the pit under active dewatering conditions, was also used in the model calibration. No RPI occurs at the site in 2011, which is also observed in the model simulations.

Predicted Dewatering Requirements

The current phase of the investigation focuses on the prediction of dewatering requirements for future mining. The key objective in designing the dewatering system is to use the minimal number of dewatering wells to achieve 'dry' working conditions over the life of the mine (LOM). Dewatering wells were simulated with assigned initial pumping rates. A "freeboard" of 25 m (the minimum required water column above the pumps) was assigned to each existing pumping well to ensure that the water level in the pumping well was maintained 25 m above the bottom of the well. For each of the new pumping wells, the bottom elevation of the well was assumed to be at 725 mamsl; and the pumping water level was assumed to be at 750 mamsl, again maintaining 25 m of "freeboard". During the dewatering simulations, if and when the simulated water level in a dewatering well reached the "freeboard" elevation, the dewatering well was then simulated as a drain boundary condition.

In order to simulate the optimum dewatering rates required for maintaining 'dry' working conditions, 16 "modeled monitoring points" were selected at various pits to compare the simulated water levels to future bench elevations. The results from the model simulations suggest that the current dewatering capacity is not sufficient to maintain 'dry' working conditions for LOM; therefore an additional 11 dewatering wells with an initial pumping capacity of 100 m³/hr are required for LOM. The maximum dewatering rate is predicted to increase from the current value of 1,500 m³/hr to approximately 2,600 m³/hr.

Future Investigations

The current model focuses on dewatering requirements. Although the model is still in the preliminary stage, it has provided valuable guidance for future project planning. Updates of the model will focus on:

- refining the localities and characteristics of structures (faults and dykes);
- assessing the relative contribution from the Chert unit and regional structures to dewatering;
- evaluating the impacts of enhanced recharge through swallets on dewatering requirements;
- developing and incorporating information of the *K* of the lower hydrogeologic units (especially the Chert zone), the

faults, and the bands of high permeability along the dykes; and

• evaluating the cumulative impacts of dewatering from Sishen and other mines on the water demands of stakeholders.

Acknowledgements

The authors thank Mr. Marnus Bester and Mr. Glen Mc Gavigan for their support of this investigation, and Mr. Reinie Meyer for his technical input of the hydrogeologic settings of the site.

References

- Azrag EA, Ugorets VI, Atkinson, LC (1998) Use of a finiteelement code to model complex mine water problems: Proceedings of symposium on mine water and environmental impacts, vol. 1, International Mine Water Association, Johannesburg, September, p. 31–42
- McGavigan, G (2009) Management of subsidence associated with the mining of the roof of the Sishen cave, An application of the slope stability radar in 2009 International Symposium on Rock Slope Stability in Open Pit Mining and Civil Engineering, Santiago, Chile, 9-11 November
- Meyer, R (2009) Development of a conceptual geohydrological model, an evaluation of the effect of dewatering and the design of a monitoring protocol, Sishen iron ore mine: Report submitted to Sishen Iron Ore Mine, June
- PHD (2007) Investigation into "sinkholes" in and adjacent to the Gamagara River and their impact on flow conditions in the river near the Sishen iron ore mine: Draft report prepared by Pulles Howard & De Lange Incorporated, February

Managing High Altitude Bog Deposits: An Investigation of the Hydrogeologic and Geotechnical Challenges associated with Andean Bofedal Sediments

Emily LUSCZ¹, Vinh-Luu LE²

Global Resource Engineering, 7000 S. Yosemite Dr., Centennial, Colorado, USA, ¹*eluscz@global-resource-eng.com,* ²*vle@global-resource-eng.com*

Abstract High altitude mine planning and development in the Andes Mountains must address the challenge of managing the low stability, low strength, high water content material found in bog deposits called bofedales. However, limited geotechnical and hydrogeologic information is available for bofedales. A testing program, geotechnical stability modeling, and groundwater modeling were used to investigate the material and develop strategies for dewatering, removing, and stockpiling of the material for reclamation.

Keywords High Altitude, Bofedal, Dewatering, Stability Analysis, Groundwater Modeling

Introduction

The Corani Project is a lead/zinc/silver mining project located in the central Andes Mountains operated by Bear Creek Mining. Throughout the site, the valleys and gently sloping terrain are often covered by deposits of glacial debris, aeolian sand deposits and post glacial lake deposits. Growing on these areas are dense mats of vegetation that over time, form deep peatlike organic soils called bofedal(es). Bofedales are characterized by dense bog-like vegetation and partial seasonal flooding which creates a hummocky terrain often punctuated with small bodies of standing water. The deposits have a high moisture retention capacity and store wet season precipitation, snowmelt, and glacial melt water eventually releasing the water as dry-season stream baseflow. Bofedales therefore sustain stream flow year-round and are an important component of the hydrologic system in the high Andes. Fig. 1 shows some of the key surface features of bofedal deposits: large spongy mats of vegetation that grow to create small pools of standing surface water.

Bofedal deposits are a significant geologic unit in the high Andes. Though potential challenges associated with bofedal arise at all stages of mine planning and development, and even though many projects in the Andes must contend with bofedal deposits, very little hydrologic or geotechnical data exists in the public domain.

There are several potential challenges associated with mine development in areas with large volumes of bofedal material. Natural bofedal material is saturated, low-strength, and compressible and consequently, is not suitable as a foundation for mining-related fa-



Fig. 1 Picture of typical bofedal landscape at the Corani Site. Photo credit: Kevin Gunesch

cilities. Standard Penetration Test (SPT) values are often below 5 blows per 6 in, and as a result, even drilling can be difficult due to the tendency of boreholes to collapse. Due to the high water content and low strength, stripping, stockpiling and management of this material are a unique challenge. Furthermore, the material's ecological value must be considered in closure planning.

At the Corani Project, bofedal is located beneath several proposed facilities including the pit, the waste rock dump, and the water supply pond. Specifically, the project must determine how to dewater bofedal so it can be excavated, stabilize bofedal in the pit excavation, and stabilize bofedal stockpiles until they are used for reclamation. In order to address these issues, a testing program, geotechnical stability modeling and groundwater modeling were performed. Based on these evaluations, the project developed a bofedal management plan to effectively manage this important material.

Methods

Field Testing and Lab Testing

Field testing was conducted to assess the *in situ* geotechnical and hydrogeologic properties of the bofedal and to determine the extent and depth of bofedal deposits. Six slug tests and a multiple well aquifer test were conducted on wells completed in the bofedal deposits. Resistivity surveys were run in the area of the pit and the main waste rock dump to determine an approximate thickness of the bofedal. In addition, Standard Penetration Tests were performed to assess the strength of the bofedal and underlying material.

Samples of the bofedal material were sent for laboratory testing to assess soil properties. Analyses included testing of moisture content, saturated hydraulic conductivity, effective porosity, and unsaturated conductivity. The same samples were tested at different densities to cover a range of potential construction uses.

Groundwater Modeling

Data from the field program and experience on this and other project sites indicated that it will be necessary to dewater the bofedal deposits prior to removal. MODFLOW-Surfact groundwater flow models were prepared to support the conceptual plan for the dewatering of the bofedal in the mine area. The purpose of the modeling was to determine the optimum approach for dewatering the bofedal deposits within the pit prior to excavating them, and also to predict the time needed for dewatering. Two methods were considered for dewatering the bofedal deposits: the excavation of shallow drainage trenches followed by staged soil removal; and alternately, a network of vertical dewatering wells. Trenches would be excavated using low-ground-pressure equipment (to \approx 2 m depth) and dewatered by gravity flow. After dewatering, equipment would be used to remove soil to the level of the lowered water table, and new deeper trenches would be dug into the newly-exposed surface. The alternative method would install vertical wells through the full depth profile of the bofedal, and dewatering would precede excavation. Models were constructed to represent each method and dewatering rates were simulated under assumptions of various trench and pumping well patterns. The results were used to determine which method was most likely to efficiently and cost-effectively dewater the area of the bofedal.

Stability Modeling

Stability sections of bofedal excavation within the mine pit, and of stockpiled bofedal material, were modeled in SLOPE/W. Both static and pseudo-static conditions were analyzed. Seismic conditions were simulated with an anticipated 475 year seismic return event – peak ground acceleration (PGA) of 0.10 g. The potential for liquefaction of the bofedal material was anticipated due to field observations during drilling and SPT testing. Residual strength parameters were thus considered in the analysis. This was considered reasonable because the main interest of the stability analyses was overall stability and not detailed deformation.

Separate stability sections were analyzed for stockpile material to be placed on existing bofedal areas. In these areas, the objective was to determine a potential placement lift height (placement rate) that would maintain foundation pore-pressure within acceptable geotechnical limits. Because SLOPE/W is a simple limit equilibrium software for analyzing factor of safety of earth and rock slopes, it cannot intrinsically model pore-pressure increase and dissipation. Under dynamic loading the stability sections were instead analyzed with FLAC. FLAC is a more powerful, two-dimensional explicit finite difference program that permits plane-strain, plane-stress, fully dynamic analysis. The program simulates behavior of soil and rock structures that may undergo plastic flow when their yield limits are reached, suggesting a factor of safety less than 1.

Results

Material Properties

Drillings and resistivity surveys suggested the average thickness of the bofedal deposits to be around 15 - 20 m thick, with a maximum thickness of 35 – 40 m near the mine pit. Core samples retrieved from drilling showed the mat-like vegetation to be composed of nearlysaturated, dark, organic-rich sediments with dense root mass extending to around a meter in depth followed by alternating layers of sand deposits and organic sediment remains. The majority of the volume of the bofedal deposit is composed of uniform sand. "Bofedal deposit" as defined by the study, refers to the unconsolidated deposits of organic sediments and fine sand. Fig. 2 shows typical drill core photos of bofedal deposits at various depths.

First-hand observations of exposed bofedal areas and drilling samples provided reasonable assessments of typical soil material characteristics. Stand Penetration Test results (ASTM D1586 method) indicated a range of *in situ* strengths ranging from strength typical for sand to negligible strength typical for saturated silt and peat. It is believed that the SPT testing resulted in liquefaction of some materials as a consequence of the testing method. The SPT method is not applicable under these conditions. However, the SPT testing demonstrated the potential sensitivity of the unconsolidated soil materials to liquefaction under dynamic loading when saturated.

The results of the field testing indicated that the bofedal and associated sediments have an average hydraulic conductivity of 9.3×10^{-4} cm/s, or 8.0×10^{-1} m/d. Slug test data was analyzed using the Cooper-Bredehoeft-Papadopulos solution. Values ranged from 8.7×10^{-5} cm/s to 2.5×10^{-3} cm/s. This is consistent with silty and fine sands. The multiple well pumping test was analyzed using the Jacob Straight Line analytical method and showed a hydraulic conductivity on the order of 10⁻⁴ cm/s. Specific yield was calculated to be 0.004. However, the low pumping rate involved makes the applicability of the result uncertain. The results of the pumping test are shown in Fig. 3.

The laboratory testing revealed a hydraulic conductivity of 1.5×10^{-4} cm/s, consistent with the field testing. It also revealed a relatively high porosity of 51 %. These characteristics make bofedal ideal cover material for the planned evapotranspiration mine waste soil covers. High porosity and low spe-



Fig. 2 Pictures of typical bofedal drill core.



cific yield suggest that the material retains water efficiently during the wet season (Fig. 4). Water is held in the pores as a result of low hydraulic conductivity and eventually evaporates, preventing water from passing through the cover to the underlying material.

Groundwater Model Results

The groundwater model results showed that trenching and passive draining is a more efficient dewatering method than the pumping well system. At the end of two years, pumping wells left a substantial volume of bofedal sediments saturated. The fundamental reason for this is that the low average hydraulic conductivity of the sediments results in formation of a steep cone of depression around each well. The low transmissibility of the formation means that the wells function as effective drains only for the sediments within a small radius of each well.

The trenching system proved to be a very effective dewatering method provided the trench density is high enough. The model predicts that under the trenching scenario, peak flow rates to the trenches could approach 1,600 m³/d, but are expected to average 165 m³/d over roughly two years. In contrast, the network of pumping wells, could only sustain a combined pumping rate of 77 m³/d. Modeled flow rates over time are shown in Fig. 4.

The results predict that after the first round of trench excavation, dewatering of the uppermost sediment layer will be essentially complete after 30 days. However, excavation of the early-drained upper part of the material could begin sooner than that, with the limiting factor being that it may not be practical to excavate in some areas where the declining water table still remains too close to the active excavation surface. Based on the maximum bofedal thickness of about 45 m (near the center of the basin), it is expected that the dewatering project will require 15 rounds of trenching, dewatering, and excavation for a total bofedal excavation time of nearly two years.

Stability Model Results

A back analysis indicated that a typical bofedal soil stockpile will require the organic-sand mixture to have a minimum friction angle of 22°, where constructed with a 3H:1V slope and a 2 m high toe berm on a bedrock foundation, to be stable. Applying this result where soil stockpiles will be placed on existing bofedal soil foundations, the maximum theoretical lift thickness was determined to be 4 m in order to avoid potential bearing capacity failure due to excess foundation pore pressure. Actual lift thickness would be limited to around 2 m in order to provide an acceptable factor-of-safety during construction.

Slope stability modeling of the areas of the pit wall where bofedal will exist revealed that the remaining 5H:1V slope would be unstable under seismic loading, and would require a waste rock buttress for stability. Fig. 4 shows the buttress required to support a typical bofedal slope at the southern edge of the mine pit.

Conclusions

The results of the field and laboratory testing showed that bofedal must be dewatered and removed prior to the construction of project facilities. SPT tests and laboratory testing suggest that the *in situ* material has the potential to liquefy under dynamic loading. Other lab testing results indicate that bofedal would make an ideal mine waste cover material. The low hydraulic conductivity and high storage will prevent infiltration by facilitating surface evaporation and runoff, and ideally, will encourage the reestablishment of bofedal flora and fauna on reclaimed surfaces.

The results of the groundwater modeling suggest that a system of trenches is the most efficient method considered for dewatering bofedal sediments prior to excavation. It is important to note that the results of the groundwater model are a numerical exercise simulating dewatering times and volumes, which does not consider construction as well as geotechnical challenges. Such challenges could include instability of the trench walls, the time required to excavate dewatered material, and the ability of some areas of the bofedal to support earth-moving vehicles, along with others. This model is designed as a construction planning tool, and additional optimization will be required upon the final design based on the mine plan.

Excavating and stockpiling bofedal material will require extensive handling. In the pit



Fig. 5 Cross section of buttress required to support bofedal slope

where thick deposits will be excavated, large volumes of waste rock will buttress the 5H:1V excavated slope. Stable stockpiling of the bofedal material can be achieved by limiting construction lift height to around 2 m to allow for foundation excess pore pressure dissipation in areas where stockpiles are placed over existing bofedal soils.

The management of bofedal deposits is a major consideration of the Corani mine plan. Dewatering bofedal deposits will require two years of work with multiple stages of trenching, dewatering, and excavation. Bofedal stockpiles will cover 1.25 km² of surface area within the mine area, and bofedal pit slopes require specialized buttressing to be stable. The requirement for managing the bofedal soils is therefore a significant cost item in the mining capital and operations' costs. Therefore, a thorough understanding of bofedal deposits-their extent, impact, strength, and best management practices, is critical to accurate mine planning and cost estimation.

Disturbed bofedal deposits must be reclaimed upon closure, and their important hydrogeologic role must be duplicated or restored. The Corani closure planning is ongoing, but current plans include the restoration of bofedal deposits over the backfilled mine pit and on the surface of the tailings storage facility. After mine closure, the total area of restored bofedal will be greater than the current bofedal extent. The project has also committed to maintaining dry-season baseflow in mine-impacted watersheds during operations and post-closure. Additional site investigation with sampling using thin-walled samplers and laboratory testing of undisturbed samples is recommended to improve and advance the present work.

Acknowledgements

The authors thank Bear Creek Mining Company for support in publishing this work.

References

- ASTM D1586-11. Standard Test Method for Standard Penetration Test (SPT) and Split-Barrel Sampling of Soils. American Society of Testing and Materials 2011.
- Benson, Craig H., William H. Albright, Arthur.C Roesler, and Tarek Abichou. "Evaluation of Final Cover Performance: Field Data from the Alternative Cover Assesment Program (ACAP)." Waste Management Conference. Tucson, Arizona 2002.
- Cooper, H.H., and C.E. Jacob. "A generalized graphical method for evaluating formation constants and summarizing well field history." American Geophysical Union Transcripts 27 (1946): 526–534.
- Cooper, H.H., J.D. Bredehoeft, and S.S. Papadopulos. "Response of a finite-diamter well to an instantaneous charge of water." Water Resources Research 3, no. 1 (1967): 263–269.
- Fetter, C.W. Applied Hydrogeology. Upper Saddle River, New Jersey: Prentice Hall 2001.
- Squeo, Francisco A., Barry G. Warner, Ramon Aravena, and Diana Espinoza. "Bofedals: high altitude peatlands of the central Andes." Revista Chilena de Hisotria Natural 79 (2006): 245–255.

Quantification of water evaporation by open pit mining lake using lysimeters

Manoel Camilo Moleiro Cabrera¹, Cristian Youlton², Edson Wendland³

¹²³ Laboratório de Hidráulica Computacional, Departamento de Hidráulica e Saneamento, Escola de Engenharia de São Carlos, Universidade de São Paulo. Av. Trabalhador São-Carlense 400, São Carlos – São Paulo – Brasil CEP 13566–590. ¹camilo@sc.usp.br, ²cristian.youlton@usp.br, ³ew@sc.usp.br

Abstract Two lysimeters and a buried evaporation tank with simple control and regulation system were designed to investigate the water loss due to soil cover change by open mining pit. The obtained results indicate that water losses through the surface increase in 1104 mm when sandy soil is converted to an open water surface. The impact increases in 1218 mm when clayey soil is converted to an open water surface. This indicates that the installation of mining pits with consequent formation of lagoons contributes to increasing evaporative water loss and decreasing underground water reserves.

Keywords Water balance, 20 m² tank, Linacre, Class A pan, mining impact

Introduction

Groundwater resources have gained attention in recent years due to environmental problems related to land degradation. Mining is a very important activity for the society, but it is the major consumer of nonrenewable natural resources, causing significant changes in the landscape and water resources and it consumes large quantities of water; only the copper mining industry alone used over 1.3 Gm³ of water in 2006 (Gunson et al. 2010). On a worldwide scale, however, mine water use accounts for a little portion of general water use. Even in countries with dry regions, intensivemining countries like Australia, Chile, and South Africa, mine water consumption is only 2-4.5 % of national water demand (Brow 2003; Bangerter et al. 2010).

Mine acid drainage is a major world environmental problem that adversely affects both surface and groundwaters, causing also problems of ecological significance. In general it occurs when pumped mine water is of poor quality. Other negative impact of mining activities is the lowering of mine water table in the vicinity of water supply or irrigation wells, both especially due to dewatering mine (Cabrera *et al.* 1984; Gray 1998; Younger and Wolkersdorfer 2004). There are studies about surface water quality and evapoconcentration, including modeling the effects in open pit mining lake and also about monitoring the stability of steep slopes of open pit mines (Yoko *et al.* 1997; Eary 1998; Han and Zhang 2009).

However, impacts on the water cycle or groundwater resources before and after installation of the mining activities (*e.g.* mining pits) are not mentioned in environmental reports, not counting changes in the amount and flow of water lost to the atmosphere.

There is strong evidence that open water surface has a direct impact on the water balance, affecting evapotranspiration and subsequently groundwater recharge. This is partly due to increased evaporation compared to vegetation cover. Evaporation from open water surfaces such lakes and wetlands often represents the largest losses in the local hydrology and is one of the main components of the hydrologic cycle (Assouline *et al.* 2008; Mengistu and Savage 2010). In Brazil, during the last years there has been a strong expansion of mining pits in the Paraíba do Sul watershed, modifying soil cover and increasing lake areas in São Paulo state.

There are no scientific studies that estimate directly changes in water balance, especially the amount of water lost to the atmosphere due to soil cover changes (grass to open water surface) by mining activities. The main objective of this study is experimentally quantify the loss of water in mining pits by monitoring the following variables in the water balance: i) evaporation; ii) rainfall; iii) drainage; iv) water replacement to maintain the water table in lysimeters and evaporation tank during one year under natural tropical weather conditions.

Methods

The study was conducted at the Lobo watershed (extreme coordinates 22°10' S lat. 22°20' S lat.; 47°45' O long. 47°55' O long.) in Itirapina, state of São Paulo, Brazil (Fig. 1).

The experiment was conducted in the Climatological Station of the University of São Paulo. The site lies at an elevation of 733 above sea level with average annual rainfall, air temperature and relative humidity of 1493 mm, 21.5 °C and 71 %, respectively.

The climate classification by Wilhem Köppen is CWA, seasoned climate due to altitude (Machado and Mattos 2001). The classification of Thornthwaite and Matter (1955) describes the climate to be B_2 r B'₃ a' (moist climate with few hydric deficiency in June, July and August)



Fig. 1 Site of experiment.

Annual potential evapotranspiration is 985 mm (Mattos *et al.* 1998).

This experiment used one buried tank and two lysimeters (Fig. 2) filled with sandy soil (lys-sand) and clayey soil (lys-clay) with water level maintained constant 1.0 m below surface. The lysimeters were made of fiberglass and have 1.88 m top diameter, 1.52 bottom diameter and 1.32 m depth. Each lysimeter has a surface area of 2.78 m². In the bottom of the lysimeter containers a drainage systems in "fish's spine" shape was installed, to drain the excess rain water. The drainage from the lysimeters and evaporation tank were measured in containers with 310 L of capacity. The water table in a supply tank (for reposition of evaporated water) was monitored every day at 07:00 am.

The evaporation tank was exactly similar in shape to the lysimeter tank. The water level inside the tank was maintained at or slightly below natural ground level. In order to study evaporation conditions at the test site two Class A pan and two 20 m² evaporimeters were surrounded by short-cut grass, 6 - 12 cm, same as the lysimeter cover.

Data loggers were also installed to record meteorological observations. The temperature and relative air humidity were obtained using one Rotronic sensor with multi plate radiation shield and naturally aspirated, about 1.8 m above ground. Solar irradiation was measured with Licor pyranometer, wind (speed) at 2.0 m above ground was obtained with Fuess anemometer, rainfall was measured with a Ville de Paris pluviometer. The meteorological observations were used to calculate evaporation according to Penman, (1948), Snyder (1992), Linacre (1993) and Penman-Villa Nova *et al.* (2006).

The sandy soil was collected from Ribeirão da Onça watershed (22°10'33.9″ S lat.; 47°57'14.0″ W long), while clayey soil was collected from a mining area localized in Uberabinha watershed (19°20'41.1″ S lat.; 47°54'46.3″ W long). Clayey soil is feedstock to make firebrick used in ovens. The soil granulometry is indicated in Table 1





Fig. 2 Lysimeter and Evaporation Tank with water supply, drainage system and float assemblage (not in scale).

Results and Discussions

The observed values of water supply to maintain the water table constant in the lysimeters are shown in Fig. 3. In the wet season (November to April) the sandy lysimeter consumed more water than the clayey lysimeter, due to the higher rain water retention in the clayey soil. During the dry season (May to October) the water supply increased strongly providing moisture to the grass covering. In this period there is no increase in water supply during the 15–20 days following an effective rain event, as observed in June. However it could be observed

Granulometry (%)			
Lys-Clay	Lys-Sand		
0.7	0.3		
2.6	8.8		
8.8	63.6		
2.4	16.4		
20.1	10.0		
65.4	10.9		
	Granuloi Lys-Clay 0.7 2.6 8.8 2.4 20.1 65.4		

Table 1 Granulometric composition of soils inlysimeters

that the grass cover in the lys-clay did not present as good adaptation as in the lys-sand.

Fig. 4 shows the accumulated drained rain excess for the evaporation tank and for the lysimeters. The drainage (mm.m⁻²) at the clayey and sandy lysimeters show identical values. The drainage at the evaporation tank follows the observed precipitation.

In this experiment the methods of Linacre (1993) and Class A pan with K_p =0.76 (Reis *et al.* 2006) present a good agreement with measurements at the evaporation tanks. The Snyder (1992), Penman-Villa Nova (2006) and Penman (1948) methods overestimated the accumulated evaporation (Fig. 5).

Conclusions

The soil cover changes (substitution of grass cover by open water surface) due to mining pits increase water losses. According with Fig. 5, the obtained results indicate that water losses through the surface increase in



Fig. 3 Comparison of accumulated water supply for the clayey and the sandy lysimeters. The rainfall in the period is shown as hanging bars.



Fig. 4 Values of drainage for the lysimeters and evaporation tank. The accumulated rainfall in the period is also shown.

Fig. 5 Comparison of accumulated evaporation measured by evaporimeters and calculated by estimation methods based on climatic data. In the bottom of the graphic the accumulated water supply in the lysimeters is shown.

1104 mm when sandy soil (covered with well watered grass) is converted to an open water surface. The impact increases in 1218 mm when clayey soil (well watered grass but with environmental stress) is converted to an open water surface. Considering the meteorological conditions in the test site the Class A pan with K_p =0.76 and the Linacre (1993) methods for evaporation estimate showed good agreement with measured accumulated evaporation during the wet and dry periods.

References

- Assouline S, Tyler SW, Tanny J, Cohen S, Bou-Zeid E, Parlange MB, Katul GG (2008) Evaporation from three water bodies of different sizes and climates: Measurements and scaling analysis. Advances in Water Resources 31:160–172
- Bangerter P, Richard E, Villegas M (2010) Improving overall usage of water in mining - A sustainable development approach. In 2nd International congress

on water management in the mining industry, p 403

- Cabrera F, Toca CG, Diaz E, Arambarri P (1984) Acid mine-water and agricultural pollution in a river skirting the Doñana National Park (Guadiamar river, South West Spain). Water Research 18:1469–1482
- Brow E (2003) Water for a sustainable minerals industry. In. Mining Conference, Brisbane, October 2003, p 3-14
- Eary LE (1998) Predicting the effects of evapoconcentration on water quality in mine pit lakes. Journal of Geochemical Exploration 64:223–236
- Gray NF (1998) Acid mine drainage composition and the implications for its impact on lotic systems. Water Research 32:2122–2134
- Gunson AJ, Klein B, Veiga M, Keevil NB (2010) Estimating global water withdrawals due to copper mining.J. Wiertz (Ed.), II International Congress on Water Management in the Mining Industry, GECAMIN
- Han X, He M, Zhang B (2009) Sensitivity analysis for parameters of a monitoring system for steep slopes

of open-pit mines. Mining Science and Technology (China) 19:441–445

- Linacre ET (1993) Data-sparse estimation of lake evaporation, using a simplified Penman equation. Agricultural and Forest Meteorology 64:237–256
- Machado RE, Mattos A (2001) Construção e instalação de um lisímetro com sistema de drenagem. Revista Brasileira de Agrometeorologia 9:147–151
- Mattos A, Ribeiro JBR, Mattos KMC, Villa EA (1998) Caracterização climática da represa do Lobo (Itirapina-SP) In Anais Reis C (ed) Congresso Brasileiro de Meteorologia, Univ de Brasília, p 43
- Mengistu MG, Savage MJ (2010) Open water evaporation estimation for a small shallow reservoir in winter using surface renewal. J Hydrology 380:27–35
- Penman HL (1948) Natural evaporation from open water, bare soil and grass. Proceedings of the Royal Society of London Mathematical and Physical Sciences 193:120–145
- Reis B, Batista J, Teixeira G, Targa MS, Catelani CS (2006) Influência das cavas de extração de areia no balanço hídrico do vale do Paraíba do Sul. Revista Escola de Minas 59:391–396

- Salazar O, Hansen S, Abrahamsen P, Hansen K, Gundersen P (2013) Changes in soil water balance following afforestation of former arable soils in Denmark as evaluated using the DAISY model. J Hydrology 484:128–139
- Snyder R (1992) Equation for evaporation pan to evapotranspiration conversions. Journal of Irrigation and Drainage Engineering 118:977–980
- Villa Nova NA, Miranda JH, Pereira AB, Silva KO (2006) Estimation of the potential evapotranspiration by a simplified penman method. Engenharia Agrícola 26:713–721
- Yoko S, Axler R, McDonald M, Wilcox D (1997) Recovery of a mine pit lake from aquacultural phosphorus enrichment: model predictions and mechanisms. Ecological Engineering 8:195–218
- Younger PL, Wolkersdorfer C (2004) Mining impacts on the fresh water environment: technical and managerial guidelines for catchment scale management. Mine water and the environment 23:s2–s80

The combined use of spinner flow logging and geotechnical information to investigate the hydraulic properties of fractured rock mass

Rosalind Pedder, Houcyne El-Idrysy

SRK Consulting (UK), 5thFloor Churchill House, Churchill Way, Cardiff, UK

Abstract Spinner flow logging is a technique used to determine vertical variation in hydraulic properties of aquifer formations. Down-hole acoustic televiewer and geotechnical core logging are usually used to determine geotechnical parameters of rock formations. A mine Feasibility Study in West Africa where both of these methods have been implemented allowed a closer insight into the relationship between the structural and hydraulic properties of the rock formations. Combining both techniques provided valuable data that enables a more accurate estimation of pit water inflows and a more cost effective design of the dewatering system and of the pit slope angles.

Keywords Spinner logging, geotechnical logging, fractured rock, hydrogeology, dewatering

Introduction

As part of a Feasibility Study (FS) for an open pit gold mine in Burkina Faso combined hydrogeological and geotechnical site investigations were carried out. The main objective of the investigations was to refine the conceptual hydrogeological understanding of the project area and obtain the required input parameters to (1) estimate potential groundwater inflows into the pits and (2) aid the design of a dewatering system. This paper focuses on how the combined use of down-hole spinner flow logging, acoustic televiewer (ATV) survey and geotechnical core logging can contribute to achieving this objective.

Spinner flow logging is a well documented technique used to determine vertical variation in hydraulic properties of aquifer formations (Molz *et al.* 1989, Hill 1990, Paillet 1998). The combination and comparison of this technique with geotechnical information is sparsely represented in literature, yet can reveal relationships between geological structures and hydraulic properties of aquifer formations, reflecting the magnitude and potential continuity of water-bearing networks of geological structures. This in turn en-

ables a more accurate assessment of the potential variation of groundwater inflow into the pit over the mine life and thus aids the design of more effective water control and management systems.

Site Background

The site is located in the southeast of Burkina Faso in a relatively flat area of sparsely vegetated steppe grassland with a semi-arid climate. The proposed final footprint of the main pit in Fig. 1 is around 9.4 km² with an ellipse shape elongated northeast-southwest. The final pit depth is planned to reach 450 m. To the southwest of the main pit a smaller pit of 1.3 km² is proposed to have a final depth of about 120 m.

Fig. 1 highlights the proximity of the pit footprint to a river which flows into a large reservoir to the east of the image boundary. Towards the end of the rainy season the northern and eastern pit boundaries of the main pit are located between 1.2 km and 0.5 km from the river respectively. The proximity of the river to the main pit mine raises the question of a potential hydraulic link between the pit and the river, which could possibly lead to in-



Fig. 1 Location of spinner tests and ATV logs in relation to the pit footprints and the river.

creased water inflows into the pit. Although the spinner tests discussed in this paper contribute to answering this question, this hydrogeological aspect of the FS is beyond the scope of the present paper: an extensive hydrogeological investigation programme has been implemented in addition to the spinner tests presented in this paper.

The local geology is dominated by granitoids. Gold mineralisation is associated with broad alteration systems within quartz schists of varying mineralogical composition. Following a northeast-southwest strike, the geological formations in the ore zone are steeply dipping toward the northwest. Mineralisation is intersected by a series of north-south trending amphibolite dykes between 3–30 m in thickness. The rock mass is fairly competent with low structure density, although there is a 30– 40 m zone of weathered material above the more competent rock.

Methods

Spinner logging has been conducted under both ambient (non-pumped) and dynamic (pumped) conditions in addition to structural core logging and ATV surveys in nine boreholes of depths between 220–420 m. Five of the holes are vertical groundwater observation wells used in the pumping tests that have been carried out as part of the FS. The other four holes are geotechnical holes inclined at 65° or 75° into the pit walls in order to intersect any structures that could potentially act as failure planes. Fig. 1 shows the location of the boreholes relative to the pit footprint and nearby river.

Spinner Logging

Each of the nine boreholes was initially logged under ambient conditions (without pumping) by lowering the calibrated spinner sonde down the borehole at a constant speed using an electric winch. The impeller could then detect any ambient flow in the borehole and the depth of occurrence. Subsequently, each borehole was logged whilst pumping at a steady state to induce a flow greater than any ambient flow that might exist. The resulting logs were manually separated into individual flow anomalies which correspond to an inflow at a discrete depth.

Transmissivity for each borehole was estimated from the steady state drawdown and total flow induced by pumping. Where the pumping rate during spinner testing was not capable of inducing enough drawdown for analysis, transmissivity was calculated from airlift recovery tests or from drawdown during pumping tests in adjacent boreholes. To estimate transmissivity for each flow anomaly the percentage contribution of each anomaly to total flow was calculated. The percentage contribution was then applied to the total transmissivity to express the transmissivity of each inflow relative to the total.

ATV Survey and Geotechnical Core Logging

The geotechnical investigations were conducted as part of a small scale structural survey to remove drilling bias created by the resource exploration holes with the primary objective of informing pit slope design. The study was conducted in parallel with the hydrogeological study.

Oriented core was obtained from each borehole. To ensure accuracy in the structural logs the ATV surveys were carried out prior to core logging so that structures could be logged from both sources simultaneously. The ATV survey involved winching the acoustic probe slowly down each borehole so accurate information on travel time and amplitude could be obtained. Open structures were recorded as open joints, open foliations, open cemented joints and shattered zones. Their dip angle and dip direction were calculated in each case. Based on drillhole orientations the impact of sampling bias was considered to be minimal.

Selecting the exact depth of change in flow from the spinner logs requires an element of judgement and the task of correlating such responses with structures in the core and ATV logs needs to be approached cautiously. However, due to the relatively low structure frequency of the rock mass the majority of inflows in the spinner logs coincided clearly with open structures in the ATV logs. In the few cases where there was no open structure that corresponded exactly to a spinner-indicated flow zone, the nearest open structure was chosen and this was always within a few centimetres.

Results

The ambient spinner tests did not detect any ambient flow, so it was concluded that there was no significant hydraulic head gradient between inflow zones. The results therefore suggest the absence of a perched water table at the top of the rock formations or a pressurised confined aquifer at the bottom. However, the impeller has a sensitivity threshold due to friction in the bearings, so if a low vertical gradient exists between the various horizons this may not have been detected.

Spinner flow depths and magnitudes are presented in Fig. 2. The dynamic spinner survey (carried out simultaneously with pumping at constant low flow rate) clearly indicated the top rock horizons as the most hydraulically conductive. The rest of the rock mass can be described as a non-aquifer. However, once again, taking into account the impeller sensitivity threshold it is likely that there may have



been low permeability structures or zones in the deep horizons that produced flow below the spinner's detection limit both under ambient conditions and during pumping. It was assumed that the contribution of these zones to the total permeability of the rock mass was insignificant in the context of this study, as micro-flow data was not required.

The spinner test results suggest the existence of a total of 21 inflow zones in nine boreholes. Inflows ranged in depth between 36 m to 276 m, although full depth of most of these boreholes ranges between 300 m and 420 m. Due to the presence of near-surface blank casing in some boreholes the depth of the shallowest inflow is not well constrained. The spinner results show that 67 % of the inflows are located at depths shallower than 85 m.

The five largest circles in Fig. 2 represent inflows in OW7, GT7, GT8 and OW11 whose transmissivity is one or two orders of magnitude greater than the next largest inflow. These high transmissivity inflows are all at depths shallower than 120 m and are all located on the eastern side of the mine pits. Equally, the two deepest inflows in OW5 and OW6 have a transmissivity that is an order of magnitude less than the next smallest inflow and are both located on the western side of the mine pits. However, when inflow transmissivity is plotted against inflow depth there seems to be no correlation between the two. This indicates that, although the occurrence of inflows themselves appears to be controlled by depth, the magnitude of their transmissivity does not appear to correlate with depth. Furthermore, there seems to be no correlation between the total borehole transmissivity and structure frequency or aperture as recorded in geotechnical logging and ATV survey.

Transmissivity values across all boreholes ranged from 0.06 m²/d at 276 m in OW6 (also the deepest inflow), to 113.5 m²/d at 120.8 m in OW7. The inflows with the highest transmissivities were found in OW7, GT7, GT8 and OW11 (Fig. 2). These boreholes only had one or two discrete inflow horizons reflecting the relatively competent nature of the rock mass with few open structures.

All inflows were produced by open joints with the exception of two open cemented joints and two shattered zones. Shattered zones are classified as fault zones in geotechnical interpretation. Although joints may appear cemented in the core, the spinner tests revealed that these features may nonetheless act as flow conduits indicating only partial cementation with sufficient connectivity of void space within the joint structure to enable groundwater to migrate.

A comparison has been made with regard to the global dip angles of the inflow structures and the logged joints as recorded from drill cores and ATV survey. The dip angle for 95 % of the structures that were associated with inflows ('inflow structures') was less than 35°. Although the data are insufficient for a robust statistical comparison, visually it is clear from Fig. 3 and Fig. 4 that the dip angles of all open structures (as recorded by ATV survey and drill core logging) are distributed across a wider range than the dip angles of the inflow structures alone. The clustered data in Fig. 4 with a dip angle greater than 30° represent the foliation trending northeast-southwest with the more strongly clustered data representing structures dipping steeply to the northwest, and the more scattered data, structures dipping steeply to the southeast. Based on the results of this investigation the structures corresponding to the foliation are unlikely to be flow conduits. Groundwater flow is predominantly associated with the sub-horizontal joint sets.

The information from the spinner testing and the geotechnical logging were used to inform a three layer conceptual model (Fig. 5) comprising the overburden, the zone in which all inflows were detected ('inflow zone'), and the rest of the rock mass where no inflows were detected. A Radial Basis Function was used to interpolate between known inflow locations to create the estimated inflow zone. The inflow zone thickens from east to west,



Fig. 3 Density concentration of poles of structures detected as inflows. A darker colour indicates a higher concentration. Sample size was 21.



Fig. 4 Density concentration of poles of all logged structures. A darker colour indicates a higher concentration. Sample size was 3103.

💒 leapfrog®



Fig. 5 Conceptual model block diagram of proposed pit shell with zone in which inflows were detected in white. Weathered zone is dark grey and the remaining rock mass is pale grey. Aspect is towards the northeast and the pit diameter at the line of cross-section is approximately 1km.

with a narrowing in the centre of the pit, although this narrowing is likely to be caused by the geographical bias of the dataset. The model highlights that, although the highest magnitude inflows have all been recorded on the eastern side of the main pit, they all occur within a relatively narrow range of thickness between 54 m to 120 m depth, and they are often the only observed inflows in the borehole. On the western side of the pit the inflow zone had a greater thickness with depths ranging between 43 m and 276 m. However, the inflows recorded along the western side of the pit have a much lower magnitude. This observed inflow pattern suggests the existence of structure zones of significant storage capacity along the eastern wall of the main pit, which would be drained with high productivity dewatering wells.

Conclusions

Spinner logging, ATV logging and geotechnical core logging were used to investigate the hydrogeological properties of the fractured rock mass at a proposed open pit gold mine in Burkina Faso. For the hydrogeological conceptual model, the spinner test results indicated the absence of a perched aquifer as well as pressurised confined aquifers, and enabled the transmissivity of inflow structures to be quantified. The addition of geotechnical information provided added resolution as to the exact depth of inflow structures, as structure depth could be measured accurately from ATV output and confirmed in the drill cores. This enabled the thickness of the highly permeable zone to be more confidently constrained in the conceptual model. This has important implications for the estimation of groundwater inflows to the pit and for the design of a more efficient and cost-effective dewatering system.

From the perspective of the geotechnical investigation the information from the spinner testing showed that there is a low likelihood of encountering high water pressures in steeply dipping structures that may impact on the pit slope stability. Spinner test results indicate that the majority of inflow structures were sub-horizontal. Sub-horizontal structures with high water pressures are much less detrimental to pit slope stability, as they are unlikely to act as potential failure planes. The combination of both spinner testing and geotechnical logging thus provided valuable input to both open pit groundwater inflows and pit slope stability studies, ultimately leading to more effective mine designs, and may have further reaching implications during the operational phase of the mine.

Acknowledgements

The authors thank Volta Resources and Kiaka Gold SARL for facilitating the research that allowed the production of this paper. Thanks also go to the geophysical logging contractor, LIM, for collecting the spinner and ATV data. Additional thanks go to Mike Palmer and James Haythornthwaite (SRK) for their work with Leapfrog, and to the SRK Geotechnical Engineers for amiably collaborating with this research.

References

- Molz, F.J., Morin, R.H., Hess, A.E., Melville, J.G. and Güven, O. 1989. The impeller meter for measuring aquifer permeability variations: evaluation and comparison with other tests. Water Resources Research. 25:(7). 1677–1683.
- Hill, A.D. 1990. Production logging theoretical and interpretive elements: Richardson, Texas. Society of Petroleum Engineers Monograph. 14.
- Paillet, F.L. 1995. Using borehole flow logging to optimize hydraulic test procedures in heterogeneous fractured aquifers. Hydrogeology Journal 3, no. 3: 4– 20.
Methodology of Quantitative Assessment of Mine Water Inflows

Naďa RAPANTOVÁ¹, Christian Wolkersdorfer², Światosław Krzeszowski³, Arnošt Grmela¹

¹ VSB – Technical University of Ostrava, Institute of clean technologies for mining and utilization of raw materials for energy use, 17. listopadu 15, 708 33 Ostrava, Czech Republic, nada.rapantova@vsb.cz ²International Mine Water Association, Ginsterweg 4, 90530 Wendelstein, Germany ³ Silesian University of Technology, Gliwice, Poland

Abstract This paper presents a methodology of quantifying different sources of water in the overall water entering a mine. The quantification is based on the hydrochemical nature of waters from individual aquifers contributing to the resulting mine water mixture in the pit. In order to solve the general mixing equation, the software tool KYBL-7 has been developed using an over determined set of linear equations (3–10 sources defined by 4–12 parameters). Its computational methodology is generally based on the balances of selected components of mine waters in steady state conditions without considering chemical reactions.

Keywords Mine water sources proportions, open-pit coal mining, mixing equation, geochemical modeling, water balance.

Introduction

Chemical compositions of mine waters are a result of several mechanisms depending on the type of mining operation and the geological setting (*e.g.* surface, underground mining, soft rock, hard rock). Knowledge of the proportional inflow rates from the individual aquifers may facilitate the prediction of chemical trends of the mine water mixtures. In numerical models, the individual inflows from different aquifer systems contributing to the overall chemistry result indirectly from the calculation results. They are based on the calibration targets of hydraulic heads, the estimated hydraulic conductivities of the aquifers, and the total dewatering rate (Rapantova *et al.* 2007).

Direct measurement of mine water flows requires the use of hydrometric techniques for measuring the flow rates of springs, streams, and rivers. Those techniques are well established and widely described in the literature with particular methods used in the mining environment (*e.g.* Brassington 2006; Wolkersdorfer 2008). Yet, many measurements tend to have a considerable degree of uncertainty given the potential diffuse flows – if they are feasible at all. Investigations in selected mines showed that many flow measurements must be considered wrong because the prerequisites of the individual methods were not accurately taken into consideration (Wolkersdorfer 2008).

This paper will present an alternative indirect method of calculating the proportions of mine water inflows into a mine water sump by using a case study from the Sokolov Coal Basin, Czech Republic. The calculations and the quantities of the various water resources contributing to the total mine water mixture are based on the hydrochemical data from groundwater in individual aquifers and the chemical composition of the mine water in the dewatering sump. To solve the general mixing equation as an overdetermined set of linear equations (3-10 sources defined by 4-12 parameters), the KYBL-7 software has been developed (Krzeszowski et al. 2005; the Czech word 'kýbl', derived from the German word 'Kübel', means 'bucket', used in mine shaft construction).

Numerical codes for mixing calculations

Basically, the philosophy of calculating the proportions of water sources in a mine water mixture used by KYBL-7 is very similar to that of the code M3 (Multivariate Mixing and Mass balance calculation; Laaksoharju et al. 1999, Laaksoharju et al. 2008). Both codes utilize hydrochemical data for calculating the proportion of the water sources in the mixture including 'sources and sinks' identification. Nevertheless, the mathematical methods applied are very different. M3 uses Principal Component Analyses (PCA) to summarize the information from the data set and for further modeling. M₃, as declared by the authors, should only be used if two principal components of the data set sum up to more than 60 % of the variability of the information in the data set. According to Gómez et al. (2008), mass balance calculations in M3 are much more sensitive to non-conservative compositional variables and their recommendation is not to use non-conservative variables with PCA-based codes if any information about reactions is to be obtained.

Another program that is commonly used to compute proportions of source waters contributing to final mixed waters is NETPATH (Plummer et al. 1994). This inverse geochemical modeling code takes into consideration two to five initial solutions. Based on a set of analyzed parameters and a user defined selection of mineral phases, a number of potential mixing models is calculated using chemical thermodynamic principles. In addition to the mixing, dilution and evaporation processes can be modeled. NETPATH has an export function to PHREEQC and the advantages of PHREEQC can be used in conjunction with NETPATH to model mixing scenarios of known sources. However, the alternative inverse modeling approach of PHREEQC might result in large sets of mixing proportions and mineral mass transfers. Consequently, the application of this methodology might become very difficult and tedious when applied to large groundwater datasets (Gómez et al. 2008).

Methods

In order to protect the Carlsbad hot springs, it is necessary to quantify and determine the proportion of the Carlsbad type waters in the drainage water of the Jiří and Družba open pit mines in the Sokolov Coal Basin (Czech Republic). Those calculations, where proportions of various waters contributing to a water sample have to be calculated, are an essential problem in applied hydrogeology. Wolkersdorfer (2008) describes the results of such a calculation for the Gernrode fluorspar mine, where the numerical code PHREEQC was used to identify the ratio of mine water and mineral water discharging from the mine.

For the source identification of the mine water in the Jiří and Družba open pit mines, chemical analyses of groundwater taken from boreholes between 2004 and 2006 were used. By means of multivariate cluster analyses the hydrogeochemical data of the groundwater from the dewatering boreholes was characterized. Cluster analysis was conducted with the Ward clustering method of MATLAB (Manly 1994), which computed a dendrogram including similarity/dissimilarity values for samples and statistical data characterizing the individual clusters. A total of ten parameters were used for the cluster analysis: total dissolved solids (TDS), Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, HCO₃⁻, NH₄⁺, and Fe²⁺. In order to transform the original set of variables (the chemical composition of the water samples) to a new set of uncorrelated variables we applied principle cluster analyses (PCA; Jolliffe 1986), which is generally applied for classification, simplification of data and finding the most important variables in a data set (Krzanowski 1988). The transformed water composition was obtained by using the centers of the clusters. To verify that the transformed composition is chemically and statistically similar to the original data, we run hierarchical cluster analyses on both the original and the transformed data matrix identifying no statistically significant difference.

In order to quantify the proportions of source waters composing the Jiří and Družba

mine waters, the previously developed numerical code KYBL-7 was used (Krzeszowski 2005, 2009, Krzeszowski *et al.* 2005). Its computational methodology is generally based on the balances of selected components of mine waters in steady state conditions without considering chemical reactions. Fig. 1 shows the conceptual model applied by means of KYBL-7.

The whole set of mathematical equations that describe the fractions of the different source waters are based on the following equations:

$$\sum_{j=1}^{J} q_j \cdot C_{1,j} = M_1$$

$$\vdots$$

$$\sum_{j=1}^{J} q_j \cdot C_{1,j} = M_1$$
(1)

where:

 $C_{i,j}$ concentration of the *i*-th component in the *j*-th water source: i = 1...I, j = 1...J).

 M_i concentration of the *i*-th component in the mine water mixture: i = 1...I,

 q_j proportion of the *j*-th mine water source in the water mixture, j = 1...J.

The main computation algorithm in KYBL-7, leading to consistent balances, is called methods of the results coordination (MRC; Adamczewski 2010). The second algorithm, which is a supporting algorithm mainly used for calculating the starting point for MRC, is based on the Cholesky's method to solve overdetermined systems of equations (MCH). Both algorithms are described in detail in Rapantová *et al.* 2012.

Results and Discussion

Mine waters in the Sokolov Coal Basin result from the mixing of hydrochemically different water sources. For the Jiří Mine, the following six potential water sources were defined: Antonín Seam waters (ANT), Sokolov Formation waters (SPA), Cypris Formation waters (CS), Mineral waters from the underlying rocks (Carlsbad type waters KV), Atmospheric rainfall waters (AS), and a potentially unidentified source (PUS; optional).

Based on the clustering results with two principal components accounting for 78 % of the variance in the dataset, averaged hydrogeochemical compositions of the source waters were calculated using the. Although twelve averaged alternatives of the source water composition were applied in the study, we present only one of those in this paper. To represent the chemical variations of the water chemistry within each group as well as measurement errors, we applied a 10 % uncertainty resulting from potential analytical or sampling errors to the mean water compositions (Table 1).

Technically, the MCH method utilizes a semi-random number generator for the generation of input data within the ranges given in Table 1. We defined the initial boundary conditions for the computations in KYBL-7 as follows: number of simulation cycles 250,000 or 500,000 (the latter only when a relatively small number of positive results were obtained); boundary condition for the proportion of the source water in the pit water between 0.95 and



Fig. 1 Diagram of the water mixture for J mine water sources with known compositions (c_{i,j}) and unknown proportions (q_j) in water mixtures with known compositions (q. M_i). Unknown variables, constituting the unknown quantities of the system are italised.

Parameter	ANT	SPA	CS	KV	AS	Mixture
TDS	6131±613.1	2274±227.4	940±94.0	9621±962.1	17±1.7	2618±261.8
Na ⁺	1297±129.7	550 ± 55.0	200 ± 20.0	2283±228.3	0.5 ± 0.0	455±45.5
K^+	38.6±3.9	36.8±3.7	9.0±0.9	80.6±8.1	1.7±0.2	26.7±2.7
Ca ²⁺	153.3±15.3	65.1±6.5	39.7±4.0	456.9±45.7	0.9±0.1	177.0±17.7
Mg^{2+}	222.7±22.3	21.3±2.1	15.1±1.5	109.0±10.9	0.8±0.1	68.5±6.9
Fe ²⁺	0.5±0.1	8.7±0.9	0.7±0.1	5.1±0.5	$0.04{\pm}0.1$	2.3±0.2
$\mathrm{NH_4}^+$	$1.00{\pm}0.1$	2.80±0.3	0.20±0.1	1.60±0.2	0.90 ± 0.1	1.37 ± 0.1
Cl	15.9±1.6	114.5 ± 11.5	7.3±0.7	$1089.0{\pm}108.9$	1.5±0.1	$114.0{\pm}11.4$
SO4 ²⁻	3277±327.7	583 ± 58.3	249±24.9	2769±276.9	4.6±0.5	1370±137.0
HCO3	1012±101.2	920±92.0	400±40.0	2779±277.9	6.3±0.6	381±38.1
K ⁺ Ca ²⁺ Mg ²⁺ Fe ²⁺ NH ₄ ⁺ Cl ⁻ SO ₄ ²⁻ HCO ₃ ⁻	$\begin{array}{c} 38.6 \pm 3.9 \\ 153.3 \pm 15.3 \\ 222.7 \pm 22.3 \\ 0.5 \pm 0.1 \\ 1.00 \pm 0.1 \\ 15.9 \pm 1.6 \\ 3277 \pm 327.7 \\ 1012 \pm 101.2 \end{array}$	36.8±3.7 65.1±6.5 21.3±2.1 8.7±0.9 2.80±0.3 114.5±11.5 583±58.3 920±92.0	9.0±0.9 39.7±4.0 15.1±1.5 0.7±0.1 0.20±0.1 7.3±0.7 249±24.9 400±40.0	80.6±8.1 456.9±45.7 109.0±10.9 5.1±0.5 1.60±0.2 1089.0±108.9 2769±276.9 2779±277.9	$\begin{array}{c} 1.7\pm 0.2\\ 0.9\pm 0.1\\ 0.8\pm 0.1\\ 0.04\pm 0.1\\ 0.90\pm 0.1\\ 1.5\pm 0.1\\ 4.6\pm 0.5\\ 6.3\pm 0.6\end{array}$	26.7±2.7 177.0±17. 68.5±6.9 2.3±0.2 1.37±0.1 114.0±11. 1370±137 381±38.

Table 1 Example of a parameter set with mean values for the different water sources. A 10 % uncer-tainty for all samples was assumed (in mg/L); ANT: Antonín Seam waters, SPA: Sokolov Formationwaters, CS: Cypris Formation waters, KV: Mineral waters from the underlying rocks (Carlsbad typewaters), AS: Atmospheric rainfall waters.

1.05; boundary condition for the mixture composition between 0.925 and 1.075; number of fitting parameters: 10 (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, $SO_4^{2^-}$, HCO₃⁻, Fe²⁺, NH4⁺, and TDS); and number of known sources in the mixture 5. Furthermore, the hypothesis of a potentially unidentified source contributing to the pit water chemistry was tested. Depending on the input options, the computation time ranged between hours and tens of hours. In total, we conducted twelve different computations with varying input parameters including and excluding the potential unidentified source.

For all valid computation solutions, we determined average deviations of the source proportions. Results of those simulations are the arithmetic averages of the valid simulations and the dispersal values of the individual solutions. Based on those resulting data, the final proportions of the sources for the mine water were calculated (Table 2) including the results' dispersions. None of the scenarios excluding the potentially unidentified source met al. l predefined criteria; therefore we preceded the calculations with a scenario including the potentially unidentified source.

Several hypotheses could explain the existence of the potentially unidentified source: (a) a natural, so far unknown source of water, (b) precipitates or secondary minerals dissolved by the mine water, (c) an imbalance in the mixture, caused by the secondary minerals precipitation due to contact of the mine water with the atmosphere (precipitates), (d) evaporation of the mixture in the sump or (e) numerical dispersion of the solver.

In principle, the MCH method cannot give a full balance for the mine water mixture. Therefore, both, the input data and output results are provided as intervals of values. Consid-

Mine water source	ANT	SPA	CS	KV	AS	PUS	Results quality
With potentially unidentified source	16.3 ± 2.4	5.0 ± 3.3	12.7 ± 9.2	3.2 ± 1.5	61.4 ± 7.6	$\begin{array}{c} 1.3 \pm \\ 0.01 \end{array}$	High

Table 2 Calculation results of proportions of mine water sources in the mine water mixture in % (achieved by the MCH method); PUS: potentially unidentified source. No geochemically viable results were obtained for models without the PUS. The results quality is a measure to describe how good the simulations comply with the accuracy criteria.

ering the common uncertainties in hydrogeological problems related to mine water, KYBL's stochastic approach can be considered an advantage over current methods. As described above, KYBL-7 employs an MRC method which provides full mass balance results of the water mixture including a calculation of the potentially unidentified source composition. It requires an initial estimate of the proportions of the mine water's sources using the results of the MCH method which is supposed to be a good approximation. As a result, the MRC method produces proportions of water sources in the mine water mixture (e.q. in the mine sump) as well as corrections of the input data within the allowed interval. Finally, KYBL calculates the amended chemical composition of the averaged sources with very small changes much below 1 % of the initial values (Table 3).

As can be seen from table 3, the ten calculated physico-chemical parameters of the PUS exceed the six associated chemical parameters of the real sources of up to two orders of magnitude. This was an indication for the PUS to be not an additional, real water source. To identify the meaning of the PUS for the overall composition of the pit water, we conducted a geochemical modeling with the chemicalthermodynamic code PHREEQC (Parkhurst and Appelo 2013). This modeling proved that the PUS is due to site specific geochemical processes and - in fact - does not represent an additional water source. Saturation indices (SI) of gypsum were relatively high in all those calculations, ranging from 1.43 to 2.09, eliminating in fact any long-term stability of such solutions. As such, the solutions would rather represent a gypsum crystal suspension, or gypsum itself, while the gypsum sediment would be settled at the bottom of the reservoir. In the case of the phases of carbonates, the saturation indices of calcite, or aragonite and dolomite, are vital. In case of carbonates, any strong oversaturation of the solutions will only appear subject to a neutral or alkaline reaction of the solutions. It can be assumed that the unknown source represents the mass balance mixture of two types of solutions. The first one comes from dissolution of pyrite weathering products (high content of sulphate and Fe, pH below 4), the second one form dissolution of mineral water evaporates (high hydrogen carbonates). Both, secondary minerals and minerals from mineral water evaporation are exposed in the pit and dissolve during precipitation, hence contributing to the final composition of the mine water mixture.

Conclusions

The paper aimed at presenting the newly developed computer code KYBL-7, exemplified by a case study from the Sokolov Coal Basin,

Source	ANT	SPA	CS	KV	AS	PUS	Mixture
Proportion (%)	16.3	5.04	12.69	3.19	61.43	1.35	-
TDS	6123.8	2273.5	939.9	9617.5	17.3	79554.8	2625.9
Na^+	1300.6	550.0	199.6	2284.9	0.5	8414.0	452.0
\mathbf{K}^+	38.6	36.8	9.0	80.6	1.7	1008.6	26.6
Ca ²⁺	152.9	65.1	39.7	456.3	0.9	9729.4	180.0
Mg^{2+}	224.3	21.3	15.1	109.1	0.8	1781.0	67.6
Fe ²⁺	0.5	8.7	0.7	5.1	0.0	108.2	2.3
$\mathrm{NH_4}^+$	1.0	2.8	0.2	1.6	0.9	30.6	1.4
Cl	15.9	114.5	7.3	1087.3	1.5	5152.4	114.6
SO_4^{2-}	3267.8	583.0	249.0	2767.7	4.6	51393.6	1380.2
HCO3	1018.3	922.0	400.8	2787.9	6.3	1437.3	375.5

Table 3 Final results after computed amendments of input data (rounded), parameters in mg/L; PUS:

 potentially unidentified source

Czech Republic. This code represents an inverse solution of the mixing equation accounting also for the variability of the initial data set (uncertainty). It encompasses calculating up to ten source proportions (defined by four to twelve hydrochemical parameters) in mine water mixtures without reducing the multiparametric information. KYBL-7 can be used as a first step in mixing and mass transfer calculations to complement chemical-thermodynamic (*e.g.* with PHREEQC) or mixing calculations (*e.g.* with NETPATH). As has been shown, those codes can supplement to the results of KYBL by using its calculated mixing proportions for the source waters.

Our methodology described in this paper has already been applied successfully at several mines in the Czech Republic and Poland. In the case of underground mines, no relevant imbalance of the results was found, whereas in open pit mines geochemical reactions typically seem to introduce imbalances in the mixing equation. While solving the sets of overdetermined mixing equations, KYBL elides geochemical reactions occurring during the mixing of individual water sources or during the water-atmosphere-contact. This distinguishes the code from chemical-thermodynamic packages (e.g. NETPATH, PHREEQC, Geochemist Workbench). KYBL is purely based on mathematical and statistical procedures to solve the general mixing equation by approximating the proportions of the individual sources to give the closest mine water composition. The guiding idea behind the development of KYBL was to provide a simple usage based on the before described approach in order to meet the applied needs of mining hydrogeologists and engineers. It takes into account the variability of the sources, natural and technological conditions in the open pit operation, anthropogenic loads, and errors in sampling and analyses.

Acknowledgments

The article has been made in connection with project ICT CZ.1.05/2.1.00/03.0082 (Institute of

clean technologies for mining and utilization of raw materials for energy use) supported by European Union and from the means of state budget by the Ministry of Education, Youth and Sports. We thank an anonymous reviewer for helpful comments.

References

- Adamczewski Z (2010) Rachunek Wyrównawczy w 15 wykładach [Adjustment Analysis in 15 lectures] 2nd edition. Oficyna Wydawnicza Politechniki Warszawskiej, Warszawa
- Brassington R (1999) Field Hydrogeology. Wiley, Chichester
- Gómez JB, Auqué LF, Gimeno MJ (2008) Sensitivity and uncertainty analysis of mixing and mass balance calculations with standard PCA-based geochemical codes. Appl Geochem 23: 1941—1956
- Jolliffe IT (1986) Principal Component Analysis. Springer, New York
- Krzanowski WJ (1988) Principles of multivariate analysis. Oxford Science Publ, Oxford
- Krzeszowski S (2005) Obliczanie składu i udziału nieznanego strumienia w mieszaninie o znanym składzie przy pomocy programu komputerowego KYBL-4 [Evaluation of the composition and proportion of an unknown source in the mixture by the computer program KYBL-4]. Zeszyty Naukowe Politechniki Śląskiej, Górnictwo z. 267: 137—146
- Krzeszowski S (2009) Badania nad określeniem składu i udziału nieznanego strumienia wody w układach wodnych na przykładzie wód kopalnianych [Research on the proportion and composition of unknown source in mine water mixture – case studies]. Disseration, Politechnika Śląska Wydz. Inżynierii Środowiska i Energetyki, Instytut Inżynierii Wody i Ścieków, Gliwice
- Krzeszowski S, Grmela A, Rapantová N, Labus K (2005) Preliminary comments on the method of estimating the composition, and portion of an unknown source in mine waters mixture. Proceedings XII. National hydrogeological congress, Ceske Budejovice, 81—86
- Laaksoharju M, Gascoyne M, Gurban I (2008) Understanding groundwater chemistry using mixing models. Appl Geochem 23:1921—1940.

- Laaksoharju M, Skårman Ch, Skårman E (1999) Multivariate mixing and mass balance (M3) calculations, a new tool for decoding hydrogeochemical information. Appl Geochem 14 (7): 861—872
- Manly BFJ (1994) Multivariate Statistical Methods A Primer. Chapman & Hall, London
- Parkhurst DL, Appelo CAJ (2013) Description of Input and Examples for PHREEQC Version 3 – A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. US Geological Survey Techniques and Methods 6(A43):1-497
- Plummer LN, Prestemon EC, Parkhurst DL (1994) An Interactive Code (NETPATH) for Modeling NET Geochemical Reactions along a Flow PATH Version 2.0.

US Geological Survey Water-Resources Investigations Report 94—4169:130.

- Rapantova N, Grmela A, Vojtek D, Halir J, Michalek B (2007): Groundwater flow modelling applications in mining hydrogeology. Mine Water Environ 26 (4): 264—271
- Rapantová N, Krzeszowski Ś, Grmela A, Wolkersdorfer C (2012): Quantitative Assessment of Mine Water Sources Based on the General Mixing Equation and Multivariate Statistics. Mine Water Environ 31 (4): 252–265.
- Wolkersdorfer Ch (2008) Water Management at Abandoned Flooded Underground Mines. Springer, Berlin

Grouting for ensuring coal mining safety above limestone aquifers with high water pressure

Wanghua SUI, Huanju CAO, Yue GAO, Gailing ZHANG

School of Resources and Geosciences, China University of Mining and Technology, Xuzhou 221008, China, suiwanghua@263.net

Abstract This paper presents a case study for ensuring coal mining safety under high confined water pressure using grouting. The Xinyi coal mine located in Henan Province, China, has been threatened by the Ordovician limestone aquifer with high confined water pressure beneath the coal seam. Based on geological investigation, characterization and evaluation of the Ordovician limestone aquifer, a grouting project was carried out. The geophysical transient electromagnetic technique was applied to inspect grouting quality. Coal seam No. 2–1 in panel 12011 was safely mined after grouting. Therefore, grouting was verified as a feasible method to ensure the coal mining safety under high confined water pressure.

Keywords water inrush, risk assessment, grouting, geophysical survey, limestone aquifers

Introduction

More than 150 mine inrush and inundation accidents occurred worldwide in coal mines during the last decade (Bringemeier 2012). China is the largest coal producing country with the production over 3,500 Mt in 2012. According to the incomplete official statistics, about 285 of 600 key coal mines in China are threatened by water inrushes during coal mining. Many coal mines in China encounter water inrush hazard from limestone aquifers which underlie coal seams with high confined water pressure (Peng 2007). Strata under coal seam would deform during mining, which increases hydraulic conductivity. Water with high confined pressure will be able to inrush from the fractures to coal mines, which always causes disastrous consequences (Sui 2011). Generally, drainage and grouting are two main methods to ensure mining safety above limestone aquifers. Drainage will decrease the water table by powerful pumping. However, this method not only increases the cost of production, but also results in environmental disasters such as shortage of water supply and subsidence of land surface (Wang 2003). Therefore, it is necessary to employ grouting project to ensure

the coal mining safety. Grouting will enforce the strength of bed rock that underlie the coal seam and seal the inherent geological structures such as faults and fractures. Moreover, grouting project is more economical and environmentally friendly than drainage.

Coal mine grouting principles

Grouting is defined as filling open voids existing in rock or soil with slurry (Bruce 2005). Coal mining resulted in situ stress releasing and induced discontinuity surfaces which are described as water-conducting failure zone as shown in Fig. 1. The formation of this zone mainly depends on length and width of mining area. Borehole and geophysical methods are often used to investigate this zone. While goaf in Fig. 1 is defined as that part of a mine from which the mineral has been partially or wholly removed. The objectives of coal mine grouting project are reducing the permeability and deformability of rocks between water-conducting failure zones and aquifer. It is also used for increasing rock strength against shearing forces.

Grouting projects have three important components including the design, implemen-





tation and quality testing of the placed grout. Grouting design requires a good knowledge of geological conditions and grout flow theory. Therefore, the investigation should be carried out to gain a good understanding of geology. In addition, choosing one appropriate grout material and applying relative grout flow theory are necessary. Based on the assumption of Laminar flow, some theories were proposed to describe a Newtonian fluid and a Bingham fluid flow in fractures (Warner 2004). The feasibility, durability, costs and time consumption are most important aspects in grouting design (Giovanni 2004). Moreover, drilling and grouting equipments are needed to implement grouting design. At final stage, grouting quality should be tested to verify the effect.

Case study

The Xinyi coal mine is located at Luoyang City, Henan Province, China, as shown in Fig. 2. The construction of this coal mine was finished on November 2005. The coal seam No. 2-1 is the main coal resource with a dip angle of 6° to 14°.

Panel 12011 was chosen as research area as shown in Fig. 3. Geology and hydrogeology of this panel are summarized in Table 1. The depth of this panel ranges from -213 m to -296 m below sea level, the length and width of this panel are, 800 m and 130 m, respectively. The coal reserves of this panel are around 800 kt.

A number of criteria have been proposed to evaluate the water inrush hazard. Water inrush index method was recommended by State Administration of Work Safety and State Administration of Coal Mine Safety of China (2009). This index is defined by water pressure bearing capacity per unit thickness of waterproof floor strata.

$$T = P/M \tag{1}$$



Fig. 2 Location of the Xinyi Coal mine

Wolkersdorfer, Brown & Figueroa (Editors)



Fig. 3 Location of Panel 12011 and ten boreholes

where T is water inrush index, MPa/m; P is water pressure, MPa; M is the thickness of waterproof strata in floor, m.

It is considered as high risk in regards to safety when the water inrush index *T* exceeds critical 0.1 MPa/m according to the statistics around Chinese coal mines.

Ten boreholes reached the Ordovician limestone in the whole coal mine as shown in Fig. 3. Water inrush indexes of these ten boreholes calculated from equation 1 are summarized in Table 2. No. 5 borehole is the only one in the research panel 12011 and its water inrush index is 0.092 close to critical 0.1. Therefore, a detailed geological investigation should be carried out in this panel to make the grouting design more effective.

A geophysical transient electromagnetic technique was used to investigate the strata below the coal seam. The principle of this method is that electric and magnetic fields are induced by transient pulses of electric current

Stratum	Thickness (m)	Distance (m)	Hydrogeology			
Coal Seam No.	0.5—12	Coal seam	Depth of coal seam: -213m to -296 masl			
2-1	Avg. 4.9	floor=0				
Sandy mudstone and mudstone	5.8—21	Avg. 10	Aquitard			
			Aquifer			
			Pressure head:+330.22 m — +336.13 masl			
I. limestone	6.3—19	6—21				
L7 IIIIestone		Avg. 12	Hydrochemistry type: HCO ₃ -Ca·Mg Specific			
		capacity: q=0.048 L/s·n	capacity: <i>q</i> =0.048 L/s⋅m Hydraulic			
			conductivity: <i>K</i> =0.1—0.551 m/d			
Bauxitic	6.5—26.12	Δυσ 13 39	Aquitard			
mudstone	Avg. 13.36	Avg. 4 5.57				
			Aquifer			
			Pressure head:+291.14 m — +375.75 masl			
The Ordovician	272	44.3—79.68				
limestone	213	Avg. 55	Hydrochemistry type: HCO ₃ -Ca·Mg			
			Specific capacity: $q=0.006-4.03$ L/s·m			
			Hydraulic conductivity: <i>K</i> =0.000451—9.2 m/d			

Table 1 Stratum and hydrogeology that underlie the coal seam No. 2-1

Borehole No.	1	2	3	4	5	6	7	8	9	10
P(MPa)	5.14	5.16	5.06	5.17	5.16	5.13	5.14	5.18	5.15	5.20
<i>M</i> (m)	56.64	56.39	46.19	47.53	56.39	53.26	53.85	57.61	54.99	59.65
T=P/M (MPa/m)	0.091	0.092	0.110	0.109	0.092	0.096	0.095	0.090	0.094	0.087

Table 2 Results of water inrush index from ten boreholes



Fig. 4 Location of two abnormal water areas and grouting boreholes



Fig. 5 Grouting borehole design. (a, left) plane view; (b, right) cross section view

and the subsequent signal attenuation response is measured. This method is suitable to detect water because of its low resistivity. Two abnormal water areas were detected as shown in Fig. 4. No.1 abnormal water area with 40 m length and 20 m width was located at railroad. No. 2 abnormal area with 130 m length and 80 m width was located near the vent tunnel.

Grouting project

Design

The grouting target is to prevent water inrush from two abnormal water areas, as well as reduce costs. Therefore, the grouting boreholes should be arranged at abnormal water areas with different depth so that the grouting slurry can form a thick barrier. Karstic rock shows the some features including large caverns extending up to several hundreds of meters and small caverns extending up to several meters. However, caverns are partly or completely filled with gravel, sand, clay or mud.

Cement was chosen as grout material because the abnormal water areas are full of Karstic fissures. Water pressure test was carried out to identify the degree of karsticity. According to hydraulic conductivity of the Ordovician limestone, the grouting radius of cement slurry in Karst stratum can be ranged from 20 to 40 m. In order to ensure safety, the grouting radius is assumed as 20 m for conservative design. Considering the effect of group boreholes grouting, three neighbor boreholes should be arranged at corner of triangle with distance no more than 35 m. Fig. 5 illustrates principle of boreholes arrangement.

Implementation

Drilling fields with the dimension of 4.5×3.5 ×3.5 m (length × width × height) were constructed to implement drilling. The borehole was drilled in three stages because the high confined water pressure. The first stage was drilled for borehole orifice-pipe with diameter of 133 mm. When the depth of this borehole exceed the coal seam floor 5 m, casing pipe with diameter of 127 mm was applied to prevent coal collapsing. The second stage was drilled for protecting pipe with diameter of 113 mm. This borehole penetrated L7 limestone with length no less than 35 m. Borehole wall in this stage was grouted to prevent water inrush from L7 Limestone. The third stage was drilled using the diamond bit with diameter of 73 mm. Borehole length in this stage was 20 m deep in the Ordovician limestone. The grouting was implemented at the pressure of 12 MPa with the volume ranges from 1 to 2 t.

Quality control

Quality control in this project includes grout material test and permeability test. Tests on grout material were conducted on water and suspension. Water's pH was 7.6 to 7.8, and hardness was 10.01 to 23.02. Suspension's Unit weight was 1.65 g/cm, viscosity was 19.6 s, setting time ranged from 16 to 35 min, compressive strength was 8 MPa.

Transient electromagnetic technique was employed to test permeability and verify the quality of this grouting project. Fig. 6 shows the resistivity of stratum after grouting. The contours of 0.2 or lower resistivity were deeper than before grouting, which means the abnormal water area was smaller than before.

Results

The water inflow rate was less than 5 m³/h during mining of this panel from December 2011 to June 2012 and around 800 kt of coals were safely excavated. This grouting project was considered as a successful case.

Conclusions

A successful grouting project was presented in this paper to illustrate the steps of grouting design, implementation and quality verification. An effective and economical grouting design should be based on comprehensive understanding of geological and hydrogeological conditions.

Drilling and Water inrush index method were employed to evaluate the risk of water in-



Fig. 6 Apparent resistivity of vertical detection of No. 1 abnormal water area

rush from the Ordovician limestone in the entire coal mine area. The geophysical transient electromagnetic technique was applied to detect the abnormal water area pre- and postgrouting in research panel. Grouting design was proposed based on the geological and hydrogeological analysis results. The quality was verified based on the reduction of the abnormal water area. Therefore, grouting can be considered as a feasible method to ensure the coal mining safety under high confined water pressure.

Acknowledgements

The authors want to acknowledge the financial support of the National Natural Science Foundation – Shenhua Group Jointly Funded Project under grant No. 51174286. This research was also supported by A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions and the Fundamental Research Funds for the Central Universities.

References

Bringemeier D (2012) Inrush and mine inundation- a real threat to Australian coal mines. International Mine Water Association Annual Conference, 25—29

- Bruce DA (2005) Glossary of Grouting Terminology. J. Geotech. Geoenviron. Eng., 131(12): 1534–1542
- Giovanni L (2004) Grouting of rock masses. ASCE Grouting and Ground Treatment: Proceedings of the Third International Conference
- Peng SP, Zhang JC (2007) Engineering geology for underground rocks. Springer Berlin Heidelberg Press, New York
- State Administration of Work Safety and State Administration of Coal Mine Safety of China (2009) Regulation of water prevention in coal mine. Beijing: Coal Industry Press.
- Sui WH, Liu JY, Yang SG, Chen ZS, Hu YS (2011) Hydrogeological analysis and salvage of a deep coal mine after a groundwater inrush. Environmental Earth Sciences, 62(4): 735—749
- Wang JA, Park HD (2003) Coal mining above a confined aquifer. International Journal of Rock Mechanics and Mining Sciences, 40(4), 537—551
- Warner J (2004) Practical handbook of grouting: soil, rock, and structures. John Wiley & Sons.

Packer Testing Program Design and Management

Eric E. Swanson¹, Brian C. Titone²

¹AquaLithos Consulting, Principal Consultant, 5360 Cole Circle, Arvada, CO 80002 Eric@Aqualithos.com ²Orogen HydroGeo, Principal Consultant, 6232 Kilmer Loop #203, Golden, CO 80403 Brian@Packertest.com

Abstract Hydraulic testing using wireline deployed water-inflated packers is becoming a common practice for groundwater characterization at mining sites. Packers, designed for diamond drilling, allow for faster, deeper, and more accurate types of testing conducted concurrently with existing coring programs. Designing and managing these testing programs requires planning, flexibility, and consideration of available methods and equipment options. This presentation explores and provides critical examination of advantages and disadvantages of the following options: 1) single or straddle packer testing, 2) injection, shut-in, withdrawal or falling head techniques, 3) discrete interval or cumulative testing, and discusses design consideration for planning a testing program.

Keywords IMWA 2013, packer testing, hydrogeology, Lugeon, wire-line packer system

Introduction

Characterizing groundwater flow systems in a modern hard rock mining environment is a complex and challenging task. The hydrogeology of many mineral deposits typically comprises complex lithology and alteration zones which can be dominated by multiple fracture sets acting as flow barriers or conduits. Many mining projects are located in complex geological environments and are pushing depth limits below the capabilities of traditional field methods. As the economic, engineering and environmental constraints of mine design become increasingly restrictive, the demand for advanced types of testing to supporting these designs increases. Increasingly, mine designs are now including pore water pressure decay determinations, advanced dewatering techniques, and modes of integrating sustainable environmental practices as required by regulatory agencies, lending entities, and as best management practices at the corporate level. The costs, time and resources budgeted to generate advanced mine design data sets are also limited. This current environment necessitates innovative tools and field techniques that "do more with less." Wireline hydraulic packer testing embodies this by facilitating discrete interval hydrogeological data acquisition as a programmatical addition to existing or planned core drilling programs.

Methods

Basic packer testing techniques are discussed in Nielsen (1991). Unlike traditional pumping tests, packer testing generates a series of discrete interval permeability values along the length of a borehole, which typically decrease with depth. Defining the relationship between permeability and depth in a statistically meaningful manner allows this relationship to be projected across the site to support mine dewatering and refilling, impacts assessment, and groundwater or geotechnical modeling efforts.

Core drilling programs are one of the principle means of collecting a variety of data types at deeper depths in a modern mining operation. Packer testing during core drilling operations can be performed with a variety of different equipment types. Optimized for core drilling, wireline hydraulic packers deploy through the drill rods without inflation lines or cables, are removed using the rig's wireline, and operate using the rigs water pump. Wireline hydraulic packers are also inflated with water, which greatly increases the depth capabilities over systems that require compressed gasses to inflate.

Single Element Testing Typical packer tests are conducted using a single packer element. The testing interval using a single packer system is bounded by the bottom of the borehole and the packer seated just below the drill bit above the bottom of the hole. To conduct the test the packer is lowered and inflated, water is either injected or withdrawn from the interval while flow rates and pressures are recorded, the packer deflated and removed, and then drilling of the next interval commences. This process is repeated until the entire borehole is tested in a series of discrete tests. Limitations to this method include the need to test immediately after the drilling a targeted test interval, which requires the packer testing team to standby while drilling takes place. This is also called "concurrent testing" as it is conducted during the drilling process.

Double Element Testing Wireline packer systems can also be deployed as a double or straddle packer system where two inflatable el-

ements are used and separated by a series of extension pipes that allow both packers to be inflated. Testing is performed on the interval between the two packer elements by injection or withdrawal (Fig. 1). Typically, straddle packer systems are used to characterize discrete intervals at the completion of a borehole by running a series of tests across selected zones of interest in the borehole, or across the entire borehole length in a series of sequential tests. One major risk is having unstable holes collapse on the lower packer causing equipment to be damaged or stuck.

Cumulative Testing Single packer tests performed at borehole completion are termed "cumulative tests", and are performed by placing the packer at various depths either starting at the top or bottom of the borehole. Cumulative tests always use the bottom of the borehole as the lower boundary of the test interval and the packer as the upper boundary. Since the test intervals are a series of overlapping zones, these tests are not considered discrete and resulting data must be mathematically processed to determine unique permeability values and remove the overlap effect. The major limitation to this approach is that zones of higher permeability at depth can mask the permeability determinations for the upper



Fig. 1. Example of testing types and data results

tests. Cumulative tests performed at hole completion and are sequential unlike concurrent tests which requires less standby time.

Types of Hydraulic Tests

The main types of hydraulic tests performed with the packer are: 1) injection or Lugeon, 2) withdrawal or airlift, 3) shut-in, and 4) falling head (Fig. 1). Each of these tests has the same net goal of determining permeability; however, the type of test to be performed is dependent on the estimated permeability, equipment availability and logistics, and data objectives. Each type of test has advantages and disadvantages, accuracy limitations, and time constraints. The decision on what type of test to perform can be made in the planning stages or as a situational decision by the field team. A conservative approach is to design a program that has the capabilities and flexibility to perform all types of tests; however, this can be logistically challenging and expensive. An expedient approach is to assume testing will be performed via a single method, although this may sacrifice data quality.

Injection Testing Injection tests are the most commonly conducted type of packer test. These tests are performed by injecting water at a constant pressure and recording the flow rate. If several pressure steps are used, the procedure is termed a Lugeon test (Lugeon 1933). Varying the pressure over several steps is relatively simple and adds a qualitative understanding of the downhole conditions, particularly in a fracture flow setting. The pressures used during an injection or Lugeon test must be high enough to induce flow, but low enough to ensure that hydraulic fracturing or dilation of existing fractures (hydro-jacking) does not occur, as this artificially increases the formation permeability. Typically, hydrofracturing or hydro-jacking does not occur in deeper tests, but may be a major limitation in shallow, fragile or soft formation conditions. Furthermore, if testing is performed in boreholes filled with cuttings or drill fluids such as polymer or bentonite drill muds, a rapid plugging response can occur which can lead to an underestimate of the permeability. Before starting injection testing, the borehole is usually flushed with clean water for a period of time to remove drill fluids from the testing interval. Both pressure and fluid flow rates are measured at the surface during the test on regular intervals; however, downhole pressure transducers can be used to accurately determine true interval pressures and increase accuracy. Advantages of injection testing are that the tests can be performed and analyzed relatively quickly, and require relatively basic packer testing equipment. These types of tests are limited in accuracy by the upper and lower values of the test interval transmissivity. In lower transmissivity intervals, accuracy is reduced due to potential system leakage and the inability to accurately measure very low flow rates. In higher transmissivity intervals, accuracy is constrained by frictional loss across the packer, and the inability to build sufficient testing pressures. In situations where high interval transmissivities limit injection testing accuracy, the test interval can be shortened or the type of testing can be changed to withdrawal tests

Withdrawal Tests Withdrawal tests with the packer system consist of rapidly removing and measuring water from the test interval for a period of time and then observing the resulting recovery of the interval water level to near static conditions. This type of test is performed in intervals that have transmissivities that are too high for injection testing, such as open fracture zones, or highly fractured zones in the shallow portions of a borehole. This method is also called an airlift test when the method of water removal is compressed air. This type of test is essentially a rising head test because the analysis involves observing head recovery data after fluid removal is completed. One advantage of withdrawal tests is that they can be completed in borehole fluids other than water, such as bentonitic mud, polymers and brine, as the method removes these fluids during the test. In situations where a heavy mud

has been used and significant borehole skin conditions occur, withdrawal tests may be the best method, even in moderate or low permeability intervals. However, airlift tests can cause borehole instability because of the removal of bentonite from the borehole walls. Since these tests require the analysis of a water level recovery curve, higher accuracy results are obtained when recovery is greater than 90 % of static conditions which can take significant time. Logistically, airlift withdrawal tests also require more resources such as a high capacity air compressor, airlift discharge heads, downhole air pipe, and transducers. However, since high permeability zone data is usually important project data, such measures are generally warranted.

Falling Head Tests Falling head tests are performed in a packer isolated interval by charging the rods with water and measuring the resulting water level decline until a nearstatic condition is observed. This test is typically done immediately after the injection test. These tests are the most simple of all types of packer tests in terms of equipment, as only a packer, pressure transducer or water level probe is required. However, in low transmissivity conditions, falling head tests can take a significant amount of time to complete, which requires drill rig standby expenses. Additionally, it may not be possible to run a falling head test in zones with a naturally high interval water level, as there may not be enough room in the rods to induce sufficient driving head for a good-quality falling head test. Finally, falling head tests through drill mud and cuttings may induce a plugging response that could result in an underestimate of the permeability of that zone. In high transmissivity conditions, a falling head test may not work efficiently due to the inability to rapidly vent air from the drill rods as water is initially placed. Falling head data can also be gathered after an injection test as a back-up or secondary means of analysis, as the drill rods are already charged with water and data acquisition is simple if a downhole transducer has been deployed.

Shut-in Tests In intervals with very low permeability or artesian conditions, shut-in type tests can be useful. A shut-in test is performed by pressurizing the testing zone, activating downhole or up-hole shut-in valve, and then monitoring the pressure decay using an uphole gauge or a downhole transducer. Since this test is essentially a zero flow test, it can remove accuracy error related to low flow measurements obtained in injection tests and from borehole storage effects. As with withdrawal tests, shut-in tests require more time to complete and are thus more expensive considering drill rig standby rates. Although these tests bypass flow measurement related error, they can also be affected by apparatus leakage error, particularly if an uphole shut in system is used. Typically, the range of permeabilities quantified by this method is below that of concern at most mining operations; however quantification of extremely low permeabilities may be required for some project objectives. New equipment has allowed Shut-in tests to be done easier and with more accuracy than ever before (Adams and Richards 2012).

Testing Program Design

Data Objectives Detailed planning for a packer testing program is probably the most important and cost-effective activity. Table 1 shows some guidelines for packer program design. The primary consideration in performing a packer testing program is having detailed data objectives and a clear end goal for the program, which surprisingly, is often overlooked. If the packer testing campaign is in support of a groundwater or geotechnical model for example, then a preliminary model using historically available data should be constructed in order to refine and optimize the overall program objectives. The data objectives should be defined by the modeling team and the end users of the data. Data objectives include items such as assessment of the data density needs, including both vertical and horizontal distributions of tests. In an ideal program, the data needs drive the location, depths, type and

		Advantages	Limitations					
_		Logistical and operational simplicity allows quicker testing Bottom of test interval constrained by borehole base						
Packer Configuration	Single Element	Longer testing intervals possible - not limited by spacer pipe	Requires less accurate cumulative methods if testing at borehole completion					
	Double	Allows discrete zone tests after borehole completion Can be done at any tme while rig is on the hole	Logistically and operationally complex, slower operation - requires addional crew training and experience					
-	Element	Control of bottom test interval placement	Testing interval limited by available spacer pipe segments					
duling	Concurent with Drilling	Most accurate and reliable method Requires least amount of delay of drilling operations Requires less crew expertise	Testing timing dictated by drilling progress Significant standby for crew between tests Slows down drilling operations					
t Sched	Completion of Borehole	No testing crew during drilling, mobilize to rig after borehole completion	Single element completion testing must be done cumulatively - lower accuracy					
Tes		Flexible scheduling and minimizes testing crew time on rig	Discrete testing requires use of double element packer equipment					
		Simplest type of test to perform	Plugging response if testing through drill mud/additives					
Injectio Lugeo	Injection or Lugeon	Supplies both quantitative and qualitative hydrogeological data Test is quickly performed and requires less equipment	Accuracy is limited for very high and very low transmissivity test intervals					
fTesting	Withdrawal	Higher accuracy in high transmissivty test intervals Can be performed through heavy drill mud	Requires more time to set-up and run Logistically complex - requires air compressor and other equipment					
Types of	Falling Head	Can be performed in conjunction with injection tests Requires the least amount of equipment Good back-up test if pump or flow manifold gear fails	May take a significant amount of time to complete Requires a use of a down hole pressure transducer Plugging response if performed through drill mud					
	Shut-in	Good for very low permeability material or artesian head conditions	Requires a down hole shut-in valve for best accuracy.					
		Yields more types of data, higher accuracy	Very low permeability quantification may be unnecessary					

Table 1. Program Design ConsiderationsControl

number of tests to be performed; an overabundance of data is an unnecessary expenditure. Similarly, a statistically inconclusive data set may require retesting – a major setback if drill rigs and key equipment and personnel are demobilized. Often the data objectives are set by a third party, such as a regulatory body, third party reviewer, or a stakeholder representative; in these cases it is recommended that all parties come to an agreement on data objective prior to the design of the program and initiation of field activities.

Design Considerations Once the data objectives for a packer testing program are defined, the packer testing program planning can begin. Elements to consider are: 1) the type, number and capabilities of the drilling equipment intended to be used; 2) the depth, location, inclination and diameter of each borehole to be drilled; 3) timing and scheduling of the packer testing; 4) staffing as well as training plans for the personnel performing the testing; 5) expectations regarding equipment, including procurement, logistics, and trans-

portation; 6) other hydrogeological activities, such as well installations, water level monitoring, transducer installations.

There are several different approaches to executing a packer testing campaign. Typically, packer testing is an activity that is added on to an existing exploration or geotechnical design program, thus certain portions of the campaign may already be fixed, such as the drilling locations and hole angles. Other times, constraints such as limited drill rig availability, key staff availability, weather or access issues may come into play. Based on these constraints, the packer testing program may be designed as a short but intensive campaign consisting of multiple drill rigs and a large testing crew, other times the program may be a long duration operation, where sporadic tests and a single drill rig are used.

Generally, the best results occur when packer testing is performed concurrently with drilling and when using a single packer configuration. Since this type of testing is relatively fast, a typical experienced packer testing crew can handle two to three drill rigs, moving gear between them, and testing as time allows. Occasional delays may occur but these are small in comparison to the advantages. Smaller capacity drill rigs in under-developed countries typically average 20 to 40 m of core drilling per day, when conditions such as mechanical breakdowns and logistical delays are factored in. A highly trained packer crew can typically perform two injection tests per shift, or one airlift test. In such a setting, with three operating drill rigs, it is reasonable to assume that testing could take place on 30 m intervals in each borehole. Since one drill rig is usually moving, installing casing, under maintenance, or drilling in rock that is outside the data objectives; it is reasonable to assume that a single packer kit plus a day and night testing crew could handle up to three drill rigs. If other activities are required of this crew, such as well installation, data analysis, access, equipment and supply sourcing; the maximum number of rigs drops considerably.

Staffing and Scheduling Staffing of packer testing programs is a key issue requiring careful planning. Packer testing can be performed by external consultants, specially trained drill crews, or by in-house staff after receiving training. Some packer testing crews consist of a single experienced individual, while others crews may have two or three inexperienced or junior people. Typical drilling operations and packer testing campaigns are a 24/7 continuous operations, so both a day and night crew is usually required. Crew duration is typically 3 to 5 weeks; even the most seasoned field crew member become ineffectual after this period of time. Generally, the most cost effective mix of personnel for a packer testing campaign is a blend of lower cost juniors, some locally sourced laborers, and at least one highly experienced individual that can troubleshoot and supervise staff. In many instances, when dealing with consultants, it is more efficient to have the project manager on-site so that planning and logistical difficulties are rapidly resolved. Packer testing, while simple in concept, can be exacting work that requires an experienced operator to supervise and troubleshoot issues that junior or inexperienced operators may have trouble managing. Underestimating this may result in poor data quality as well as potentially long rig standby times and associated costs.

Conclusions

Recent innovations in packer systems has reduced cost and increased accessibility for versatile, deep testing equipment. Incorporating a wireline hydraulic packer testing program into a core drilling program is advantageous in that it enables the acquisition of discrete interval hydraulic testing during exploration, geotechnical, infill or other core drilling operations. Although it does require some additional equipment and personnel, the cost advantages of including this type of testing into an existing core drilling campaign far outweigh those associated with a standalone, dedicated hydrogeological drilling and testing program.

The types of testing, packer configuration and test scheduling are flexible program design elements. In designing a packer testing program, these elements must be optimized to both meet the data objectives of the program and minimize overall budget. It is important to get the advice of a packer testing expert familiar with this type of testing to help design a successful program.

Acknowledgements

Thanks to Brent Johnson of Interralogic for manuscript review.

References

Adams J, Roberts R (2012). Advances in hydrogeologic testing of mineral exploration boreholes. – In: Mc-Cullough CD, Lund MA, Wyse L: IMWA Symposium. – p. 357–364; Bunbury, Australia.

Lugeon M (1933) Barrage et Géologie. Dunod. Paris Nielsen DM (1991). Practical Handbook of Ground

Water Monitoring, Second Edition. CRC Press 1991.

Stream-aquifer interaction in mining conditions using a groundwater flow model

Jacek Szczepinski

Poltegor-projekt Sp z o.o. Wyścigowa 56f, 53–012 Wrocław, Poland, j.szczepinski@poltegor.pl

Abstract In some areas, particularly those under mine dewatering, streams become dry due to lowering of the groundwater table. On the other hand, mine water pumped out from the mine dewatering system additionally discharges into rivers and streams, increasing their streamflow. This phenomenon can be represented in MODFLOW by the Stream Package, which simulates interaction between streams and aquifers. In this paper the Stream Package has been used in the modeling studies for future open pit dewatering. The numerical model has been developed for pre-mining conditions and for mining conditions.

Keywords Modflow, mine dewatering, mathematical model, surface water, groundwater

Introduction

In some areas, particularly those under mine dewatering, streams become dry due to lowering of the groundwater table. On the other hand, mine water pumped out from the mine additionally discharges into rivers or streams, increasing their streamflow. To simulate the stream-aquifer relation in a three-dimensional groundwater flow computer program MOD-FLOW (McDonald and Harbaugh 1988), the River Package (RIV) and the Drain Package (DRN) are most often used. The main drawback of the River Package is that it only accounts for leakage to or from the rivers. It does not permit rivers to go dry during a given period of simulation. On the other hand, the Drain Package simulates the effects of features such as small courses, which remove water from the aquifer so long as the head in the aquifer is above the streambed elevation. But it has no effect if the head falls below that level. Neither package tracks the amount of flow in the rivers, nor do they permit simulating mine water discharge into streams. This can be done by using the Stream Package (STR; Prudic 1989), that tracks the flow in one or more streams which interacts with groundwater. It represents the mixed boundary condition. The package can be particularly useful in areas

under the influence of mine drainage, where some parts of streams dry up but others increase their streamflow due to mine water discharge. The purpose of this paper is to present the ability of the Stream Package to simulate the impact of the proposed open pit dewatering on stream as well as the influence of mine water discharge on groundwater.

Site description

The proposed open pit mine is located in the north part of the Pleistocene upland area, which is a ground moraine of glacial sediments. Glaciofluvial and glacial till deposits range in thickness from 40 to 60 m. The underlying bedrock consists of fractured cretaceous marls, sometimes with mudstone. It is a predominantly flat area with the ground level between 85 to 100 m a.s.l., lowered to the north towards the River X flowing through the ice – marginal valley with a flow of about 60 m³/s and being on the level of 75–80 m a.s.l. The average annual precipitation amounts to 550 mm and the land evaporation is 471 mm. The baseflow for this area is $1.0 - 1.5 \text{ L/s/km}^2$.

Within the area of the deposit, the hydrological system is poorly developed and its principal elements are the left-bank tributaries filled with Holocene deposits about 5 m thick. The Streams A, B, C and D flow in a north direction towards the River X. The ephemeral course, namely Stream B, with flow up to $1 \text{ m}^3/\text{s}$, is regarded as a body of water where the discharge from the dewatering system will be released (Fig. 1).

There are three aquifers within the area: the unconfined quaternary water table aquifer, the neogen-paleogen aquifer and the Mesozoic aquifer – both confined. The water table aquifer consists of the quaternary sandy formations with an average thickness of 5 m and hydraulic conductivity from 3×10^{-5} to 1.2×10^{-5} m/s, the average being 7×10^{-5} m/s, while the specific yield is from 0.1 to 0.13. The groundwater flow direction is towards the north and is determined by the River X. The glacial till, clays, silts and argil under this aquifer have a thickness of about 20–40 m and act as a confining unit (Fig. 2).

Directly under the glacial aquitard neogen-paleogen, fine and medium-sized



Fig. 1 Hydroizohipses of the water table quaternary aquifer. Explanations: 1 – watershed, 2 – mine water discharge direction, 3 – hydroisohipses, 4 – open pit area, 5 – hydrogeological cross-section

sands occur lying on the silts and mudstones, or directly on the cretaceous formations. The sands are up to 20 m thick, the average being 12 m, while the hydraulic conductivity is on average 8×10^{-5} m/s. The storativity is from 4.91×10^{-4} to 2×10^{-3} , while the specific yield is 0.14. The lowest fractured cretaceous aquifer is represented by marls, sometimes with mudstone layers with a thickness of 80 m and the hvdraulic average conductivity of 4.4 \times 10⁻⁵ m/s, while the storativity is 3.68 \times 10⁻³. Slight isolation enables hydraulic contacts between the cretaceous and neogen-paleogen aquifer, which is provided by the similar water table level. The upper unconfined aquifer is recharged directly from precipitations and discharged by the river and streams. The lower aquifers are recharged by leakage of water from the upper aquifer or directly through the hydrogeological windows. The general groundwater flow direction is towards the north.

Methods

A 3-dimensional finite difference model has been used based on MODFLOW code (McDonald and Harbaugh 1988) in conjunction with the MODFLOW-Surfact (Version 3) code to allow for both saturated and unsaturated flow conditions. The modeling has been undertaken using the Groundwater Vistas (Version 5.36) software package (ESI 2006). The concep-



Fig. 2 The hydrogeological cross-section through the deposit area (S–N). Explanations: 1 – fine and medium sands, 2 – clays, 3 – silts, 4 – argils, 5 – marls, 6 – deposit, 7 – quaternary water table in natural conditions, Q – Quaternary; Ng – Neogene; Cr – Cretaceous

tual model for the area is based on investigations undertaken by the Geological Institute and mining company. A three-dimensional five-lavered numerical model has been developed, which covers an area of 660 km². The model is discretized with a uniform 100 m by 100 m grid, which gives a grid mesh of 255 rows and 300 columns. It is divided into five vertical layers - three aquifers and two aquitards. The aquifers represent: 1. the water table quaternary aquifer, 2. the neogen-paleogen over-deposit porous aguifer and 3. the porous – interstice aguifer which includes the cretaceous marls and mudstones. Between the aquifers, there are two layers represented by aquitards comprised of clays and silts. The effective infiltration Q = const. varies over the area from 4.6 to 15.3 % of average annual precipitation. Head dependent flow boundaries (MODFLOW GHB cells) have been used in all layers to represent external regional flows into and out of the model domain. The River X on the north has been represented using Modflow's River cells. The water level in the River X has been set from the topographic map 1: 25 000.

All streams in the study area including the Stream B flowing through the deposit area, were simulated only in the layer I by mixed boundary condition represented by the Stream Package. This package enables computing the flow between the stream and aquifer using Darcy's law as presented by McDonald and Harbaugh (1988; 1). The value of leakage between the aquifer and the stream is added to or subtracted from the flow of the stream, which allows calculating the water level in each cell representing the stream, using the Manning formula as described by Ozbilgin and Dickerman (1984; 2, 3). All parameters for using the Stream Package - stage of stream, width of stream, streambed elevation, slope of stream channel and streambed conductance - have been collected during the field investigation. Roughness coefficient was estimated from the tables (White 1979).

$$Q = \text{CSTR}(H_s - H_a)$$

where:

Q – leakage to or from the aquifer through the streambed, (L³/T),

 $H_{\rm S}$ – head in the stream, (L),

H_a – head in aquifer side of streambed, (L),

 $CSTR-conductance \ of \ the \ streambed, \ (L^2/T).$

$$Q = \frac{C}{n} \left(A R^{\frac{2}{3}} S^{\frac{1}{2}} \right)$$
 (2)

where:

Q – stream discharge, (L³/T),

n – Manning's roughness coefficient, dimensionless,

A – cross-sectional area of the stream, (L²), R – hydraulic radius, (L),

S – slope of the stream channel, (L/L),

C – a constant, (L^{1/3}/T), which is 1.486 for units of cubic feet per second or 1.0 for cubic meters per second.

$$d = \left[\frac{Qn}{\sqrt{Cws}}\right]^{\frac{3}{5}}$$
(3)

where:

d – depth of the water in the stream, (L),

w – width of the channel, (L).

The groundwater model was developed in steady state mode. Steady state calibration has been based on the available water level data recorded during field investigations in 450 dug wells located in the water table aquifer. The water level data from deeper aquifers represents long term average aquifer conditions. The steady state conditions were achieved with sequential model runs by manually adjusting the horizontal and vertical conductivity and recharge values until the best fit between the simulated and measured water levels was attained. Transient model calibration was not run but the heads from steady-state runs calculated for pre-mining conditions were used as initial conditions for the transient simulation. The predictive simulation has been carried out in transient conditions for the 8-year period of the open pit dewatering, by lowering the groundwater level within the deposit area of 30 - 45 m. The dewatering operation was

(1)

modeled by progressive assignment of Modflow the Time-Variant Specified Head cells H =f (*t*) to active mining areas in accordance with the respective project mine plans. It was assumed that the mine water from the pit dewatering will be discharged into the Stream B.

Results and Discussion

For the average Stream B parameters obtained during field investigations – channel width of 4 m, riverbed conductance of 1.2×10^{-6} m/s, hydraulic gradient of 1.6×10^{-3} and roughness coefficient of 0.01 as well as taking into account measurements of the stream stage and groundwater level in 450 wells – the Stream Package enables simulating its total streamflow (0.07 m³/s) in the steady state conditions. Moreover it evaluated the interaction between the stream and the aquifer in each cell (Fig. 3). The results of the modeling study reveal that the streamflow occurs 3000 m downstream from the beginning of the streambed, which confirms the field investigation (Fig. 4). In the next step, the streamflow and flow between the stream and the aquifer has been simulated in mining conditions under transient conditions. In this case the Stream B, regarded as a body of water where the discharge from the dewatering system will be released, has been divided into two segments. The first segment covered a section of the Stream B located upstream of the proposed pit. The second segment involved a part of the Stream B situated downstream.

Two variants have been analyzed. The first one assumed that the mine water will not be discharged into the Stream B. In this case the streambed will be out of water at a range of 4500 m from the pit. When the groundwater level is above the bottom of the streambed, the process of groundwater drainage by the Stream B will begin and the streamflow will start (Fig. 5).

In the second scenario mine water will be discharged into the Stream B downstream of the pit at the rate of 0.5 m^3 /s. In this case stream-







Fig. 4 The Stream B – streambed (left) and streamflow (right)

flow was accounted for by specifying flow for the first cell in the segment located downstream from the dewatering system (north boundary of the pit), and then computing the streamflow to adjacent downstream cells as equal to the inflow in the upstream cell plus or minus leakage from or to the aquifer in the upstream cell (Prudic 1988). In this case the highest streamflow will take place right in the first cell downstream the north boundary of the pit. In the cells located downstream, the flow will decrease because of the aquifer recharge with surface water (Fig. 6). Groundwater recharge from the surface water reduced the range of the cone of depression of 1000 m. The simulation revealed that due to mine water discharge the water stage in the Stream B will increase by 0.1 m, compared to natural conditions.

In both of simulated variants, south from the open pit boundary *i.e.* in a segment of the

Stream B located upstream of the proposed pit, the Stream B changes from a gaining into a losing stream. At a distance of 4000 m from the south edge of the pit the streamflow in the Stream B will stop due to mine dewatering impact (Fig. 7).

Conclusions

The impact of mine drainage on the surface water results in streamflow reduction, and even drying up. On the other hand, discharge of mine water to streams increases the streamflow, stream stage and can reduce the cone depression by interaction with the aquifer. In order to assess stream-aquifer interaction the Stream Package can be used. It is a lot more powerful than the commonly used River Package and Drain Package, allowing calculation of the streamflow and water stage change as well allowing estimating the lengths of the



Fig. 5 Streamflow (left) and leakage between the Stream B and the aquifer (right) in dewatering conditions, downstream of the open pit without mine water discharge



Fig. 6 Streamflow (left) and leakage between the Stream B and the aquifer (right) in dewatering conditions, downstream of the open pit with mine water discharge 0.5 m³/s



Fig. 7 Streamflow (left) and leakage between the Stream B and the aquifer (right) in dewatering conditions, upstream of the open pit

streambed subject to a total loss of water. However, to get a feasible solution it is necessary to acquire additional data: stream parameters (width of stream, roughness coefficient, slope of stream channel), stream stage and the groundwater level in the upper aquifer, essential for the stream-aquifer relations. The results of the modeling study reveal that the Stream Package is particularly useful in areas under the influence of mine drainage and mine water discharge. In addition to calculating the streamflow, flow between stream and aquifer and the stream stage, it permits streams to go dry during a given period of simulation as well as to simulate subtraction or additional inflow to surface water, which is not included in the River Package. The Stream Package has some limitations that may affect the solution (Prudic 1989). It does not include a time function for routing flows specified for the first cell; it calculates the water level in the stream assuming a rectangular channel and constant streambed conductance and makes the assumption of the instantaneous leakage from the stream to the aquifer. Some of these restrictions have been removed in newer versions of the Stream Package. The possibility of varying the geometry of the streambed in its cross section has been included in the Streamflow-Routing Package (SFR1) Package (Prudic et al. 2004), and the presence of the unsaturated zone beneath the streambed, in a subsequent modification - in the Streamflow-Routing Package (SRF2) Package (Niswonger and Prudic 2006).

References

- ESI (2000–2007) Groundwater Vistas. Version 5. User's manual.
- Hydrogeologic, Inc. (1998) MODFLOW-SURFACT v. 3.0, A Comprehensive MODFLOW-Based Flow and Transport Simulator. Code Documentation Report. HydroGeoLogic, Reston VA.
- McDonald MG, Harbaugh AW (1988) A modular threedimensional finite difference ground-water flow model, USGS Techniques of Water-Resources Investigations Book 6, Chapter A1.
- Ozbilgin MM, Dickerman DC (1984) A modification of the finite difference model for simulation of two dimensional ground-water flow to include surfaceground water relationships, USGS Water-Resources Investigations Report 83–4251.
- Niswonger RG, Prudic DE (2006) Documentation of the Streamflow-Routing (SFR2) Package to Include Unsaturated Flow Beneath Streams – A modification to SRF1. US Geological Survey, Techniques and Methods 6-A13, Nevada.
- Prudic DE (1989) Documentation of a computer program to simulate stream-aquifer relations using a modular, finite-difference, ground-water flow model. US Geological Survey, Open-File Report 88– 729, Nevada.
- Prudic DE, Konikow LF, Banta ER (2004) A new Streamflow-Routing (SFR1) Package to Simulate Stream-Aquifer Interaction with Modflow 2000. US Geological Survey, Open-File Report 2004–1042, Nevada.
- White FM, ed. (1979) Fluid mechanics, New York, Mc-Graw-Hill.

Integrating Less-Common Data Sources to Improve Groundwater Model Calibration

Keith Thompson¹, Sonya Cadle²

¹Tetra Tech, Inc., 3801 Automation Way, Fort Collins, Colorado, USA, keith.thompson@tetratech.com ²Tetra Tech, Inc., 363 Centennial Parkway, Suite 210, Louisville, Colorado, USA, sonya.cadle@tetratech.com

Abstract MODFLOW-SURFACT was used to create and calibrate a three-dimensional groundwater flow model to simulate the effects of Nevada Copper Corp.'s proposed Pumpkin Hollow mining project on the local and regional hydrogeologic system. This model illustrates the value of (1) incorporating existing accepted models, where possible, (2) using anecdotal evidence in conjunction with hydrogeological data to guide model construction, and (3) using GIS, database and automated calibration tools to streamline the process of incorporating both public and sitespecific data.

Keywords groundwater, modeling, calibration, dewatering

Introduction

When beginning a regional-scale groundwater modeling project, little data may be available from the client regarding regional hydrogeologic conditions. However, public data sources often can provide information for model construction and calibration. These data sources may not be utilized because of the time and cost to confirm and organize the data. For example, separate governmental agencies may have different data records for the same well, but under different names and with different estimated coordinates. Collating and correlating these data sources can be a daunting task. However, with the aid of databases, spreadsheet tools, and GIS, the data manipulation can ultimately reduce the time and cost of model construction and calibration while improving the model's accuracy and lending additional credence and defensibility to the model.

Nevada Copper Corp.'s proposed Pumpkin Hollow mining project in west-central Nevada, USA provides a case study in which numerous public data sources were combined with sitespecific data to create a well-calibrated regional groundwater flow model (NCC model). Fig. 1 provides a site location map for the modeled area. One of the concerns with the proposed mining project was the potential to impact water supplies in the nearby Mason Valley, an intensively developed agricultural area that relies on irrigation from groundwater and surface water sources. An additional concern was the project's location within the Walker River Basin. Walker Lake, the terminus of the Walker River, is a closed-basin lake that has experi-



Fig. 1 Model Location Map.

enced more than 45 m of water level decline since 1882 as a result of agricultural diversions. Consequently, prediction of potential impacts from the project was critical, and the goal during model development was to create a wellcalibrated model based to the extent possible on publicly available data that had undergone thorough quality assurance review.

Methods

At the start of the project, in conjunction with review of data provided by the client, a detailed literature review and data search was conducted to identify publicly available data sources. Public data sources included:

- An integrated surface water and groundwater model of Mason Valley, constructed and calibrated by the Desert Research Institute [DRI](Carroll *et al.* 2010, Collopy and Thomas 2010)
- United States Geological Survey (USGS) Digital Elevation Model (DEM),
- Geologic maps (Bingler 1978, Proffett and Dilles 1984),
- Geologic data sets in GIS format from Nevada Bureau of Mines and Geology (NBMG),
- Hydrogeologic data sets in GIS format from the USGS (Maurer *et al.* 2004),
- USGS and DRI studies compiling well pumping records (Huxel and Harris 1969, Schaefer 1980, Lopes and Allander 2009a and 2009b, Carroll *et al.* 2010, Collopy and Thomas 2010),
- Nevada Division of Water Resources (NDWR) well permits and point-of-diversion (POD) information, and
- Groundwater elevation and stream flow data from the USGS.

Many of the data sets necessary for model construction were accumulated by downloading from the internet. Some well and geologic data were hand-entered or digitized from the associated studies and maps. The majority of the DRI model electronic files were obtained by requesting them from DRI directly, but for confidentiality reasons not all files could be provided. Those that could not be directly provided were summarized numerically by DRI in such a manner that confidentiality was preserved.

After all data sets were obtained, significant formatting, generalization and correlation had to be performed to create a unified MODFLOW-SURFACT model. The DRI model of the Mason Valley formed the western half of the NCC model. The DRI model discretization was generalized laterally to fit the scale of the NCC model, but the estimates and distributions of all of the water balance components were retained from the DRI model. The NCC model grid was selected to be more refined in the proposed mine area (100 × 100 m) and telescope out to 500 m elsewhere. GIS was used to generalize the DRI grid from its original uniform 100×100 m to the new, variable grid. GIS was also used to generalize or aggregate (if applicable) all the other DRI model inputs including stream flow routing, ditch flows and PODs, evapotranspiration, irrigation-related recharge, hydraulic conductivity, and mountain block recharge to match the new grid. The seasonal component of DRI's model was averaged to represent steady-state conditions, since the NCC model covered a multi-decade time frame.

Next, the steady-state observation data set to be used for model calibration was constructed. This represented a significant challenge, because many of the observation wells were the same wells used for irrigation and were represented in several different databases that sometimes used different coordinate systems as well as different estimated coordinates. All the observation and irrigation well data for the region were imported into a single database. Wells represented using the Public Land Survey System (PLSS) were assigned coordinates using GIS based on the centroid of the PLSS polygon. The database was used to match up wells based on application number and permit number. After as many matches as possible were made and the matched wells combined, all well data were imported into GIS for spatial evaluation. Additional wells were then matched based on spatial proximity combined with depth, installation date, or other criteria. Depth information was necessary for target layer assignment and pumping layer assignment for irrigation wells. If no depth information was available from any database for a particular well, average depths and screened intervals were assigned based on other wells spatially nearby that well. Then, a weighting scheme was employed for the observation data set which incorporated the uncertainties due to missing information.

The vertical discretization was designed to accommodate the proposed mining plan. The NCC model has 22 layers, which are for the most part flat and extend far below DRI's original two layers. This construction greatly simplified the incorporation of both regional and local geologic information but resulted in a cube with inactive (no-flow) cells representing the elevations above ground surface. This complicated the incorporation of DRI's top model layer, which had variable elevation. Irrigation wells, streams, ditches, and evapotranspiration had to be assigned to the correct layaccomplished ers. This was using combination of GIS and database processing to match the elevations of the features to the correct model layer. The results of the irrigation well evaluation performed as part of the target data set construction were used to guide the layer placements of irrigation well screened intervals.

The hydraulic property distribution was assigned based on regional and local geology and USGS divisions of hydrogeologic units in Nevada, for which a GIS dataset was available (Maurer *et al.* 2004). Geologic cross-sections were used to generalize the regional lithologic units into Quaternary alluvium, Tertiary volcanics and sediments, Mesozoic intrusives, and Mesozoic volcanics and sediments. A three-dimensional geologic model was created from the cross-sections and other available geologic information, such as well logs and surface geologic maps. The model was created in Mining Visualization System (MVS) with cooperation from Tetra Tech and Nevada Copper geologists with experience in the local geology. The geologists felt that the boundary zone between the Tertiary and Mesozoic units (likely erosional or faulted) should be called out as a separate unit, due to anecdotal evidence from resource drilling that it was more highly fractured, potentially leading to a more transmissive unit. The regional lithologic units were used where the DRI model was not present, but DRI model lithologic units were used wherever they were present. Limited aquifer testing data were available, particularly as related to the large fault structures that cross the model domain. Anecdotal evidence and numerous cross-sections provided by mine site geologists were crucial in incorporating both the faults and the extensive geologic information near the proposed mine site. As a result, in the immediate vicinity of the mine, a number of previously unmapped faults and additional lithologic units such as hornfels and endoskarn were included.

Two methods were used to estimate precipitation-related recharge from the mountains in the model. For the portions of the model that corresponded to DRI's model, the DRI mountain block recharge values were represented as below-ground injection wells, mimicking the DRI method. For the area where the DRI model connected to the Wassuk Range and adjoined the proposed mine site, recharge was represented differently. The Precipitation Zone Method (PZM) of the USGS (Lopes and Medina 2007) was used to estimate average annual precipitation on the Wassuk Range. The elevation-based precipitation zones were calculated from the USGS DEM. Then, the calculated precipitation was converted to estimated recharge using the Maxey-Eakin recharge categories (Maxey and Eakin 1949). The portion of recharge that would flow out of the Wassuk Range and into the Mason Valley was compared to the DRI estimate for recharge in that

same area, and the calculated recharge was adjusted using a multiplier to match the calibrated DRI mountain block recharge. That multiplier was applied to the calculated recharge for the portion of the Wassuk Range that fell within the model boundaries. DRI's values for irrigation-related recharge in Mason Valley were incorporated directly into the NCC model.

In addition to the steady-state hydraulic head observation targets, the model was calibrated to steady-state stream flow and transient drawdown data. Stream flow targets were obtained by downloading the data for USGS stream gages within the model domain from the USGS website. An average stream flow was calculated for each gage to use as a steady state stream flow target. Transient drawdown targets were created by calculating the drawdown over time from two long-term pumping tests conducted at the proposed mine site. The steady state model and transient model were calibrated in tandem using PEST (Doherty 2010) as an automated calibration tool to improve the efficiency and accuracy of the calibration process.

Results

The incorporation of DRI's model materially improved the NCC model's representation of Mason Valley. Initial model simulations indicated that the DRI portion of the model was already well calibrated due to scrupulously maintaining DRI's calibrated input parameters to the maximum extent possible. Hence, the DRI parameter zones were excluded from any adjustments, greatly simplifying the remaining calibration effort. The use of PEST in the NCC model calibration significantly reduced the time necessary to complete calibration. PEST was first used to identify the parameters to which the calibration was sensitive. Then, PEST was used to optimize those parameter values, and the results were assessed for reasonableness and consistency with available data. Insensitive parameters were not subjected to optimization but were fixed at reasonable values based on available data.

The final calibration statistics for the steady-state hydraulic heads, transient drawdowns, and steady-state stream flow data sets are shown in Table 1. The steady state model was calibrated to within about 5 % and the transient model to within about 9 %. The steady state stream flow targets were primarily used qualitatively, since the actual magnitude and location of diversions inside Mason Valley was confidential and very little information was available regarding diversions downstream in the Walker Valley. Also, DRI used a complex Fortran code to determine return flows back into the Walker River; the NCC model simply simulates the return-flow ditches as streams draining excess water. The NCC model was expected to over-predict streamflow as a result, particularly outside the Mason Valley where diversions were not well-characterized. However, despite the uncertainties regarding stream flow, the numerical match was within 4 % in the Mason Valley and within 18 % overall. Fig. 2 is a plot of the measured versus simulated steadystate hydraulic head targets, and Fig. 3 illustrates the measured versus simulated drawdown in one of the two pumping tests.

Residual Statistics by Data	Hydraulic	Drawdown	Stream Flow	-
Set	Head (meters)	(meters)	(cubic meters per	
			day)	-
Mean	3.62	-0.061	-96654	
Absolute Mean	7.43	0.61	98359	
Standard Deviation	24.78	0.91	105636	
Number of Data Points	357	6371	11	
Standard Deviation/Range	0.054	0.087	0.18	
Absolute Mean/Range	0.016	0.059	0.17	Table 1 Final calibration sta-
Range of Calibration Data	461.47	10.42	584737	tistics for NCC model, 2013

On Fig. 2, the close fit to the 1:1 line and lack of excessive scatter indicate that the model is well-calibrated. Layers 3 and 4 have the most deviation from the 1:1 line, possibly because the targets had only one data point apiece, the most recent of which was from 1965. It is probable that conditions have changed since that date. Also, those were the uppermost points in the model and were near the top of the Wassuk Range. Because of the high gradients between the summit and foot of the mountains, such data points are hard to match.

On Fig. 3, the first pumping test calibration is visually good for NC07-19, NC10-GT02, and NC07-26. However, NC08-MW03 showed an unusual lack of recovery in the observed data, while the modeled drawdown data show typical drawdown and recovery behavior. There appears to have been a localized factor influencing drawdown at the well, since it would ordinarily be expected to recover after cessation of pumping. Without further information, the model could not include this local influence and would not be expected to reproduce the unusual recovery pattern observed in that well.

The calibration results for the second pumping test (not shown in Fig. 3) were similar, in that overall the matches were quite good, but an unusual fracture-related effect was observed in a set of three wells. Those wells had similar drawdowns even though they varied in distance between 28 and 203 meters from the pumped well. An equivalent porous medium model such as this regionalscale finite-difference model cannot reasonably incorporate these small-scale fracture-related effects.

Conclusions

The NCC model incorporated a number of data sets not commonly used in other modeling efforts. These included publicly available irrigation well and water level data sets that often are not used due to the time and expense necessary to reconcile inconsistencies between data sets. In addition, the existing DRI model was a rarely-available and highly useful data source. Finally, the extensive field investigation conducted at the site and close communication with the client's geological and other staff provided valuable anecdotal evidence regarding the local geology and faulting, which informed and greatly improved the geological representation in the NCC model. The use of the DRI model, the estimates of fault and aquifer properties based on anecdotal information, and the use of GIS, database tools and PEST resulted in a well-calibrated and defensi-



Fig. 2 Observed versus model-simulated steadystate hydraulic heads.



Fig. 3 NCC model observed versus simulated drawdown for first pumping test data set.

ble MODFLOW-SURFACT model that can be used to support engineering and permitting activities for the project, such as mine dewatering design and geochemical assessment of post-mining pit lake formation. Incorporating such less-commonly-used data sources can ultimately reduce the costs and improve the quality of a groundwater flow model.

Acknowledgements

Both the model and the extensive field work that went into gathering the data to create and calibrate the model were supported financially by Nevada Copper Corp. The authors wish to thank Nevada Copper Corp., and in particular Greg French and Tim Dyhr, for significant and insightful review, comments and discussion provided during model development, calibration and revision.

References

- Bingler EC (1978) Geologic Map of the Schurz Quadrangle. Nevada Bureau of Mines and Geology Map 60. Scale 1:48,000
- Carroll RWH, Pohll G, McGraw D, Garner C, Knust A, Boyle D, Minor T, Bassett S, Pohlmann K (2010) Mason Valley Groundwater Model: Linking Surface Water and Groundwater in the Walker River Basin, Nevada. Journal of the American Water Resources Association (JAWRA) Paper No. JAWRA-09-0081-P. 20 pp
- Collopy MW, Thomas JM (2010) Restoration of a Desert Lake in an Agriculturally Dominated Watershed: The Walker Lake Basin. Prepared by Desert Research Institute and University of Nevada, Reno. April 2010. 1,273 pp
- Doherty J (2010) PEST Model-Independent Parameter Estimation User Manual: 5th Edition. 336 pp

Huxel CJ, Harris EE (1969) Water Resources Develop-

ment in Mason Valley, Lyon and Mineral Counties 1948–65. Nevada Department of Conservation and Natural Resources, Division of Water Resources Water Resources Bulletin 38

- Hydrogeologic Inc., (2010) MODFLOW-SURFACT Software (Version 3.0) Overview: Installation, Registration, and Running Procedures. Herndon, Virginia, 548 pp
- Lopes TJ, Allander KK (2009a) Hydrologic Setting and Conceptual Hydrologic Model of the Walker River Basin, West-Central Nevada. U.S. Geological Survey Scientific Investigations Report 2009–5155, 84 pp
- Lopes TJ, Allander KK (2009b) Water Budgets of the Walker River Basin and Walker Lake, California and Nevada. U.S. Geological Survey Scientific Investigations Report 2009–5157, 44 pp
- Lopes TJ, Medina RL (2007) Precipitation Zones of West-Central Nevada. Journal of the Nevada Water Resources Association 4(2), 1–19
- Maurer DK, Lopes TL, Medina RL, Smith JL (2004) Hydrogeology and Hydrologic Landscape Regions of Nevada. U. S. Geological Survey Scnientific Investigations Report 2004–5131, 35 pp
- Maxey GB, Eakin TE (1949) Groundwater in White River Valley, White Pine, Nye and Lincoln Counties, Nevada. Nevada State Engineer, Water Resources Bulletin 8, 53 pp
- Proffett JM, Dilles JH (1984) Geologic Map of the Yerington District, Nevada. Nevada Bureau of Mines and Geology Map 77
- Schaefer DH (1980) An Appraisal of the Water Resources of the Walker River Indian Reservation, Nevada. U. S. Geological Survey Open-File Report 80– 427, 65 pp

Groundwater Modelling and Site Investigations to Evaluate Groundwater Supply Availability and Withdrawal Impacts for a Proposed Gold Mine in Yukon, Canada

Randi THOMPSON¹, Katherine JOHNSTON¹, Trevor CROZIER¹, Stephen WILBUR²

¹BGC Engineering Inc., Suite 800 – 1045 Howe Street, Vancouver B.C. V6Z 2A9, Canada, rthompson@bgcengineering.ca, kjohnston@bgcengineering.ca, tcrozier@bgcengineering.ca ²Victoria Gold Corp., Suite 584 – Bentall Four, 1055 Dunsmuir, Vancouver B.C. V7X 1KB, Canada, swilbur@vitgoldcorp.com

Abstract The Eagle Gold Project located in central Yukon, Canada is in the process of development. Bedrock groundwater supply wells will be required to meet water supply demands throughout mine construction and operations. A groundwater flow model was developed to evaluate aquifer yield, groundwater supply sustainability, and potential hydrogeologic impacts of groundwater extraction and mining on surface water flows. A bedrock groundwater supply well was later installed and a 10-day pumping test was carried out. The groundwater model was subsequently bench marked against the results of the pumping test showing reasonable agreement with the independent data set.

Keywords groundwater supply, numerical model, pumping test

Introduction

Victoria Gold Corporation is in the process of developing the Eagle Gold Project (the "Project") at their Dublin Gulch Property located in the center of the Yukon, Canada (Fig. 1). The Project focuses on the Eagle Gold Zone, which contains vein-hosted gold mineralization (Wardrop 2012). The Project will occur over a



Fig. 1 Project location and proposed mine layout.

27-year period in four phases: a 25 month preproduction (construction) phase, a 10 year operations mining phase, and a 10 year closure and reclamation phase, followed by a post-closure and monitoring phase. Mine infrastructure includes an open pit, a lined heap leach facility (HLF), two Waste Rock Storage Areas (WRSAs), a mine water treatment plant (MWTP), and the Dublin Gulch diversion channel (DGDC), which will be constructed to route non-contact water from upstream of the Project area within the Dublin Gulch watershed to Haggart Creek (Fig. 1). Bedrock groundwater supply wells located adjacent to Haggart Creek in the lower Dublin Gulch valley will be required to supplement the makeup water supply demands throughout mine construction and operations.

A three dimensional (3-D) MODFLOW-SURFACT numerical groundwater flow model was developed for the Project area at the Dublin Gulch watershed-scale (*i.e.* a roughly 10 km² watershed within a 65 km² model domain) to meet the current industry standards and regulatory requirements. This paper describes the development and use of the groundwater model to evaluate the aquifer yield, to assess the ability for groundwater to sustainably meet the Project water supply demands, and to predict the potential hydrogeologic impact of mining and groundwater extraction on surface water flows. In addition, subsequent field investigations and model bench marking are presented.

Conceptual Hydrogeologic Model

The Project lies within the upper regions of the Haggart Creek drainage basin, within the Dublin Gulch and Eagle Creek sub-basins (Fig. 2). Haggart Creek flows to the south, ultimately flowing into the South McQuesten River. The average annual precipitation for the Project is estimated to be 557 mm, with approximately 50 % of the annual precipitation falling as snow. The hydrology of the region is generally characterized by large snowmelt runoffs during the freshet, which quickly taper off to low summer stream flows interspersed with periodic increases in flow associated with intense rainfall events.

Placer mining has been conducted in both Haggart Creek and the Dublin Gulch basins



Fig. 2 Groundwater flow model domain.

Wolkersdorfer, Brown & Figueroa (Editors)

over the past century. Surficial materials are generally composed of a veneer of colluvium in the uplands; while alluvium and reworked placer tailings dominate in the valley bottoms and generally vary from 10 to 30 m thick between Eagle Pup and Haggart Creek. The Project area is underlain by Upper Proterozoic to Mississippian sedimentary rocks of the Selwyn Basin (Smit et al. 1995). The bedrock of the Project area can be broadly divided into the Hyland Group metasediments and intrusive rocks of the Dublin Gulch Stock. Results from hydrogeologic tests (i.e. over 80 slug tests and packer tests in over 50 boreholes and four pumping tests) conducted in the bedrock suggest that the hydraulic conductivity of the intrusive and metasediment units is generally similar, and a general trend of decreasing permeability with depth is discernible from the data.

The observed water table is a subdued replica of topography, with depths to groundwater typically being greater in the uplands relative to the valley bottom. Groundwater enters the flow system from infiltration of precipitation and snowmelt, as well as by surface water infiltration in creeks and gullies. Groundwater discharge occurs to creeks, gullies, and at breaks in slope. Groundwater elevations are observed to decline through the winter and spring, and are highest during the summer and fall quarter. The seasonal variation in groundwater levels is consistent with the seasonal precipitation and temperature trends.

Groundwater extraction wells will be required within the lower Dublin Gulch valley to supplement the Project makeup water supply demands. Under average conditions, groundwater supply requirements will be approximately 200 m³/d during construction and operations, but will peak annually during late spring (typically April, when observed stream flows are low) at rates from 1,600 m³/d to 2,500 m³/d. Also, the hydrogeologic regime of the mine site will change during construction and operations due to the open pit advance and mine dewatering, overburden dewatering and removal, surface water diversions, and changes in land use (*e.g.* placement of a lined HLF and underdrains beneath the WRSAs which may reduce groundwater recharge).

Numerical Groundwater Model Development and Results

The domain of the 3D groundwater flow model developed for the Project encompasses the area shown in Fig. 2. The model domain is bounded by a combination of Haggart Creek and a topographic divide in Fisher Gulch along the north edge, by Lynx Creek in the south, by topographic divides to the west, and by a combination of drainage channels and a topographic divide in the east. Eight model layers were used to discretize the domain in the vertical dimension. The upper layer of the model was divided into six overburden units which included alluvium deposits, colluvium deposits, bedrock with colluvium veneer, glaciofluvial terrace deposits, placer tailings, and glacial till. Layers 2 to 8 were divided into intrusive and metasediments bedrock hydrostratigraphic units based on local geologic mapping. In addition, Layer 2 was assigned as an overburden deposit within the Dublin Gulch valley where surficial material is the deepest.

The groundwater flow model was calibrated to available site data, including average and seasonal hydraulic heads, estimated mean monthly stream flows, and pumping test data. Streams in the model domain were simulated using the Streamflow-Routing (SFR) package (Niswonger and Prudic 2005) and monthly stress periods were used to represent seasonality during calibration, and to evaluate the seasonal effects of the Project during predictive simulations. Assigned boundary conditions were modified on a monthly basis for the transient predictive simulations to represent fluctuating groundwater extraction well water supply demands, the open pit advance and mine dewatering, overburden dewatering and removal, surface water diversions, and changes in land use (e.g. modified recharge rates beneath HLF and WRSA footprints).

The results of the predictive simulations indicate that one to two groundwater supply wells installed in the bedrock of the lower Dublin Gulch Valley will be able to sustain the groundwater supply demands. Model results also predict that mine development will cause a reduction in hydraulic heads (*i.e.* drawdown) within the Project area sub-basins of the Haggart Creek watershed. The predicted drawdown will alter groundwater gradients and therefore groundwater flow.

Stream station W5 is located south of the Project footprint on Haggart Creek (Project compliance point, Fig. 2). Estimated pre-development mean monthly flows at stream station W5 range from lows of 11,800 m³/d in March just before freshet, to highs of 275,000 m³/d in May. The changes to the monthly model water budget through closure including: 1) reductions in groundwater discharge to streams, and 2) increased leakage from streams, were combined to present the net change to baseflow. Net baseflow reduction was compared to model calibrated mean monthly pre-development stream flows as rates (Fig. 3A) and as percentages (Fig. 3B). The net baseflow reduction at W5 is up to 1,400 m^3/d during operations, but typically varies from $600 \text{ m}^3/\text{d}$ to 1,100 m³/d during construction and operations and from approximately 400 m³/d to $1,100 \text{ m}^3/\text{d}$ during the closure periods. During operations, the predicted reductions to stream flow at W5 are generally less than 1 % from May through October to 3 % to 6 % from December to April (Fig. 3B). During closure, the net baseflow reduction is estimated to decrease stream flow at W5 by less than 1 % to 2 % from May through November, and by 2 % to 5 % from December to April. Predicted reductions to stream flow peak during construction, but per-



Fig. 3 Model predicted reductions to stream flow as (A) m^3/d and (B) % of mean monthly stream flow.
sist through closure due to the overall changes to land use simulated (*i.e.* reduced groundwater recharge beneath HLF and WRSA footprints).

Field Investigations and Model Benchmarking

Following the groundwater modelling study, a 407 mm (16 in) diameter bedrock groundwater supply well (PW-BGC12-04) was installed in the Lower Dublin Gulch valley adjacent to Haggart Creek to confirm well constructability and to evaluate safe well yield. The well was constructed by simultaneously drilling and casing through alluvial overburden and metasedimentary bedrock using the dual rotary drilling method. The well was completed with 31 m telescoping screen installed from 52 to 83 meters below ground, and draws water from highly fractured zones within the metasediments bedrock. This bedrock aquifer is interpreted to be a leaky confined aquifer system recharged from the overlying alluvial sediments and adjacent uplands. This zone corresponds to Layers 3 and 4 in the groundwater model.

A step-rate pumping test followed by a 10day constant rate pumping test was carried out at a rate of 2500 m³/d to evaluate the safe well yield. Aquifer drawdown during the pumping test was monitored using electronic dataloggers at 17 locations around the site including nine monitoring wells, five vibrating wire piezometers and three stream gauging stations (Fig. 2).

The monitoring wells and vibrating wire piezometers used for aquifer test monitoring are screened in both alluvial overburden and metasediments bedrock. The three stream gauging stations were located on Haggart Creek upstream and downstream of the pumping well. Pumping test observed drawdowns at the pumping well and observation wells with measurable drawdown are included as Fig. 4.

Drawdown was measured a maximum distance of 700 m away from the pumping well in bedrock monitoring well BH-BGC11-33 (Fig. 2). Discernible drawdown was not measured in Haggart Creek; however since winter freeze-up was taking place during the pumping test there was significant ice build-up at the stream gauging stations. Aquifer transmissivity interpreted from this long term pumping test was on the order of 50 – 900 m²/d, consistent with previous pumping test results from the site.

As the data collected during drilling and testing PW-BGC12-04 was not used to build or calibrate the numerical model, it could be used



Fig. 4 Observed drawdowns for PW-BGC12-04 Long Term Pumping Test

	Distance from	Observed	Simulated
Well ID	Pumping Well	Drawdown	Drawdown
	(m)	(m)	(m)
PW-BGC12-04	-	25.2	46.3
BH-BGC11-68-S	40	2.4	12.2
BH-BGC11-68-M	40	11.2	13.2
BH-BGC11-68-D	40	12.7	1.3
BH-BGC11-72	218	3.0	0.2
BH-BGC11-74	256	1.9	0.1
BH-BGC11-32	348	0.2	0.1
3H-BGC11-33	720	0.1	0.0
MW09-DG4	210	0.7	0.6
BH-BGC11-54	580	0.0	0.0
MW10-AG3, MW96-13A	1672, 1606	0.0	0.0
MW96-13B, 09-GTH-BGC-02a-D	1606, 2411	0.0	0.0

Table 1 Simulated versus ob

 served total draw

as an independent data set to evaluate the groundwater model as a predictive decision making tool (Konikow and Bredehoft 1992). Of particular interest for this aspect of the project are model simulated impacts to Haggart Creek on the operational time scale.

Observed and simulated results are in general agreement (Table 1), and show similar areal extents for the cone of depression and reasonable agreement in drawdown values. These results show that the groundwater flow model can reasonably reproduce the water levels and drawdown observed during the 10-day constant rate pumping test. This increases confidence in the long term (25 year) prediction results from the groundwater model, especially in the lower valley area.

Conclusions

A MODFLOW-SURFACT groundwater flow model was developed to evaluate impacts of mine development on the groundwater flow regime at the Eagle Gold site including the effects of groundwater extraction on nearby Haggart Creek. Monthly stress periods were used to evaluate the net baseflow reduction to Haggart Creek. Predicted results indicate peak stream flow reductions at station W5 of 6 % during the low flow months during operations and an average reduction of 2 % during closure and post-closure. Following model development, a bedrock groundwater supply well was installed and tested to evaluate well constructability and aquifer yield. The well construction and pumping test data was subsequently used to benchmark the groundwater model and showed reasonable agreement with the independent dataset.

Acknowledgements

The authors thank Victoria Gold Corporation for involving them in the project.

References

- Konikow LF, Bredehoft JD (1992). Groundwater Models Cannot be Validated. Advances in Water Resources 15, 75 – 83.
- Niswonger RG, Prudic DE (2005) Documentation of the Streamflow-Routing (SFR2) Package to include unsaturated flow beneath streams – A modification to SFR1. U.S. Geological Survey Techniques and Methods, Book 6, Chapter A13, 47 p
- Smit H, Sieb M, Swanson C (1995) Summary information on the Dublin Gulch Project, Yukon Territory. In: Yukon Exploration and Geology. Exploration and Geological Services Division, Yukon, Indian and Northern Affairs Canada. Pgs. 33-36
- Wardrop a Tetra Tech Company (2012) Technical Report
 Feasibility Study Eagle Gold Project, Yukon, Prepared for Victoria Gold Corp. Document No. 1154860100-REP-R0008-02

Integrated methods to determine the optimal underlying grouting strata against hazardous waterinrush (China) – a case study

Changshen WANG, Haibo BAI, Xianbiao MAO, Shucai LIU, Jingcun LIU, Yong LIU

China University of Mining and Technology, Xuzhou, 221116, China, cougar3wcs@163.com

Abstract Floor grouting reinforcement technique is widely and successfully used by many coal mines in North China to prevent upwelling disasters from the underlying late Paleozoic karst aquifers. However, this technique failed to avoid mine flooding and excessive grouting fluid consumption for two coal mines in Yanlong coalfield. On the basis of a finished project, the article showed an integrated method to optimized their grouting technique. The late Carboniferous Benxi formation actually doesn't serve as a traditional aquifuge, but a real aquifer. It's the Benxi that consumed the excessive grouting fluid. Benxi is the optimized target grouting layer.

Keywords underlying karst aquifer, fragmented aquifuge, water inrush, strata reinforcement, optimal grouting strata;

Extended Abstract Since 1950s, coal mines in the Carboniferous-Permian coalfields of North China platform have been yearly contributing most of the annual coal production of China. However the geologic structures of these coal mines are complicated and the carboniferous coal seams have to undertake great water pressure of underlying early Palaeozoic carbonate karst aquifers. Coal mining of China is somewhat the history of coal mines in North China to fight against early Palaeozoic karst water upwelling disasters.

During these years, floor grouting-reinforcement technique was developed in order to strengthen the coal floor formations into effective aquifuges against accidents of the underlying karst water inrush. So far, the technique has been widely and successfully adopted by coal mines of Feicheng, Jiaozuo, Fengfeng, Huaibei and the like mining areas in North China, who had ever been well-known for their excessive mine water inflows and frequent mine water disasters.

Yanlong coalfield locates in the south edge of North China platform and had been undergoing strong geologic actions from the Caledonian to Himalayan period. Geologic structures of this coalfield can be characterized by layer-slip structures, tectonic coal, and overgrown faults. Its depositation sequence consists chiefly of the Cambrian neritic carbonate rocks, the late Carboniferous paralic thin-coalseam-bearing deposits with 4-7 limestone interlayers, the early Permian terrestrial coal deposits, the late Permian terrestrial clay-siltsand rocks, and the Pleistocene non-consolidated deposits. The only workable 2-1 coal seam in the lower Permians belongs to mylonitic anthracitic coal. Hydrogeologically, the Cambrian aquifers are the regional karst water reservoir; the early Permian limestone interlayers are also nonuniformally water-bearing and inclined to conduct and burst the Cambrian karst water into coal faces when mining.

Changcun and Longmen are the two active coal mines in Yanlong coalfield. They adopt conventional machine mining. Floor grouting-reinforcement technique is the only choice for them to prevent hazardous karst water upwelling. However, even so the Longmen mine had ever been flooded three times before 2000 and the Changcun mine was inundated again in 2007. Another big issue is excessive grout consumption. Sometimes one grouting hole can eat up over 10⁴ t of grouting fluid. Therefore, it is imperative for the two mines to improve floor grouting efficiency and reduce grout consumption.

From 2011 to 2013, we accomplished the project, sponsored by the two mines, to optimize their floor-grouting-reinforcement technique. (1) We analyzed the past drilling and grouting data from the two mines to reveal the water yielding and grouting consumption features of underlying formations. (2) Supplementary hydrogeologic drillings and lithologic analysis were used to calibrate and uniform the early Permian thin limestone aguifers; (3) Hydrogeochemical analysis and hydrological isotope tracing were used to identify the hydrologic connections between the early Permian limestone interlayers and the Cambrian karst aquifers; (4) By tracing the fractures along the underground incline drifts for 6 months, we investigated the attitude, density, filling and water-bearing features of joints and fissures in the floor strata. (5) Virgin ground stress and geologic structure analysis were conducted to judge how excessive faults and layer-slip structures to control floor grouting. (6) In situ test and mechanical numerical simulation were used to identify the underlying mining-induced fissure zones (7) Mercury porosimeter was used to test the type and quantity of tiny void of the rock.

The results showed that

1. it is owing to complicated geologic struc-

ture, fragmented and thin floor aquifuges, and high Cambrian karst water pressure that floor grouting in Yanlong coalfield can't ideally work.

- 2. Judging from the grouting holes, the water yield of the underlying late Carboniferous thin limestone aquifers accounts for 56 % of the total grouting hole inflow, that of the late Carboniferous Bensi silt-clay rocks accounts for 18%, and that of the top Cambrian accounts for 26 % (Fig. 1). It indicates that the Carboniferous limestone aquifers have the biggest water availability. Bensi formation doesn't traditionally serve as aquifuge, but a real aquifer. For a single grouting hole, it often vields the minimum water when piercing into the top Cambrian. Not as the regional karst aquifer, the top Cambrian is only weak water bearing.
- **3.** From the perspective of grouting fluid consumption, the grouting holes consume 41 % of the total grouting fluid in the Carboniferous limestone aquifers, 41 % in the Benxi silt-clay formation, and 18 % in the top Cambrian (Fig. 2). It showed that the Carboniferous limestone aquifers and the Benxi formation consumed most the total grouting fluid and the top Cambrian used a little. The excessive grouting consumption happened in Benxi formation. The top Cambrian is not the target







grouting strata. The thin carbonate strata don't uniformly occurs in the two coal mines and the two mines actually grouted different strata.

- 4. Hydrogeochemical analysis and hydrological isotope tracing showed that the two coal mines lie in the discharge area of the regional Cambrian karst system, all the underlying aquifers have similar water fingerprint, and excessive fissures and faults make it possible for the water interaction. Most of fractures in target strata strike northeast, are half filled with calcite, weakly contain water.
- 5. In situ test and mechanical numerical simulation showed that the underlying mining-induced fissure zones is 14 m in depth. Only under the precondition that the Benxi formation be solidly reinforced, the floor of 2_1 coal seam can be enough to stand 2.5-3.5 Mpa water pressure of the Cambrian karst aquifer. Benxi formation is the optimized target grouting strata.

Our integrated work indicated that it is the specific geologic and hydrogeologic backgrounds of Yanlong coalfield that made the floor grouting-reinforcement technique not ideally work. Benxi formations in Yanlong coalfield is not only the targeted but also the easily ignored grouting strata. Timely optimizing the targeted grouting strata is necessary and an effective way to overcome the water control inefficiency.

Acknowledgements

This work is supported by the National Basic Research Program of China (973 Program NO. 2013CB227900).

Water Balances and their Role in Operational Mine Water Management

Michael WILTON¹, John LUPO²

Newmont Mining Corporation, 6363 S. Fiddler's Green Circle Suite 800, Greenwood Village, Colorado, USA; ¹Michael.Wilton@Newmont.com, ²John.Lupo@Newmont.com

Abstract Water balances are an important tool in mine water management yet there are a number of common pitfalls that can reduce the usefulness and value of a model. Water balances may 1) be too complicated to be of use or too simple to represent real conditions; 2) not be used due to an inability to see or understand the logic in the model; 3) not provide the answers that the user requires; 4) not be updated or calibrated; 5) not include all site water; and, 6) not be seen as valuable and therefore not used.

Keywords mine water management, water balance, useful models, update, calibration

Introduction

Efficient and effective water management at mine sites is critical to ensuring successful and sustainable operations. Mine water management at operating mines can be a complex problem given the various components that contribute or remove water from the overall system. A water balance is an important tool in mine water management that in its simplest form, tracks inflow and outflow from the mine water system. Water balance models vary from simple spreadsheets that track annual or monthly flows between major mine facilities to complex simulations that include numerous components and estimate flows on a daily basis from probabilistic and actual mine (e.g. ore production) input.

While water balances play an important role in mine water management, they are often incomplete or misunderstood. Water balances may be too complicated to be used in a practical sense, or too simple to represent operational conditions. With the exception of climate, water balances are often created assuming static conditions such as constant watershed size, constant mining rate and mill throughput, and constant groundwater inflow, but actual conditions at mines are much more dynamic. The dynamic nature of inflows and outflows can have a significant impact on the water balance, and on overall water management strategy. For most projects, the water balance is developed prior to the mine being constructed as part of the mine study to quantify water use. However, these models are often not updated after the mine has been put into production. Depending on conditions, this can lead to models that no longer reflect the actual mining situation, and produce results that are no longer meaningful. A robust water balance must be adaptable to the ever changing mining environment so that it can be calibrated with measured data and updated with actual conditions throughout operation to be a useful component of the mine water management system.

This paper discusses a number of common pitfalls that can reduce the value and usefulness of water balance models. Examples are included to demonstrate how useful and adaptable water balance models can be developed and utilized in the mining environment.

Common Water Balance Pitfalls

Some of the more common pitfalls with water balances are listed below and described in more detail in the following sections:

• Incorrect level of complexity – models may be too complicated to be of use or too

simple to represent actual conditions;

- Nontransparent or incomprehensible models may not be used due to an inability on behalf of the user to see or understand the logic employed in the model;
- Irrelevant results models may not provide the answers that the user requires;
- Static models may not be updated or calibrated to account for dynamic conditions and therefore not provide useful results;
- Not integrated models may not include all site water inflows and outflows; and,
- Not valued models may not be seen as valuable operational tools by mine staff and management.

Incorrect Level of Complexity

The level of complexity for a water balance should reflect the system that it represents, and the data from which it is built. If very little information is available (*i.e.* early stage study), the water balance may be relatively simple. However, in advance stage studies or operations, the water balance complexity should reflect the actual site conditions within reason. A water balance should be detailed enough to provide results that account for the site conditions, but simple enough to be understood and efficiently used by site personnel. A water balance that is too complicated or overly detailed to be updated regularly has little value. On the other hand, a model that is too simple will not provide results that allow for good design and operation decisions to be made. As a project progresses through the development cycle and into operation, the water balance model should become more descriptive, which generally requires more complexity, but the model developer should continually try to maintain a balance between complexity and over simplification.

For example, the selection of the time step (e.g. yearly, quarterly, monthly, daily) used in the model should be based on trying to balance the level of resolution required and the time required to develop, run, and update the model. Fig. 1 shows an example for the volume of water in a water treatment plant surge pond for a given year. If the model user wants to determine the order of magnitude of the maximum volume in the pond, the quarterly or monthly time step model may suffice. However, if the model user wants to determine the maximum volume in the pond for design calculations, a daily time step would be preferable so that the design can match the level of risk. A yearly time step is clearly too simple for this case as it does not give any indication of the need for a surge pond, because the volume in the surge pond at the start and end of the year is zero.

Nontransparent or Incomprehensible

A water balance model should be clearly understood by the users of the model. Therefore,



Wolkersdorfer, Brown & Figueroa (Editors)

the model should be developed for the intended audience to allow users to view and understand the logic and calculations that the model performs. If site staff are unable to view or to understand the water balance calculations, there will be much less support for using the results of the water balance at an operation. While it may be necessary to have an external party develop and update the water balance due to lack of time or proficiency of the site staff, the model should be developed using a program that allows mine operators to view the calculations and results, and at least make minor modifications relatively easily. It is important that the water balance users clearly understand the intent of the water balance. Water balances are developed for a number of reasons (e.g. permitting, water treatment, make-up water estimation), but the intent of the water balances is sometimes not clearly conveyed to the users. This can lead to applications of the models outside of their original intention, resulting in poor performance or predictive capabilities.

A water balance should be developed and presented in a manner that allows users to understand the calculations that are being performed. Explanations of the model should be included within the model program, where possible, and documented in a user manual. Site users should be trained in the use of the model, as required.

Irrelevant Results

A water balance should provide results that enable site staff to make good operating and risk decisions. A water balance that provides numerous detailed results but does not answer the questions required to operate the water management systems at the mine is of little value.

The results of the water balance should be presented in a way that allows users to clearly understand their meaning. For example, if a water balance model presents probabilistic results from numerous model runs, the model developer should ensure that there is clear documentation to explain the significance of the results. Fig. 2 shows probabilistic results for a sump that collects runoff from rainfall in an open pit prior to pumping the water to a water treatment facility. The 95th percentile daily sump volume represents the volume below which 95 % of the model runs are found for a given day. The 95th percentile annual maximum sump volume represents the volume below which 95 % of the model runs are found for the highest volume in the sump during the year. If the water balance model shows only the 95th percentile daily sump volumes, the mine operators may size the sump to the highest value shown for the year and then incorrectly assume that the probability of the sump overtopping and mine operations being negatively impacted is 5 % for the year.



Fig. 2 Example of probabilistic results for a sump.

Wolkersdorfer, Brown & Figueroa (Editors)

As shown by the 95th percentile annual maximum sump volume, the sump would be required to be significantly larger than the highest 95th percentile daily sump volume to actually have a 5 % probability of overtopping in the year.

In this example, this significant difference is due to the sumps filling up quickly following rainfall events and then emptying relatively quickly after the event by pumping. In the individual model runs, rainfall events occur intermittently during the wet season, with most days having no rainfall. Therefore, on any given day, most of the model runs have very little water in the sump, but almost all model runs have at least one day with significant rainfall during the wet season and therefore, significant water volume in the sump. Therefore, it is critical that the model users clearly understand what the results represent and how the results can be applied to the mine water management system.

Static Models vs. Dynamic Models

To be of any practical use at an operating mine, a water balance must be regularly calibrated and updated in order to reflect actual conditions. Therefore, the water balance should be developed to be adaptable and allow for the user to calibrate the model based on actual measurements and update key inputs as they change through the mine life.

Key inputs to the model, such as precipitation and runoff parameters, can be calibrated based on site measurements. Precipitation is often the key input to determine the amount of water entering the mine water management system and therefore, should be regularly updated as additional site precipitation data become available. Most water balance models include a calculation to determine the amount of runoff from a catchment as a result of precipitation. This runoff calculation can be calibrated by comparing actual measurements of precipitation and stream flow, where available. If stream flow measurements are not available, it may be possible to calibrate the runoff calculation based on measurements of reservoir water levels that receive flow from upstream catchments.

The water balance model will include a number of inputs related to the mine plan such as footprint areas for mine facilities (e.g. pits, waste rock, heap leach, tailings), volumes of materials (e.q. waste rock, ore, tailings), mining rate, mill throughput, leaching rates, makeup water, and domestic water use. Since these inputs will determine the amount of water entering and exiting the mine water management systems, they should be regularly updated to reflect the latest mine plan. The water balance model will also include a number of operations flows such as dewatering flows from the open pit or underground mine, and flows within the process system. The water balance model should be regularly updated to include actual flows from, and capacities of these systems.

A dynamic, adaptable model will allow the model user to update key inputs and determine how these changes may impact the mine operations and water management risk. Like a bank account, a water balance can move relatively quickly from a positive balance to a negative balance based on relatively minor changes to inflows and outflows. For example, Fig. 3 shows the water volume in a tailings pond. It can be seen that the water volume remains below the spillway level throughout the year and therefore the pond does not discharge. Make-up water is required for the process during much of the year. Fig. 4 shows the water volume in the tailings pond with less water losses due to a decrease in mill throughput. In this case, the water balance model estimates that the tailings pond would overtop. Regular updates to water balance models potentially allow mine operators to foresee these changes in operating conditions and take required steps to prepare for these changes, such as obtaining discharge permits and constructing water treatment plants for the discharge flow.

Not Integrated

A water balance model should include all relevant water inflows, outflows, and processes, which again highlights the importance of understanding and communicating the intent of the model. While it may be necessary to have more detailed water balance models for specific areas such as a heap leach facility or process plant, the site should have an overall, integrated, site-wide water balance model that allows staff to fully understand the water interaction between the different mine facilities. This integrated model should allow for evaluations of how changes in water management in one area of the site may impact other areas, such that water management risks that are critical to operations can be identified.

An integrated, site-wide model may also

allow mine operators to identify and implement more efficient water use methodologies. For example, the base case presented in Fig. 3 shows a requirement for make-up water during a significant portion of the year. Fig. 5 shows this make-up flow and assumes that the same mine site treats water from the pit and waste rock facilities and discharges this treated water to the environment. An integrated, sitewide water balance model would allow the operators to evaluate the impact of using the treatment discharge to reduce the amount of make-up water required, as shown in the modified case in Fig. 5.

Not Valued

A water balance model must be seen as a valuable operations tool by users and manage-





Fig. 5 Example of an integrated model resulting in more efficient water use.

ment. Often a water balance is under-valued and not considered as an important component. However, water use and efficient water management are critical for sustainable mining operations. Developing, calibrating, updating, and using a water balance model can involve significant effort, and if the results are not valued, the resources required to maintain the model will not be included in the operating budget for the mine. Model developers and users can ensure that key stakeholders appreciate the importance of the model by avoiding the pitfalls mentioned above and by effectively communicating the results and advantages of the model.

Conclusions

A water balance is an important tool in mine water management. For a water balance to be useful and of value to mine operations, it should 1) be detailed enough to provide results with sufficient accuracy but simple enough to be understood and efficiently used by site personnel; 2) be transparent and understood by the users of the model; 3) provide results that enable site staff to make good operating decisions; 4) be regularly calibrated and updated to reflect actual conditions at the mine site; 5) include all relevant water inflows, outflows, and processes at site; and, 6) be seen as a valuable operations tool by users and management so that it is used. A water balance model that achieves these goals will support efficient and effective water management practices at operating mine sites.

Practical Application and Design Considerations for Fully Grouted Vibrating Wire Piezometers in Mine Water Investigations.

Grace Yungwirth ¹, Martin Preene¹, Michal Dobr², Felipe Forero Garcia³

¹Golder Associates (UK) Ltd, 1 Alie St., London, E1 8DE, United Kingdom, gyungwirth@golder.com; mpreene@golder.com ²Golder Associates Ltd, 500 – 4260 Still Creek Drive, Burnaby, British Columbia, Canada V5C 6C6, Canada, mdobr@golder.com ³Golder Associates Colombia S.A.S., Calle 127 No. 13A – 32 piso 5°, Bogotá, Colombia, felipe ForeroGarcia@golder.com

Abstract Fully grouted vibrating wire piezometer sensors have proven to be particularly useful in mine water investigations where the use of traditional standpipe piezometers may have practical drawbacks, such as low conductivity of the formations, depth, borehole diameter and inclination. Design considerations are presented for implementation of the method to many applications in mine water investigations.

Keywords Fully grouted vibrating wire piezometers, design considerations, piezometeric head

Introduction

In-situ measurement of groundwater levels and piezometric pressures is an important part of many mine water investigations. In order to collect accurate and representative data, it is essential that the design of the monitoring instrumentation is individually adjusted to the actual site conditions. The traditional standpipe groundwater monitoring well design has the disadvantage that a finite volume of water must flow into or out of the borehole to register a change in water level. This creates a time lag between the piezometric pressure in the strata and the monitoring well. In strata of low hydraulic conductivity the equilibration rate may be too slow to provide useful information within a reasonable time.

Since the 1980s the standpipe piezometers have been replaced for some applications with vibrating wire pressure (VWP) sensors. These sensors respond to groundwater pressure changes, at the sensor location. For early applications VWP design included a sand pack around the sensor, similar to the conventional standpipe design. However, in the last two decades the "fully grouted" installation method has been developed, where multiple VWP sensors are set in a low permeability grout within the borehole, without a sand pack.

Considerable experience in installation and monitoring has been gained with this type of instrumentation in the mining industry since this methodology was first developed, but some questions remain over the installation requirements and technical limitations.

This paper provides a review of the general installation methodology, and the conditions when this type of instrumentation can offer advantages over the traditional design. A project case study is presented to describe challenges associated with the installation of the fully grouted piezometers. This discussion is intended to be useful for mine water practitioners planning groundwater investigations in complex hydrogeological conditions, particularly where strata of low hydraulic conductivity are present.

Development of Rapid Response Piezometer Methods

The traditional form of groundwater monitoring piezometer comprises an open tube (termed a standpipe) with a perforated section to allow water to enter the well at the depths of interest (Fig. 1a). These piezometers in strata of moderate to low permeability will respond slowly to changes in pore water pressure, because a finite volume of water must flow into or out of the piezometer to register the change in pressure. This leads to a 'time lag' between changes in water pressure in the strata and the registering of that change in the piezometer. The time lag is greater in strata of lower permeability, and is greater for piezometers using larger diameter tubing, where larger volume flows are needed to register pressure changes.

To avoid the time lag problem various 'rapid response' piezometer instruments were developed. In the 1960s hydraulic and pneumatic piezometers were developed, where the movement of small volumes of fluid (water or air, respectively) in closed systems inside the instrument was used to balance external water pressure, allowing external groundwater pressure to be determined. Unfortunately these instruments were difficult to set up correctly and intolerant of extreme field temperatures.

Since the 1980s and 1990s the vibrating wire pressure transducer (often known as a vibrating wire piezometer or VWP) is widely used for monitoring of hydraulic pressures and water levels. These instruments contain a metal diaphragm in hydraulic connection with the groundwater. Inside the instrument a taut wire is stretched between the diaphragm and a stable datum. The wire is activated by passing a controlled frequency electrical pulse along it. The wire resonates at a frequency related to its tension which can be related to the deflection of the diaphragm, and the water pressure on the diaphragm.

When VWP instruments were originally applied for field use, each instrument was typically installed in a discrete filter sand response zone in a similar way to a standpipe piezometer (Fig. 1b). This approach is effective but difficult, and time consuming. In the 1990s an alternative approach, known as the 'fully



grouted method' (McKenna 1995) was developed where the VWP instruments are installed in the borehole surrounded by cement-bentonite grout (Fig. 1c). This method is possible because VWP instruments require only a very small volume equalisation (10^{-6} to 10^{-7} m³) to respond to water pressure changes, and an appropriate cement-bentonite grout is able to transmit the pressure change over the short distance which separates the VWP instrument from the ground around the borehole.

Guidance for Installation Requirements and Technical Limitations

VWP sensors can be installed within boreholes in both soil and rock and therefore suit all applications where pore pressure monitoring is desired. The sensors register the pore pressure at the location of the VWP diaphragm. This creates a specific point at which the pore pressure can be monitored, rather than monitoring the average pore pressure across a screened interval within a standpipe piezometer or sensor installed within a sand pocket. This allows the design of very specific response zones, for example to target discrete fractured zones in fractured rock systems, or in complex soil and rock lithologies where pore pressures are expected to vary across short distances.

Given the ability to target specific locations for pore pressure measurements, the greatest benefit from sensor placement comes when a good understanding of the lithology has been developed. For this reason it is most beneficial in ground investigations to install the sensors within a cored borehole where the recovered core can be used to identify the specific target lithologies for sensor installation, or where reliable geophysics has been used. This is particularly true when VWPs are used in ground investigations where the exact nature of the target materials may be unknown prior to the sensor installation as opposed to dam and embankment applications.

Field and laboratory tests of hydrodynamic response times of VWP sensors in fully grouted installation have been shown to be very quick. Contreras *et al.* (2012) report responses of less than two minutes in a 100 mm diameter borehole backfilled with a water:cement:bentonite grout (1:2.5:0.3); Mickelson and Green (2003) present similar results.

Suitable Applications for Grouted VWP Sensors

Given the nature of VWP sensors, fully grouted methods are best suited for use in the following applications:

- monitoring within low hydraulic conductivity formations where a short hydrodynamic time lag is desired;
- monitoring at locations that could be affected by surface freezing conditions (Contreras *et al.* 2012), provided the sensors are installed below the ground freezing depth;
- deep, inclined, or horizontal installations in which a discrete sand pack interval might be difficult to place;
- artesian or flowing borehole conditions in which discrete sand pack intervals and bentonite pellets might be difficult to place; and
- small diameter boreholes where multiple monitoring points are desired. Multiple sensors can be placed within a single borehole where space might limit the number and amount of standpipe piezometers which can be installed within a single borehole.

There is a practical limit on the number of sensors which can be installed within a single borehole. This is generally much greater than the number of standpipe piezometers, however the number of practicable installations depends on the borehole and sensor diameter, and support design used to place the sensors in the borehole. It is the authors' experience that in general installations of three to four sensors in 75.8 mm (NQ) diameter boreholes, and four to five sensors in 96 mm (HQ) diameter boreholes are practicable.

Overview of Installation Methods

The VWP sensors are positioned downhole attached to cables which run from the sensor to surface where they can either be connected to a datalogger or can be read with a portable unit. Fully grouted VWP sensor installation procedures are described in detail by Mikkelsen and Green (2003). The sensors are often installed attached to a support structure such as a sacrificial tremie pipe which supports the weight of the installation, and allows for placement of the grout from the bottom of the hole up. If a grout plant is not available, the grout is prepared in a drum or mud tank and mixed either by separate mixer or by circulating the mixture with the driller's pump using a suction hose and jet nozzle. Once suitably mixed, the grout is pumped in place through the tremie pipe/hose filling the borehole to surface and allowed to cure. A suitable surface housing should be installed to protect the cables and/or dataloggers at surface.

VWP Sensor Installation Design Considerations

Key factors in the design of installations of fully grouted VWP sensors include:

- **1.** Choosing the appropriate VWP sensors;
- **2.** Structural support of the installation;
- **3.** Design of the grout mixture;
- 4. Placement of the grout;
- 5. Additional Installation challenges; and
- **6.** Installation costs.

Choosing the Appropriate VWP Sensors

Sensors should be chosen based on the range of pressure that the sensor is expected to measure when installed, with sufficient range to withstand the additional pressure applied during grouting. When the expected pressure is unknown it can be approximated based on the installation depth. As with most commercially available pressure transducers, the greater the sensor range the greater the potential systematic error in the readings. Therefore for the most accurate readings, sensors should be chosen to have the lowest appropriate range that can still withstand the pressure applied during grouting.

The nature of VWP sensors allows for the length of cable to be adjusted without any degradation of the signal. Most manufacturers will supply easy to use splice kits which can be used to extend the cable length, and similarly the cables can be easily cut and shortened. This means that materials can be procured in advance of the investigation based on expected installation depths and adjusted based on conditions encountered.

Structural Support of the WVP Sensor String

VWP sensors can be installed by hanging them within a borehole or by guiding them into place using a support structure such as a driller's wireline or a tremie-pipe/hose. The purpose of the support structure is for depth control as well as support of the installation to avoid cable stretch or damage. During installation, care must be taken not to damage the cables. Installation on the outside of a tremiepipe is useful in inclined or horizontal boreholes where gravity alone cannot be used to place the sensors. The tremie pipe can be left in place for the dual purpose of sensor support, and then be used to deliver the grout from the base of the borehole to surface.

The use of sacrificial tremie pipe may not be appropriate for use in soft ground where a large amount of vertical compression is expected. Contreras *et al.* (2012) has shown that the behavior of the fully-grouted installation using a sacrificial grout pipe in soft ground is adequate when the amount of vertical compression expected is less than 15 %.

Design of the Grout Mixture

When using the fully grouted method, sensors should be placed within a grout that is matched to the permeability of the surrounding formation (Mikkelsen and Green 2003). Cement-bentonite grout mixtures for fully grouted VWP applications have been investigated and described in detail by Mikkelsen (2002) and in field and laboratory experiments by Contreras *et al.* (2008, 2012) with recommended mixtures presented below in Table 1.

The amount of bentonite required will vary depending on the type of bentonite, the amount of mixing, and the water quality such as pH and temperature (Mikkelsen 2002). Mikkelsen (2002) describes the grout consistency as "drops of grout should barely come off a dipped finger and should form "craters" in the fluid surface."

Control of the water-cement ratio is essential when designing the mixture as it controls the compressive strength and void ratio of the grout and thus the permeability (Contreras *et al.* 2008). Bentonite is added to assist with suspension of the cement, to control shrinkage and bleeding, and therefore grout component separation on setting. The ability to pump the grout is also a contributing factor in the design.

Contrary to the original theoretical work done by Vaughan (1969) which suggested that grout should be no more than one order of magnitude greater than the permeability of the surrounding formation, Contreras *et al.* (2008, 2012) have shown that grout permeability can be up to three orders of magnitude greater than the surrounding soil and rock without inducing significant error in the measured pore water pressure. This leaves a significant amount of flexibility in the properties of the grout mixture for most applications.

It is the authors' experience that the grout mixture presented in tab. 1. for use in hard soils is suitable for use in most fractured rock systems. Additional information on the per-

	Hard To M	edium Soils	Soft Soils		
Material	Weight	Ratio by Weight	Weight	Ratio by Weight	
Cement	40 kg	1	40 kg	1	
Water	100 L	2.5	264 L	6.6	
Bentonite	12 kg	0.3	16 kg	0.4	

Table 1 Recommended Cement-Bentonite GroutMixtures (after Mikkelsen 2002).

meability and properties of cement-bentonite mixes can be found in Contreras *et al.* (2008).

Placement of the Grout

Cement-bentonite grout can be placed into the borehole through the drill string or a tremie pipe. Tremie pipe should typically be fitted with ports in the lower section of the pipe through which the grout can escape when it is pumped downhole. Grouting the borehole from the bottom up to surface using the tremie pipe is preferred to ensure that the grout is consistently placed with no voids or separation. Factors to consider when placing the grout are:

- ensure the tremie pipe contains sufficient ports for grout delivery;
- check the suitability of the tremie pipe to withstand grouting pressures and support the weight of the instrumentation;
- check the back pressure within the tremie pipe or rods when pumping the grout;
- check the suitability of the grout pump to handle the pressures required to place the grout;
- where several batches of grout must be delivered, can they be delivered quickly enough to avoid partial setting or separation of the previous batches; and
- can the pumping pressure be controlled to avoid overpressuring of the VWP sensors.

It is recommended that the VWP sensors are monitored during grout placement to ensure the grouting pressure does not cause significant overpressuring of the VWP sensors, and that the grout has been placed properly. Overpressuring during grouting is one of the key causes of VWP sensor malfunction (Marcil 2006). Downhole grout pressures can be minimized by slowing the delivery of the grout.

Other Installation Challenges

There are several additional challenges commonly encountered when performing VWP installations which can be accounted for in the installation design.

- 1. Borehole stability issues. Where possible, sensors should be lowered into place within the drill string which will support the borehole during installation and can subsequently be removed leaving the sensors in place.
- 2. Damaged cables during sensor placement. In addition to testing of the VWP sensors on surface, a robust quality assurance and quality control ("QA/QC") procedure should require testing of the VWP sensors once they are in place in the borehole, but before grouting activities commence. It is possible that VWP sensor cables become cut or damaged during placement. If this is identified during the QA/QC check prior to grouting, the installation could be removed and the damaged cable removed and repaired prior to grouting.
- **3.** Difficulty in attachment of the sensors and cables to the support structure under high temperature and depth conditions. For shallow installations (less than 300 m), it is normally sufficient to attach sensors to the support structure using tape. However in conditions where high temperature or greater depth is expected, the tape may not be strong enough to support the weight of the cables, and a more robust attachment method should be considered.
- 4. Strength of the tremie pipe or support structure. Care must be taken to ensure that the tremie pipe used is robust enough to support its own weight and the weight of the instrumentation as well as the expected grout pressures. This is particularly relevant for deep vertical installations.

Cost Considerations

The cost of the materials should be considered when designing a VWP sensor installation

(costs below are 2013 costs): Sensors typically cost \$US350–500; sensor cable typically costs \$US4–6 per metre depending on type; support structures such as PVC tremie pipe cost \$US5– 10 per 3 m length; grouting materials such as cement cost \$US7–10 per 25 kg bag, bentonite cost \$US10–15 per 25 kg bag and water; and dataloggers or readout units necessary to collect the data typically cost approximately \$900 USD per unit depending on type.

Installation of VWP sensors by the fully grouted method is often quicker than the placement of sand and bentonite for traditional standpipe piezometers, thus limiting drill rig support costs.

Case Study – Deep VWP Installation for Mine Water Investigation

The following case study presents an example of the application of the fully grouted method to illustrate the challenging conditions that can be expected in mining investigations.

A hydrogeologic investigation was undertaken in a vertical, 155.6 mm diameter exploration borehole designed to investigate a coal bearing formation of alternating sandstone, siltstone, and mudstones from 500 to 1200 m depth below ground surface. Single well pressure response testing using borehole packers equipped with a shut in tool was undertaken over depth intervals from 665 to 1670 m. Calculated hydraulic conductivities were of the order of 5×10^{-11} m/s. Borehole stability and the potential for the generation of coal gas limited testing times to 12 h before the borehole had to be reconditioned with drilling muds. This was sufficient testing time over which hydraulic conductivities could be estimated, however it was not always long enough to allow the pressure within the system to equilibrate to the average interval pore pressures.

A VWP sensor string was installed to determine equilibrated pore pressures within different lithological units in support of the testing program, and to be used for long term monitoring. A typical setup at the drill rig during installation activities is depicted in Fig. 2.



Challenges to the installation included borehole stability, the depth of the installation, and the high formation temperatures, measured at depth from 32 °C to 50 °C. These challenges were overcome by designing the installation using robust steel rods to support the increased weight of the installation and expected grouting pressures. Metal banding was

used to secure the cables and sensors to the tremie pipe to withstand the increased temperature and weight. A dedicated high performance pump was used to inject the grout through the pipe and backfill the borehole from depth to surface. The grout placement was undertaken by pumping several batches of grout in series within a short enough timeframe to allow placement before the grout had set. Fig. 3 depicts VWP sensor readings during grout placement and stabilization of piezometric levels as the grout is set.

VWP sensors were successfully installed to depths of approximately 600 m, 750 m and 900 m below ground surface and subsequently measured piezometric heads of approximately 50 m, 80 m and 190 m below ground surface respectively. The results were comparable with a second installation undertaken in the same formation from approximately 650– 1000 m depth approximately 3 km away. These sensors have been functioning well since their installation in mid 2012.

Conclusions

Monitoring boreholes installed with fully grouted vibrating wire piezometers can have significant advantages over conventional standpipe wells. This paper has discussed installation and design methods, and used a case study to highlight typical installation challenges.

References

- Contreras IA, Grosser AT, VerStrate RH (2008) The Use of the Fully-grouted Method for Piezometer Installation Part 1 and Part 2. Geotechnical News June 2008, 30–37
- Contreras IA, Grosser AT, VerStrate RH (2012) Update of the Fully-grouted Method of Piezometer Installation. Geotechnical News June 2012, 20–25
- Marcil L (2006) Discussions of "Karkheh Dam Instrumentation System-Some Experiences" Geotechnical News June 2006, 36–37
- McKenna GT (1995) Grouted-in Installation of Piezometers in Boreholes. Canadian Geotechnical Journal 32, 355–363
- Mikkelsen PE (2002) Cement-Bentonite Grout Backfill for Borehole Instruments. Geotechnical News. December 2002, 38–42
- Mikkelsen PE, Green EG (2003) Piezometers in Fully Grouted Boreholes. International Symposium on Geomechanics. Oslo, Norway. September 2003
- Vaughan PR (1969) A Note on Sealing Piezometers in Boreholes. Géotechnique, 19(3), 405–413

The AA leach pad cover design – a successful reclamation project at a Nevada gold mine

Guosheng Zhan¹, Mike Milczarek², Jason Keller³, Joe Giraudo⁴

¹Barrick Gold of North America, Inc., Salt Lake City, Utah, USA, jzhan@barrick.com
 ²GeoSystems Analysis, Inc., Tucson, Arizona, USA, mike@gsanalysis.com
 ³GeoSystems Analysis, Inc., Hood River, Oregon, USA, jason@gsanalysis.com
 ⁴Barrick Gold of North America, Inc., Salt Lake City, Utah, USA, jgiraudo@barrick.com

Abstract The AA Leach Pad at Barrick Goldstrike Mine was reclaimed using an evapotranspiration (ET) cover designed to limit meteorological infiltration. Monitoring of the sensors installed in the facility continued for eleven years. Data indicates that the cover is limiting net percolation to less than 1 % of precipitation. AA Leach Pad is the first large-scale closed mine waste facility which has been robustly monitored for a long time in Nevada. Results from the study provide an understanding of ET cover system performance for closure of other mine waste facilities, and offer guidance for ET cover system requirements in other arid regions.

Keywords Evapotranspiration (ET) cover, cover performance, leach pad, mine closure

Introduction

The Barrick Goldstrike Mines Inc. (BGMI), located 60 km northwest of Elko in north-central Nevada, is a large open pit and underground gold mining operation. The AA Leach Pad (AA Pad) at BGMI operated from 1987 through 1999 and at the end of operation consisted of 55 Mt of run-of-mine leached ore. The facility covers approximately 100 ha.

The climate at the site is semi-arid with hot summers and cold winters. Average annual daily temperature is about 9 °C. The majority of precipitation falls between December and May as snow. Annual precipitation is about 300 mm. Average annual pan evaporation is about 1500 mm.

The AA Pad was reclaimed in 2000/2001 using an evapotranspiration (ET) cover. ET extracts water from the cover layer predominantly during warmer periods (summer and fall), leaving a moisture-depleted plant root zone by fall, which then stores water in winter and spring.

Cover Design

Hydrological Design and Test

1. Laboratory Tests: Hydrologic property tests, including, saturated hydraulic conduc-

tivity (K_{sat}) and soil water characteristic curves (SWCC) were originally conducted on leach ore material and potential cover materials (Tertiary Carlin Formation Siltsone (TCS) and topsoil) at Daniel B. Stephens & Associates, Inc. (DBS) in Albuquerque, New Mexico. In the laboratory tests, the gravel portion was first removed from the samples and the test results were then adjusted with a published gravelcorrection method. To avoid the potential errors induced by gravel-correction, leach pad ores and potential cover materials were retested with the gravel portion included using large diameter columns $(150 \times 300 \text{ mm})$ at GeoSystems Analysis, Inc. in Tucson, Arizona.

2. One-dimensional Simulation: Several unsaturated numerical codes were evaluated for the cover design and SoilCover (Geo-Analysis 1997) was chosen for the simulations. Soil-Cover is a one-dimensional (1D), finite element package that models transient conditions. The model is based on Darcy's and Fick's Laws, which describe the flow of liquid water and water vapor, and Fourier's law to describe conductive heat flow in the soil profile and soil/atmosphere boundary. The numerical analyses demonstrated that topsoil and TCS, have sufficient water holding capacity to be used for an ET cover. Additionally, the leach pad material was shown to be suitable as a capillary barrier layer when overlain by TCS/topsoil materials. The numerical analyses concluded that 90 cm of TCS/topsoil cover placed over the leach pad material would effectively minimize meteoric water percolating through the reclaimed leach pad (Zhan *et al.* 2000).

3. Two-dimensional Simulation: Since the AA Pad has long slopes, the real behavior of a cover system can be different than the idealized 1D model. A particular concern was moisture that builds up above the cover-leach ore interface could flow along the slope, and at a certain point the cover material could become wet enough to allow infiltration into the coarser leach ore. This point is called the Down Dip Limit (DDL) point. In order to examine whether or not the DDL would be reached, a two-dimensional (2D) simulation was conducted using the software HYDRUS2D (Simunek et al. 1999). The 2D simulated results demonstrated that in a normal precipitation year net percolation (infiltration minus ET) into the cover was close to zero and suction heads at the cover-leach ore interface were higher than the water entry value of spent ore material. Therefore, it was concluded the DDL will not occur along the slope under these conditions. In order to evaluate ET cover behavior during extreme precipitation events a separate risk assessment simulation was performed in which 10 days with no evapotranspiration was assumed and three 100-year return frequency storm events occurred Day 1, 2 and 3 respectively. The risk assessment simulation predicted that at all locations along the slope, the water content and pressure profiles at the bottom of the cover did not increase significantly to exceed the water pressure entry value of the leach ore. In other words, the capillary barrier would not be broken and water would not seep into the leach ore under these extreme precipitation conditions (Zhan *et al.* 2001a).

4. Pilot Field Test: Prior to full-scale cover installation a pilot study was conducted on a small-scale test cover plot placed on the AA Pad to examine the cover performance simulated rainfall conditions. For this test, a 7×7.5 m cover test plot with a thickness of 60 cm of TCS was constructed on the 3(H):1(V) east-facing slope of the AA Pad (Fig. 1). After the cover was put in place, drip irrigation tubes were installed on the surface of the cover. Water content sensors (time-domain reflectometry, TDR) and matric potential sensors (heat dissipation sensors, HDS) were installed on the lower part of the test slope since surface water run on makes these areas more susceptible to net percolation. Performance testing simulated intermittent irrigation of Approximately 227 cm of water (equal to about 7.6 years of precipitation) during the period of July to September 2000. The 1D numerical model was then calibrated to the observed data (Zhan *et al.* 2001b).

The volumetric water content of the cover reached as high as 0.30, during irrigation periods. Simulated volumetric water content corresponding to wilting point of 4 MPa, which is representative of desert plant communities in the Great Basin (Zhan *et al.* 2006), was 0.17, in-



Fig. 1 AA Leach Pad 2000 pilot field test: irrigated area (left) and data acquisition system (right).

Wolkersdorfer, Brown & Figueroa (Editors)

dicating a storage capacity of the cover equal to $0.13 \text{ cm}^3/\text{cm}^3$ (0.30 - 0.17). Consequently, a TCS cover thickness of 90 - 120 cm was predicted to be able to store 12 - 16 cm of water, independent of evaporation and lateral drainage. Based upon this analysis, the holding capacity of the cover would have sufficient volume to retain 3 continuous one-hundred year storm events (approximately 24 cm of water), assuming half the precipitation runs off the cover. Therefore, the cover would operate as designed even under extreme precipitation conditions.

Engineering Design

The engineering aspects associated with the closure of the AA Pad facility consisted of the following:

- Design of a permanent toe drain facility that would collect and isolate any water flux from the reclaimed heap leach pad over time.
- Preparation of a grading plan that would provide for adequate support and function of the soil cover, optimize revegetation and reclamation potential, minimize erosion risk and sediment yield, and provide a landform compatible with the natural landforms.
- Design of a drainage network on the cover surface which would safely and efficiently collect and remove surface runoff from the new landform, incorporating a natural looking configuration of drainages for the control of erosion and sediment yield (Fig. 2).
- Balancing earthwork quantities and construction pathways to minimize construction costs and provide adequate space for the ET cover layer construction.
- Design of a perimeter storm drainage network capable of safely collecting and removing storm water runoff from the recontoured heap surface.

Details about engineering design can be found from Myer *et al.* (2001). The geotechnical



Fig. 2 Freshly reclaimed AA Leach Pad showing drainage network on the cover surface (looking northwest).

integrity of the cover system remains unchanged after having been in place for more than 10 years and experiencing numerous storms of varying intensity levels.

Vegetation Design

Planted vegetation at AA Pad included grass, forbs and shrubs. The seed mix was based on 5 years of site specific research of vegetation data. In March of 2001, the seedbed was prepared and then broadcast seeded 18 kg/ha of the selected seed Mix and then harrowed a second time to lightly cover seed. An organic mulch and tackifier were hydraulically applied over the entire unit at a rate of 9 t/ha and 168 kg/ha, respectively (Fig. 3).

Cover Monitoring Instrumentation

In different areas on the facility, the cover is composed of different materials of different thicknesses, with variable slope positions, solar aspects, and proximity to drainage channels. Cover system performance monitoring systems were installed between 2001 and 2005 on the AA Pad. Fourteen monitoring stations were located along three transects (East, West, and South, Fig. 2), with six, five, and three stations, respectively. At each transect, sensor stations were located near the crest, mid-slope, and foot-slope of the AA Pad, and in addition, adjacent to stormwater runoff channels at the East transect. Instruments include HDS to measure matric potential and temperature,



Fig. 3 AA Leach Pad plant seeding (left) and organic mulch application (right).

TDR or capacitance (ECH₂O) sensors to measure water content. Schematic diagrams showing sensor installation are shown in Fig. 4. Because both water content and matric potential sensors were installed as pairs at same depths, *in situ* SWCC could also be obtained.

Monitoring Data Precipitation

Precipitation totals over the monitoring period from water year (WY, Oct 1 through September 30) 2002 to WY 2012 ranged from 201 to 493 mm, averaging 332 mm, 16 mm higher than the 316 mm long-term average. WYs were classified into average, wet, or dry years by defining a wet year as one with a WY precipitation total greater than one standard deviation above the long-term average, and a dry year as one with a total less than one standard deviation below the average. WYs 2005, 2006 and 2011 were wet years; 2008 was a dry year; and all other WYs were average years.

Vegetation

More than 10 years of AA Pad vegetation data indicates that plant succession is progressing in a positive direction, and the AA Pad vegetation appears to be stable and self-sustaining, as well as resistant to erosion. Total plant cover in 2011 was 52.1 % with 44.4 % being derived from perennial species (Fig. 5). By comparison the reference area only displayed 19.1 % perennial cover out of 58.4 % total plant cover. An example of the exemplary status of this reclamation effort is the 5.6 % composition contributed by bitterbrush (Purshia tridentata), an extremely important, but difficult to establish component of the northern Nevada rangeland.

Drain-down data

AA Pad is a synthetically lined facility and its drain-down data have been collected on a regularly basis: bimonthly or monthly through 2009 and quarterly since January 2010. Draindown data are missing from January through November 2006. Data generally indicate seasonal increases in drainage rates in response to spring snowmelt (March-May) followed by declining rates over the summer and fall months.

Assuming that the October drain-down rates approximate residual drainage from the leach heap (baseflow) drain-down rates exceeding baseflow should then approximate the area-averaged net percolation rate through the AA Pad cover system into the underlying leach ore. Fig. 6 shows the average difference between the baseflow rate and the increased drainage rates in response to spring melt was 3.2 mm/a (0.94 % of precipitation) from October 2002 to October 2012.



Fig. 4 Installation schematic for cover performance monitoring stations.



Fig. 5 AA Leach Pad Perennial Plant Cover (2001–2011).

High flow rates measured in December 2006 in response to the very wet precipitation year, indicate that significant net percolation may also have occurred in response to the above-average precipitation in WY 2006.

Estimates of Net Flux

After 11 years of monitoring, the cover performance is well understood. Consequentially, all stations were decommissioned in October 2012. Net percolation flux is defined as meteoric water that infiltrates into the cover and is not removed by ET. Net percolation flux will eventually exit the base of the AA Pad as draindown.

Net percolation flux of meteoric water near the cover-leach ore contact was estimated at each monitoring station by calculating the 1D vertical flux. Flux rates were calculated from matric potential data measured from the two deepest HDS located at each station, together with matric potential versus water content relations (SWWC) and saturated and unsaturated hydraulic conductivity values measured in the laboratory. Flux rates calculated in this manner are referred to as matricpotential-based (MPB)-calculated flux.

The MPB-calculated flux data indicate that most flux occurred in wet WYs 2005, 2006, and 2011; whereas during average WYs, near-zero MPB flux values were calculated at most stations; stations near stormwater runoff channels recorded the highest MPB-calculated flux values of all the AA Pad stations. Weighting the MPB-calculated flux for the entire AA Pad with respect to the amount of surface area occupied by each monitoring station slope position (crest, mid-slope, foot-slope, and channels) is approximately 2.2 mm/a (0.63 % of precipitation). This value is very similar to the esti-



Fig. 6 Predicted and measured drain-down from AA Leach Pad.

mated net percolation flux calculated from the draindown data.

Conclusions

Eleven years of cover monitoring data at AA Pad indicate that the cover is limiting average annual net percolation flux through the cover to 2.2 mm/a (0.63 % of precipitation), based on the area weighted average MPB-calculated flux. Estimated average annual flux from seasonal increases in AA Pad drain-down rates in response to spring melt are slightly higher than the MPB-calculated flux, being 3.2 mm/a (0.94 % of precipitation). Considering the small difference, it is reasonable to conclude that net peculation through the cover is less than 1 % of the precipitation.

Eleven years of vegetation surveys indicate that plant succession is progressing in a positive direction and plants within these areas are self-sustaining and reclaimed sites appear at least as stable and resistant to erosion as nearby, undisturbed areas.

Acknowledgements

This paper is generated from the AA Leach Pad reclamation program of BGMI. The inputs from all team members are gratefully acknowledged. Authors thank Dr. Mark Ankeny from Daniel B. Stephens & Associates, Mr. Steven Viert from Cedar Creek Associates, Dr. Dale Hammermeister from GeoSystem Analysis, Inc., Mr. Greg Newman from Newmans Geotechnique Inc., Ms. Mayana Kissiova from Golder, Professor Michel Aubertin from École Polytechnique de Montréal for their valuable contributions to this project. Finally, special thanks to Barrick Gold Corporation for providing permission to publish this technical summary.

References

- Geo-Analysis 2000 Ltd. (1997) SoilCover User's Manual Version 4.01
- Myers KL, Espell R, Karl Burke K. (2001) Reclamation and closure of the AA Heap Leach Pad at Barrick's Goldstrike Mine, SME Transaction 2001, 310: 12 pp
- Simunek J, Sejna M, van Genuchten M Th. (1999) Simulating Water Flow and Solute Transport in Two-Dimensional Variable Saturated Media, Version 2.0. HYDRUS2D/MESHGEN2D. U.S. Salinity Laboratory, Riverside, California
- Zhan G, Mayer A, McMullen J, Aubertin M (2000) Capillary cover design for a spent leach pad. Proceedings of International Symposium on Hydrology and the Environment, October 17 –21, Wuhan, Hubei, China, p 144–150
- Zhan G, Mayer A, McMullen J, Aubertin M (2001a) Slope effect study on the capillary cover design for a spent leach pad. Proceedings of Tails and Mine Waste'01, January 16 –19, Colorado State University, Front Collins, Colorado, USA, p 179–187
- Zhan G, Aubertin M, Mayer A, Burke K, McMullen J (2001b) Capillary cover design for leach pad closure. SME Transaction 2001, 310: 104–110
- Zhan G, Schafer W, Milczarek M, Myers K, Giraudo J, Espell R (2006) The evolution of evapotranspiration cover system at Barrick Goldstrike Mines. Proceedings of 7th International Conference on Acid Rock Drainage (ICARD), March 26–29, St. Louis, Missouri, USA, p 2585–2603

RELIABLE MINE WATER GEOCHEMISTRY RELIABLE MINE WATER GEOCHEMISTRY





Using Humidity Cells Tests to Evaluate an ARD Minimization Approach in Santa Catarina Coal Field, Brazil

Juarez R. do Amaral Filho¹, Jéssica Weiler¹, Ivo A. H. Schneider¹, Jennifer L. Broadhurst²

¹Universidade Federal do Rio Grande do Sul, LTM-DEMIN-PPGE3M, Av. Bento Gonçalves 9500, Porto Alegre, RS, Brazil.juarez.amaral@ufrgs.br, jessica.weiler18@gmail.com, ivo.andre@ufrgs.br ²Minerals to Metals, University of Cape Town, South Africa, jlb@absamail.co.za

Abstract The aim of this work was to use humidity cells tests to evaluate the effectiveness of an ARD minimisation approach for coal discard from the Santa Catarina coal field, Brazil. Coal waste sample was obtained from a typical beneficiation plant and separated into three density fractions, using a ferrosilicon medium. Further characterisation of these density fractions indicated that the low (<2.2 g/cm³) and high (> 2.7 g/cm³) density fractions are potentially suitable for energy and sulfuric acid production respectively. The waste fraction of intermediate density (2.2-2.7 g/cm³) had a reduced sulphide sulfur content, and it was postulated that it may be suitable for land disposal with minimum risk to the surrounding environment. This hypothesis was tested using laboratory-scale static and humidity cell tests. The results of these tests indicated that, whilst the intermediate density waste fraction remained acid generating, the release of metals, salts and acidity into solution was considerably lower than that obtained for the discards before density separation. This has important implication in terms of reagent requirements and sludge generation during subsequent ARD treatment.

Keywords humidity cells tests, coal waste, ARD, prevention

Introduction

The grade of coal deposits in Brazil is relatively low, and approximately 65 % of the run-ofmine (ROM) coal extracted from underground mines in the carboniferous regions of Santa Catarina, Brazil, is discarded as waste in dump deposits. These waste discards contain sulfide minerals, particularly pyrite, which oxidize and give rise to acid rock drainage (ARD).

Currently, the Brazilian coal mining operations emphasise an end-of-pipe treatment approach to coal waste and ARD management. Chemical ARD treatment techniques such as lime neutralisation typically consume large amounts of expensive reagents, generate significant quantities of sludge requiring further treatment as well as disposal, and are only effective in reducing ARD risks in the short term. As pointed out by Kontopulos (1998), many of these shortcomings can be overcome by implementing ARD preventative techniques which are aimed at minimising the generation as well as subsequent dispersion of ARD from waste dump deposits over the long-term. One such approach entails the pre-disposal removal of ARD generating sulfide minerals, by means of physical separation techniques such as flotation and density separation (Amaral Filho 2010, Benzaazoua *et al.* 2000, Hesketh *et al.* 2010, Kazadi Mbamba *et al.* 2012). Apart from reducing ARD risk, integration of a sulfide removal step into the beneficiation circuit also offers opportunity for additional value recovery (Amaral Filho 2010; Hesketh *et al.* 2010, Kazadi Mbamba *et al.* 2012).

The ability to accurately predict the ARD generating potential of wastes plays an important and essential role in the development of effective approaches and technologies for mitigating associated impacts and liabilities. Methods for quantifying the ARD potential of sulfide wastes can be classified as either "static" or "kinetic" tests. Static testing methods are short term (hours to days) tests which do not take into account the relative rates of acid forming and neutralising reactions, whilst kinetic testing methods are long term (month to years) tests which allow for the study of the dynamic factors influencing ARD generation (Sapsford *et al.* 2009, Lengke *et al.* 2010). Although a number of kinetic test protocols have been developed, only humidity cell tests follow standard procedures (ASTM 2007).

The objective of this study was to use standard static and humidity cell ARD tests in order to verify the effectiveness of an intervention based on sulphur removal and low-grade coal recovery, in terms of metals leaching and acidity reduction.

Methods

The coal waste was collected from the coal preparation plant of the "Verdinho Mine", Santa Catarina State-Brazil, which extracts the "Barro Branco" seam. The material was subjected to laboratory-scale dense medium (Fe-Si) separation processing to produce three density fractions, namely < 2.2 g/cm³, 2.2-2.7g/cm³, and > 2.7 g/cm³. All size fractions were subjected to standard proximate (ASTM 2007a), ultimate (ASTM 2009), and chemical speciation (ASTM 2002) analysis.

ARD prediction tests were carried out on the bulk (pre-separation) discard and intermediate density fraction (2.2-2.7 g/cm³) samples in order to evaluate and compare their acid generating potentials. Traditional and modified acid base accounting (ABA) procedures were carried out according to the method prescribed by Sobek (Sobek 1978, EPA 1994). These tests measure the net neutralising potential (NNP), which represents the balance between the sample's maximum acid production potential (AP) and its neutralization potential (NP). The net neutralization potential (NNP) was calculated from the difference between NP and AP. A sample is classified as acid forming when it has NNP values less than -20 kg CaCO₃/t and as non-acid forming when it has NNP values greater than +20 kg CaCO₃/t. Samples are classified as uncertain when their values range from –20 to +20 kg CaCO₃/t. These samples were also subjected to long-term humidity cell tests in accordance with the ASTM "Standard Test Method for Accelerated Weathering of Solid Materials Using a Modified Humidity Cell" procedure (ASTM 2007b). Humidity cell leach solutions were analysed over 52 weeks in terms of pH, redox potential (Eh), acidity, and concentrations of sulphate and metals (Al, Mn, Zn, Fe).

Results and Discussion

Results of the density separation tests (Fig. 1) indicate that 17 % of the coal discards has a density of < 2.2 g/cm³, 69 % a density of between 2.2 and 2.7 g/cm³, and 14 % a density of >2.7 g/cm³.

The characterization results for the bulk discards and discard fractions after density separation are shown in Table 1.

Whilst all samples had a relatively high total ash content, the low density fraction (< 2.2 g/cm³) was enriched in carbonaceous matter (16.4 % carbon) and depleted in sulfur (1.8 % total sulphur).Previous studies (Li *et al.* 2006, Li *et al.* 2011, Muthuraman *et al.* 2010) have demonstrated the feasibility of co-combusting high ash coal with carbonaceous wastes to produce energy. The majority of the pyritic sulfur (>70 %) was reported to the high density frac-





	Bulk discards	Low density fraction ¹¹⁷	Intermediate densityfraction ² ⁶⁹	High density fraction ^{3 14}	-
a) Proximate analysis %					-
Ash (%)	82.7	75.8	88.3	64.8	
Volatile Matter (%)	12.1	11.6	8.4	27.6	
Fixed Carbon (%)	3.4	10.5	1.0	6.9	
Moisture (%)	1.8	2.1	2.3	0.7	
b) Ultimate analysis %*					
C (%)	6.7	16.4	3.9	8.9	Table 1 Characteristics of
Н (%)	1.2	1.8	1.1	0.9	the downstream discards
N (%)	0.3	0.5	0.3	0.3	the downstream discurds
S (%)	6.2	1.8	1.1	37.7	samples pre-intervention
c) Forms of sulfur %					and after gravity separa-
Pyritic sulfur	6.0	1.3	0.7	32.5	tion by ferrosilicon
Sulfate sulfur	0.1	0.2	0.1	0.4	modium donao
Organic sulfur	0.9	0.3	0.3	4.8	meatum dense.

tion. This fraction had a pyritic sulfur content of 32.5 %, equivalent to 60.4 % pyrite. Pyrite roasting has been used in Brazil and it is a wellknown technology to produce sulfuric acid worldwide (Runkel and Sturm 2009). Although comprising the bulk of the discard material (69 % by mass), the pyritic sulfur content in the fraction of intermediate density (2.2-2.7 g/cm³) was relatively low (0.7 %), amounting to less than 10 % of the pyritic sulfur in the feed discards.

The results of the subsequent static ARD tests, conducted on the bulk discards (before density separation) and the intermediate density fraction $(2.2-2.7 \text{ g/cm}^3)$, are summarised in Table 2. In accordance with both the traditional and modified ABA test results, all samples were classified as acid forming. This can be attributed to the negligible neutralising capacity (NP=0) of both samples, indicative of the absence of reactive neutralising minerals such as carbonates. Nevertheless, a comparison of the static test results indicate that the fraction of intermediate density has a significantly lower acid production potential (AP) and higher net neutralising potential (NNP) than the bulk discards, which can be attributed largely to the reduced pyritic sulfur content.

The time-related profiles for the humidity cells tests (HCT) conducted on the bulk discard and intermediate density fraction samples are summarized in Fig. 2. Both samples generated slightly acidic leachates from the beginning of the tests, with pH values in the region of 4.5. These pH values continued to decline steadily, stabilising at values of approximately 2-2.5 after 30 weeks. The bulk discard sample presented with slightly lower pH values than the intermediate density fraction sample throughout the experiment. Redox potentials increased from initially low values of around 300 mV to peak values of between 550 and 600mV after 13 and 22 weeks for the bulk discard and intermediate density fraction samples respectively. Redox potentials of >550-600 mV at pH values <3 are generally indicative of rapid oxidation of ferrous iron and sulfide minerals, and are normally associated with microbial activity

	AP (kg CaCO₃/t)		NP (kg CaCO₃/t)		NNP (kg CaCO ₃ /t)	
	Trad.	Modif.	Trad.	Modif.	Trad.	Modif.
Bulk discards	217.3	196.9	0.0	0.0	-217.3	-196.9
Intermediate density fraction	35.0	22.5	0.0	0.0	-35.0	-22.5

Table 2 Static ARDprediction tests for the bulk coal discards and intermediate density fraction samples.



Fig. 2 Plot of Humidity Cells Tests profiles for the bulk discard and intermediate density fraction (2.2–2.7 g/cm³) samples.

	Bulk discards	Intermediate density fraction	Reduction (%)	
Fe (mg/kg)	7630	3338	56	
Al (mg/kg)	403	158	61	Table 3 Comparison of
Zn (mg/kg)	96	25	74	
Mn (mg/kg)	46	43	7	the accumulated release
Acidity(mg/kg CaCO ₃)	56715	24840	56	values over the 52 week
Sulfate (mg/kg)	80928	40765	50	leach period.

(Acharya et al. 2001, Hesketh et al. 2010, Kazadi Mbamba et al. 2012). The significant increases in the soluble iron, sulfate and acidity values after 13 and 22 weeks for the bulk discard and intermediate fractions respectively are consistent with the on-set of rapid and extensive pyrite oxidation at these time intervals. Similar leach profiles were obtained for the trace metals, with the on-set of rapid pyrite oxidation being accompanied by a significant increase in the soluble concentrations of trace metals (Al, Zn and Mn). A comparison of the humidity cell leach profiles for the bulk discards and intermediate density fractions indicates that the leaching of concentrations and release of acidity occurs at a faster rate and to a significantly greater extent in the case of the bulk discard sample. A comparison of the accumulated release values over the 52 week leach period (Tab. 3), confirms that density separation results in a decrease in soluble metal concentrations of up to 65 %, as well as a decrease in the release of sulfate salts (50 %) and acidity (56 %). Considering raw waste cells, at 52 weeks 7630 mg/kg of accumulated iron were leached whilst accumulated released of Mn. Zn and Al were: 46 mg/kg, 96 mg/kg and 403 mg/kg respectively. In contrast, considering processed samples, at 52 weeks 3338 mg/L of accumulated iron were leached whilst accumulated released Mn, Zn and Al were 43 mg/kg, 25 mg/kg and 158 mg/kg respectively.

Conclusions

The results of this test work show that pre-separation of coal waste discards into different density fractions has the potential to generate useful by-products for energy (density $<2.2 \text{ g/cm}^3$) and sulphuric acid (density > 2.7 g/cm^3) production, whilst reducing the amount of waste requiring disposal by 69 % (*i.e.* with a density of 2.2-2.7 g/cm³). Static and humidity cell tests indicate, furthermore, that this separated waste fraction also has a significantly lower ARD generating potential than the bulk discard sample, resulting in reduced release of metals, salts and acidity into solution over the long-term. This, in turn, will reduce the amount of neutralising reagents required and sludge produced during subsequent ARD treatment.

Acknowledgements

The authors thank Brazilian Coal Network, CNPq, FINEP and ABCM for the support provided for this research.

References

- Acherya C, Kar RN, Sukla LB (2001) Bacterial removal of sulphur from three different coals. Fuel 80: 2207– 2216
- Amaral Filho JR, Schneider IAH, Tubino RMC, BrumIAS, Miltzarek G, Sampaio CH, Schneider CH, Characterization of a coal tailing deposit for zero waste mine in the Brazilian coal field of Santa Catarina. In: Wolkersdorfer, Ch. & Freund, A (Eds) 2010 Mine Water & Innovative Thinking,Cape Breton Universty, p 639–643
- American Society for Testing and Material (2002) ASTM D 2492. Standard Test Method for Forms of Sulfur in Coal. 7pp.
- American Society for Testing and Material (2007a) ASTM D 3172. Standard Test Method for Proximate Analysis of Coal and Coke. 4pp.
- American Society for Testing and Material (2007b) ASTM D 5744: Standard Test Method for Accelerated Weathering of Solid Materials Using a Modified Humidity Cell. 19pp.
- American Society for Testing and Material (2009) ASTM D 3176. Standard Test Method for Ultimate Analysis of Coal and Coke. 6pp.
- Benzaazoua M, Bussière B, Kongolo M (2000) Environmental desulphurization of four Canadian mine tailings using froth flotation. International Journal of Mineral Processing 60 (1): 57–74
- Brazilian Mining and Energy Ministry (2010) National Mining Report 2030, Brazil, 174pp
- Hesketh AH, Broadhurst JL, Harrison STL (2010) Mitigating the generation of acid mine drainage from copper sulfide tailings impoundments in perpetuity: A case study for an integrated management strategy. Minerals Engineering 23: 225–229
- Kazadi Mbamba C, Harrison STL, Franzidis JP, Broadhurst JL (2012) Mitigating acid rock drainage risks while recovering low-sulfur coal from ultrafine col-

liery wastes using froth flotation. Minerals Engineering 29:13–21

Kontopoulos A (1998) Acid mine drainagecontrol. In: Castro SH, Vergara F, Sánchez MA (Eds) 1998 Effluent treatment in the mining industry, University of Concepciòn, 57–118

- Lengke MF, Davis A, Bucknam C (2010) Improving Management of Potentially Acid Generating Waste Rock. Mine Water Environment 29: 29–44
- Li XG, Lv Y, Ma BG, Jian SW, Tan HB (2011) Thermogravimetric investigation on co-combustion characteristics of tobacco residue and high-ash anthracite coal. Bioresource Technology 102: 9783–9787
- Li XG, Ma BG, Xu L, Hu ZW, Wang XG (2006) Thermogravimetric analysis of the co-combustion of the blends with high ash coal and waste tyres. ThermochimicaActa 441: 79–83
- Muthuraman M, Namioka T, Yoshikawa K (2010) A comparative study on co-combustion performance of municipal solid waste and Indonesian coal with

high ash Indian coal: A thermogravimetric analysis. Fuel Processing Technology 91: 550–558

- Runkel M, Sturm P (2009) Pyrite roasting, an alternative to sulphur burning. The Journal of the Southern African Institute of Mining and Metallurgy 109: 491–496
- Sapsford DJ, Bowell RJ, Dey M, Williams KP (2009) Humidity cell tests for the prediction of acid rock drainage. Minerals Engineering 22: 25–36
- Sobek AA, Schuller WA, Freeman JR, Smith RM (1978) Field and Laboratory Methods Applicable to Overburden and Minesoils. EPA 600/2-78-054, 203 p.
- US Environmental Protection Agency (1994) Acid mine drainageprediction. EPA-530-R-94-036, Washington, DC, USA, 52 pp.

Role of Professional Judgement and Scaling in Interpretation of Water Quality Model Results

Paul Beddoes¹, Michael Herrell², Jerry VANDENBERG³

¹Golder Associates Ltd., Burnaby, BC, V5C 6C6, Canada, paul_beddoes@golder.com ²Golder Associates Ltd., Burnaby, BC, V5C 6C6, Canada, mherrell@golder.com ³ Golder Associates Ltd., Kelowna, BC, V1Y 5V5, Canada, jvandenberg@golder.com

Abstract Water quality models are routinely used to identify issues of concern, develop monitoring programs, and establish mitigation strategies for mining projects. Model results are a function of several inputs which introduce uncertainty. Mass loading rates determined from laboratory tests are common inputs to water quality models. These rates require scaling from laboratory conditions to estimate ambient rates. Scaling factors introduce additional uncertainty in results and professional judgement is required in interpretation of those results. This paper presents common water quality modeling challenges associated with laboratory loading rates and scaling factors. Methods for addressing unrealistic model results and the use of professional judgement are discussed.

Keywords water quality modeling, mine water quality, best practices, scaling factors

Introduction

Water quality models are routinely used to identify key issues of concern, develop monitoring programs, and establish mitigation strategies for proposed mining projects. Results of these models are used to provide estimates of expected drainage qualities from proposed mine facilities such as waste rock piles and tailings storage facilities throughout the mine life and into closure. These estimates are based, in part, on geochemical input data from laboratory testing of mine waste material.

Mass loading rates (mass of solute released per unit mass material per unit time) obtained from humidity cell tests (HCTs) are commonly used to represent the solute mass released into water from expected mine materials (*e.g.* tailings, waste rock). Since loading rates under laboratory conditions may not be representative of ambient site conditions, results from these tests generally require some type of scaling factor when used as inputs to environmental models.

Differences between laboratory and ambient site conditions can be addressed through the use of scaling factors (Kempton 2012) that account for the following characteristics: grain size of test material (SF_{size}), channelization/ water contact (SF_{contact}), temperature (SF_{temp}), oxygen concentration (SF_{O2}), and moisture content (SF_{moist}). Kempton (2012) presented the following equation for calculating field loading rates (R_{field}), which is equal to laboratory loading rates (R_{lab}) multiplied by appropriate scaling factors:

$$R_{field} =$$

$$R_{lab} \times SF_{size} \times SF_{contact} \times$$

$$SF_{temp} \times SF_{O_2} \times SF_{moist}$$
(1)

Application of scaling factors can involve the use of any combination of these factors, and each factor can reduce the field loading rate by orders of magnitude. Therefore, developing a reasonable scaling approach is essential to predicting realistic water qualities. Site-specific information (*e.g.* temperature, precipitation) must be used to inform the approach; however, ultimately this selection of scaling factors will be based, in part, on professional judgement. The development of realistic scaling approaches can be iterative; factors may have to be added, eliminated, or modified to achieve reasonable model results. Modeling in general should also be iterative and input assumptions (*e.g.* scaling approach)should be modified to more closely represent ambient conditions as additional site data and monitoring information become available. However, water quality modeling is often based on limited information for projects that are still in planning as well as design stages.

While validation of model inputs is always preferable, it is often not possible for proposed projects. In the absence of site-specific water quality monitoring data, the reasonableness of model results can be assessed by comparing model results to expected water quality ranges provided in the literature (e.g. Plumlee et al. 1999) as well as to observed water qualities at analogous mine sites. Sensitivity analyses and multiple model scenarios can also be used to evaluate the validity of a water quality model. Multiple model scenarios can be run to evaluate water quality under a range of plausible climatic conditions, mine plan changes, or changes to other site variables. Predicted water qualities should be within, or similar to, the expected range for the deposit type for all modeled scenarios, unless site specific conditions dictate otherwise.

This paper examines the differences in water quality model results using combinations of scaling factors introduced above. A case study of a hypothetical copper mine in Arctic Canada is used to evaluate how selection of the scaling approach can affect model results.

Methods

A mass-balance water quality model was developed using the GoldSim[™] Contaminant Transport Module (GoldSim 2010) for a hypothetical project at a copper porphyry deposit in Arctic Canada. This model is described in greater detail in Herrell (2012). The model was designed to predict water quality in a collection pond downstream of a Tailings Storage Facility (TSF). The collection pond receives runoff from the TSF tailings beach area.

Average winter temperatures at site were assumed to be approximately -10 °C (October to April), and approximately 10 °C in the summer (May to September). Rainfall was assumed to be distributed from May to September. Precipitation was assumed to be pure water containing no metals. Loadings of metals from the TSF were assumed to be stored over winter and released during freshet each May. Water in the TSF collection pond was assumed to be circum-neutral. Sulphide-sulphur concentrations in the tailings were assumed to be as high as 5 %. Two precipitation scenarios were used to evaluate model sensitivity to climate (Table 1).

Hypothetical HCT results representative of tailings material from a porphyry deposit were used to develop mass loading rate inputs to the model. For the purposes of this paper, model inputs and results are limited to three parameters: copper, iron, and zinc. Inputs are presented in Table 2.

The synthetic loadings rates are used to determine field loading rates for input to the water quality model using Equation 1. The laboratory loading rate was calculated as the average measured loading rate over the 56th to 60th week. The scaling factors used to calculate the field loading rates are presented in Table 3.

Ν	Nodel Scenario	Precipitation (mm/a)	Evaporation (mm/a)	TSF Footprint (km²)	TSF Collection Pond Area (km ²)	Pond Capacity (m ³)
А	Net Surplus	840	550	1.0	0.1	115,000
В	Net Evaporative	400	550	1.0	0.1	115,000

 Table 1 Model Sensitivity Analysis Details.
Grain size (SF_{size}) and moisture content (SFmoist) factors were not included in the water quality model. The tailings grain size in the HCT is expected to be similar to tailings deposited in the TSF at site and the moisture content of the tailings is not expected to be low enough to warrant scaling based on moisture content.

To evaluate model output sensitivity to application of these scaling factors, several model simulations were performed using different combinations of the scaling factors presented in Table 4. There is a range of reasonvalues able SFO2 in rock with а sulphide-sulphur concentration of $\approx 1-5$ % (Kempton 2012). Two simulations were performed to evaluate model sensitivity using SF_{O2} values of 0.2 (SF_{O2-A}) and 0.5 (SF_{O2-B}).

Results

Monthly maximum predicted metal concentrations in the TSF collection pond water for two climate scenarios (Table 1) and four scaling factor simulations (Table 4) are illustrated in Fig. 1. Results are compared to expected concentrations in circum-neutral drainage from copper porphyry deposits presented in Plumlee *et al.* (1999).

The following observations can be made based on the water quality model results:

- Iron concentrations were within the expected range for copper porphyry deposits for both climate scenarios and all model simulations.
- When only a channelization factor (SFcontact) is applied, the maximum predicted concentration of copper is above the expected range for copper porphyry deposits for both climate secnarios, while the maximum predicted concentration of zinc is above the expected range for copper porphyry deposits in the net evaporative climate scenario (Scenario B).

Parameter	Units	Week	Week	Week	Week	Week	Model Source
		56	57	58	59	60	Term (R _{lab})
Copper (Cu)	mg/kg/week	0.0018	0.0023	0.0029	0.0026	0.0028	0.0025
Iron (Fe)	mg/kg/week	0.017	0.022	0.023	0.019	0.025	0.021
Zinc (Zn)	mg/kg/week	0.00012	0.00011	0.00012	0.00011	0.00012	0.0012

Results are hypothetical based on a one kilogram charge sample and one litre of water flushed per week.

Model source term is based on the average of the last five weeks of testing.

Scaling Fact	or	Value	Description/Rationale					
Channelization/ Water Contact	$SF_{contact}$	0.1	Reflects the difference in flow pathways under laboratory relative to ambient conditions. Synthetic loading rates reduced by a factor of 10 to account for preferential flow paths.					
Temperature	SF_{temp}	0.37 (Summer) 0.04 (Winter)	Calculated using the Arrhenius equation* to account for differences in reaction rates between laboratory (20 °C) and ambient temperatures (MEND 2006).					
Oxygen Content	SF ₀₂	0.2, 0.5	Reflects differences in oxidation rate due to oxygen content in test conditions relative to ambient; factors between 0.2 and 0.5 are reasonable in high sulphide conditions (Kempton 2012).					

Table 2 Hypothetical Geochemical Source Terms.

*An activation energy of 69 kJ/mol was used

Table 3 Scaling Factors Used in Water Quality Modeling of a HypotheticalCopper Mine in Arctic Canada.

Simulation	Scaling Factors Applied
1	SF _{contact}
2	$SF_{contact}, SF_{temp}$
3	SF _{contact} , SF _{temp} , SF _{O2-A}
4	SF _{contact} ,SF _{temp} , SF _{O2-B}

Table 4 Model Simulations Using Various ScalingApproaches.

- Maximum predicted concentrations for all modeled parameters are within the expected range for copper porphyry deposits when both the channelization (SF_{contact}) and temperature (SF_{temp}) scaling factors are applied for both climate scenarios.
- If $anSF_{O2}$ factor of 0.5 (SF_{O2-B}) is applied with the channelization ($SF_{contact}$) and temperature (SF_{temp}) factors, copper, iron and zinc concentrations are within the expected range for copper porphyry deposits for both climate scenarios.
- When a lower oxygen content scaling factor (SF_{O2-B} = 0.2) is applied with the channelization (SF_{contact}) and temperature (SF_{temp}) factors, the maximum predicted concentration of copper is below the expected range for copper porphyry deposits for both climate scenarios.

• Depending on the selection of scaling factors, model results can vary by almost two orders of magnitude.

Discussion and Conclusions

Selection of an appropriate scaling method can be challenging because site-specific information may not be available when scaling factors need to be determined. Therefore, professional judgement is used to select scaling factors based on the available information and the current understanding of the system being modeled. Depending on site conditions, some scaling factors may be inappropriate, while others are necessary to develop a reasonable representation of the system.

To evaluate whether water quality model results are reasonable, they can be compared to the range of drainage water quality from similar deposit types (Plumlee *et al.* 1999) or to analogous mine sites. Plumlee *et al.* (1999) presents a range of natural drainage chemistries from mineralized zones of several deposit types. While this information does not directly represent the operational drainage water quality from a mine site, it provides a useful benchmark to assess the reasonableness of model results in the absence of sitespecific water quality.



Fig. 1 Maximum predicted metal concentrations in TSF collection pond water for climate scenarios A (net surplus, left) and B (net evaporative, right). Results are compared to expected concentration ranges for circum-neutral drainage presented in Plumlee et al. (1999) for copper porphyry deposits (boxes).

A comparison of application of different scaling factors indicates that model results can be sensitive to the use of different scaling factors. When only a channelization factor (SF_{contact}) was applied to scale loading rates, predicted maximum concentrations of copper and zinc were above the expected range of concentrations for porphyry copper deposits (Fig. 1). As expected, simulated concentrations decrease as additional scaling factors (*i.e.* SF_{temp} and SF_{O2})are applied.

Due to the sensitivity of water quality model results to scaling factors (Fig. 1), it is the role of the modeler to exercise professional judgement, not only when selecting which factors to apply, but also when determining the value for each scaling factor. For example, when an SF_{O2} of 0.5 was applied to HCT loading rates, maximum copper and zinc concentrations were within the expected range for copper porphyry deposits (Plumlee et al. 1999). However, concentrations of copper and zinc were less than the minimum concentrations for this deposit type when the SF_{O2}was decreased to 0.2 (Fig 1). Based on the model assumptions, both of these factors would be considered reasonable (Kempton 2012).

Given the large range of possible model results (*i.e.* orders of magnitude) that can result from the use of different scaling factors, the results of such an exercise can be presented as a sensitivity analysis when there is uncertainty about which rate to apply. In doing so, the modeler can present the most plausible realizations or results as being "likely", whereas upper and lower bounds can be presented as "unlikely" or "possible". Mine water managers can thus be made aware of the uncertainty inherent in such model predictions, and decisions regarding monitoring and mitigation will be more well informed.

Model development is an iterative process. Water quality models are often initially developed using conservative assumptions and if the model results indicate that the projected water quality is unreasonable, further refinement to the model assumptions is required. This is usually addressed through the modification of scaling factors. However, it is not the purpose of scaling to adjust model results until they match an expected water quality but rather, to generate reasonable and conservative representations of systems being modeled. Water quality models should be frequently updated throughout the life of mine with operational water quality monitoring results. This way, the results can be validated or corrected through refinement of model input assumptions, such as scaling factors that are often initially selected based on professional judgement.

It has been shown, using a water quality model for a hypothetical TSF, that use of inappropriate scaling factors can lead to unrealistically high or low water quality results when compared to the range of drainage water quality for a copper porphyry deposit (Plumlee *et al.* 1999). Despite limited site information, a reasonable scaling approach can be selected using professional judgement. Even in the absence of site-specific, field measurements, this approach can be used to produce realistic and conservative water quality results which can be used to inform decision making processes in planning and permitting of mining projects.

References

GoldSim (GoldSim Technology Group) (2010) GoldSim User's Guide.Version 10.5.

- Herrell MK, Salzsauler K, McRae C (2012) A Practical Application of Mass-Balance Methods for Predicting Mine Drainage Water Quality – Climate Influences and Best Practices. Proceedings of the9th International Conference on Acid Rock Drainage (ICARD), Ottawa, Ontario, Canada, May 20 – 26, 2012.
- Kempton H (2012) A Review of Scale Factors for Estimating Waste Rock Weathering from Laboratory Tests. Proceedings of the 9th International Conference on Acid Rock Drainage (ICARD), Ottawa, Ontario, Canada, May 20 – 26, 2012.
- Mine Effluent Neutral Drainage Network (MEND) (2006) Update on Cold Temperature Effects on Geochemical Weathering. MEND Report 1.61.6, October 2006.

Plumlee GS, Smith KS, Montour MR, Ficklin WH, Mosier EL (1999) Geologic Controls on the Composition of Natural Waters and Mine Waters Draining Diverse Mineral-Deposit Types. In: Reviews in Economic Geology, Society of Economic Geologists (SEG), 1999, pg. 373 -407.

Hydrogeochemistry of the Mine Water from "Bochnia" Salt Mine (Kraków Region, South Poland)

Andrzej Bezkorowajny¹, Mariusz CZOP², Bernadetta STOCHEL³, Magdalena WORSA-KOZAK³

¹AB&Flint, ul. Glowackiego 18a, 32–800 Brzesko, Poland, abflint@poczta.onet.pl ²AGH University of Science and Technology, al. Mickiewicza 30, 30–059 Krakow,Poland, mariucz@agh.edu.pl ³KGHM Cuprum R&D Centre, ul. Gen. Wl. Sikorskiego 2–8, 53–659 Wroclaw, Poland, bstochel@cuprum.wroc.pl, mworsa@cuprum.wroc.pl

Abstract "Bochnia" salt mine, located about 40 km east from Kraków, is one of the world oldest mines with about 765 years old history. The amount of water inflow into the mine from the surrounding rocks range from 9.11 to 14.59 m³/d, averaging 11.24 m³/d. Total dissolved solids in the mine water from "Bochnia" mine range from 5.6 g/L to about 311 g/L. The lowest values of the TDS are observed for the inflows in the shallow mining levels and highest TDS in a deepest levels. As a consequence of salt dissolution mine water possessed Na-Cl type.

Keywords hydro-geochemistry, mine water, salt mine, Bochnia, Poland

Introduction

"Bochnia" salt mine is located in the south of Poland about 40 km east from Kraków (fig. 1). It is one of the world oldest mines, operating continuously since 1248. Rock salt mining was indeed finished in 1992, but the operations related to maintaining the mining infrastructure have been still carried on, since the mine is now a tourist facility with a big accommodation, didactic and spa center. "Bochnia" mine has three shafts Trinitais, Campi and Sutoris, and their openings are located at the depth from 76 m to 330 m below the surface.

"Bochnia" salt mine is located within the



Wolkersdorfer, Brown & Figueroa (Editors)

series of practically impermeable rocks. However, some water from the rocks surrounding the mine, mainly from the overburden, inflows into the mine. The water inflow to the salt mine is potentially dangerous for stability of the ground over underground workings. As a consequence of the intensive salt dissolution catastrophic events with mine and surface failures were observed in the past. In Poland in the 1970s the Wapno Salt Mine located in a salt dome was completely destroyed by the catastrophic inflow of low TDS groundwater from gypsum-clay cap formation. In the 1990s also the famous Wieliczka Salt Mine had the event with hazard inflow of groundwater originating from the outside surrounding rocks not related to the impermeable gypsum-clay cover formation. The methodology of detailed research on the groundwater inflows, hydrogeochemistry and isotopic composition was started in Polish salt mining industry after Wapno Salt Mine catastrophe. This research is especially important for the historical mines (Wieliczka and Bochnia) which are operating also as tourist centers.

Geology and Hydrogeology

"Bochnia" salt deposit occurs on the Carpathian Foredeep, in its south part within the so-called allochthonous Miocene folded on Carpathian foreland. The equally famous "Wieliczka" salt mine is located there as well, about 30 km west from Bochnia (fig. 1).

"Bochnia" salt mine is located in the north side of the steep fold (Bochnia fold) within allochthonous Miocene (fig. 2). The Miocene formation is represented by claystone with silty and sandy intercalations (over-salt series – Chodenice beds), gray claystones with salt and anhydrite (salt series) and claystones (Skawina beds) underlying the salt series. In the core of Bochnia anticline, additionally flysch (Cretaceous-Tertiary) rocks composed of the alternating beds of sandstones and claystones occur there (Garlicki 1968, Wagner *et al.* 2010).

"Bochnia" salt mine is located within the series of claystones, which are practically impermeable. However, some water from the rocks surrounding the mine, mainly from the Quaternary formations, Chodenice beds (Tr) and flysch rocks (Cr-Tr) being a part of Bochnia anticline core, inflows into the mine.

Mine Water

Inflow of water from the layers occurring above the deposit formation takes place through the old workings or abandoned shafts since lots of them have been excavated during 765 years of mining operations. Most of those excavations have been self-closed by collapse or compression, but those areas are the preferred ways of underground water flows, allow-



Fig. 2 Geological cross-section of the "Bochnia" salt deposit (Garlicki 1968)



Fig. 3 Scheme of the groundwater inflow zones to the "Bochnia" salt mine

ing the inflow of infiltration waters directly from the surface (fig. 3).

The amount of water inflow into the mine from 2001 to 2011 ranged from 9.11 to 14.59 m³/d, averaging 11.24 m³/d. Main inflows into "Bochnia" salt mine are concentrated on the shallowest mining level *i.e.* Danielowiec level. Only part of this inflow is directly taken, while the rest of water penetrates down to the deeper parts of the mine.

Mine Water Chemistry

Chemical composition of the water inflowing into "Bochnia" salt mine is very varied. Total of dissolved solids in the mine water from "Bochnia" mine range from 5.6 g/L to about 311 g/L (Table 1). The chlorides and sodium are of the highest values among all other elements and impacts strongly the water TDS. Chlorides in mine water from "Bochnia" mine range from 1.4 g/L (D-1) to 190.1 g/L (A-5). In the same

Consulato	14/4	TDS	Na	К	Li	Ca	Mg	Sr	SO_4	HCO ₃	CI	SiO ₂		
SampleiD	wtype	[g/dm ³]	[mg/dm ³]											
A1	Na-Cl	287.4	109096.4	348.5	3.5	613.7	1089.5	15.4	5474.1	346.6	170408.3	2.64		
A2"	Na-Cl	257.7	95310.1	143.8	1.3	643.8	435.1	13.3	2908.7	137.1	158045.2	1.38		
A3	Na-Cl	267.6	98529.4	273.6	3.6	665.6	916.2	15.6	5612.6	266.4	161600.4	2.48		
A4	Na-Cl	261.9	101360.4	262.8	3.9	456.6	1000.0	10.8	4397.1	256.1	154106.7	1.65		
A5	Na-Cl	311.1	112280.8	577.4	9.0	1254.9	1972.6	34.7	4660.6	129.3	190121.9	1.46		
A6	Na-Cl	260.1	93402.6	625.0	11.7	1045.0	1339.8	25.8	3078.0	294.8	160260.1	2.05		
D1	Na-Cl	26.6	8681.4	147.9	0.8	607.9	177.4	11.3	3842.9	605.2	13063.75	13.71		
D10	Na-Cl	234.3	86583.3	110.4	1.7	769.4	438.3	10.5	2965.6	256.1	143104.2	1.09		
D11	Na-Cl	310.9	118200.7	248.2	4.0	855.0	603.5	22.6	6619.6	170.7	184321.6	1.14		
D12	Na-Cl	281.2	104901.7	173.2	2.8	615.2	442.6	16.7	4729.0	178.5	170314.0	2.42		
D13	Na-Cl	305.1	112830.3	319.9	4.1	920.3	473.7	25.8	5604.1	131.9	184894.4	1.32		
D14	Na-Cl	161.9	58067.8	694.9	6.7	3171.7	645.4	100.4	2936.8	121.6	96170.9	7.53		
D2	Na-Ca-Cl-SO ₄	5.1	1139.1	19.0	0.1	601.4	66.2	8.2	1693.3	488.8	1491.9	24.56		
D3	Na-Cl	34.5	11450.7	125.0	0.9	752.1	204.8	13.9	4882.8	615.6	17087.4	6.59		
D5	Na-Cl	57.0	19081.4	145.4	1.2	1289.2	334.4	31.4	4176.0	1761.3	31722.8	11.63		
K1	Na-Cl	288.5	106143.8	154.3	2.6	692.7	654.5	16.6	6772.2	239.2	174009.9	1.07		
Kanalek	Na-Cl	305.5	109938.6	454.5	9.1	500.9	1553.0	16.6	9943.7	253.5	183035.1	0.86		
OS1	Na-Cl	308.6	115279.0	300.2	3.0	1073.5	888.6	23.8	5229.5	175.9	185610.5	1.13		
P2	Na-Cl	304.2	106995.8	774.8	10.3	630.7	2755.1	22.3	7812.3	162.9	185041.4	1.55		
P3	Na-Cl	308.1	112593.0	769.4	9.6	879.0	2062.2	24.0	6127.6	186.2	185467.3	1.55		
P4	Na-Cl	303.5	111553.6	770.8	7.9	876.0	2149.2	25.5	5983.3	385.4	181743.6	5.37		
P5	Na-Cl	308.7	114689.0	783.2	9.7	913.2	1952.1	30.2	6077.6	240.5	183963.5	3.83		
Pompownia	Na-Cl	266.5	99054.7	434.8	3.7	1100.8	1483.6	21.0	4025.7	232.8	160046.1	12.18		
Regis	Na-Cl-SO ₄	67.9	22554.6	389.3	3.7	671.4	485.8	13.4	12699.2	266.4	31080.8	3.69		
SO2	Na-Cl	311.1	115200.4	606.7	11.0	1518.8	2039.5	44.2	4069.1	212.1	187329.1	68.68		
W1	Na-Cl	292.4	106044.1	185.9	1.5	1008.9	519.9	19.8	4244.0	297.4	180169.8	0.10		

Table 1 Mine water chemistry for the samples from "Bochnia" mine. inflow (D-1), the minimum concentration of sodium, equal to 1.1 g/L (D-1) was also observed, but the maximum value of this constituent, about 118.2 g/L, was measured in the D-11 inflow.

A relatively high concentration of sulfate, observed in the concentration between 1.7 g/L (D-2) and 12.7 g/L (Regis) is an important feature of the mine water from "Bochnia" mine is. In case of this sample, sulfate ion is incorporated into the water type so D-2 sample is a Na-Ca-Cl-SO₄ type and Regis sample is of Na-Cl-SO₄ type. Calcium and magnesium concentrations in all samples vary with the wide range, from dozens to a few hundreds mg/L to about 1–2 g/L.

The chemical composition of the mine water from "Bochnia" mine results from dissolution process of halite (Na Cl). Water inflowing to the underground working from the surrounding rock formation in contact with Na Cl increased the concentrations of chloride and sodium, and also TDS. Longer residence time of water within the mine workings increases the amount of dissolved salt. So, all mine water samples form "Bochnia" mine are located on



Fig. 4 Chloride and sodium concentrations in mine water from "Bochnia" mine

the theoretical line of the halite (Na Cl) dissolution (fig. 4).

Halite dissolution is the main process of mine water chemistry formation in case of "Bochnia" mine, but other processes, especially in the shallow part of the mine are also important. Inflow of the groundwater from the overlaying formations to the mine's underground workings is connected with complete change of hydrogeochemistry. The sample D-2 from Danielowiec level has the lowest TDS, in the whole population of the samples, and this state is certainly connected with its origin from the Quaternary aquifer (sands and sandy loam). The water type in this point Na-Ca-Cl-SO₄ indicates that a process of dissolution both of halite and also gypsum is occurring.

Groundwater from the Quaternary deposits flow to the mine through fracture or discontinuity zones within gypsum-clay cover formation. Changes of the Quaternary water within "Bochnia" salt mine in the shallow Danielowiec level occur not only due to successive dissolution of halite (Na Cl) but also magnesium salts, mainly sulfate (MgSO₄). According to this process the increasing trend of the Mg/Ca ratio can be observed in the population of the Danielowiec level samples. Increasing trend in magnesium concentrations with relation to calcite is also connected with limitation of Ca level by gypsum solubility. In a spite of relative increase of Mg/Ca ratio the intensive dissolution of relatively pure halite results in decreasing of Mg/Na ratio(fig. 5).

Population of the mine water samples collected in the deeper levels of "Bochnia" mine originate from the Quaternary groundwater inflows to the main shafts (Sutoris, Regis, Gazaris and Bochneris). The water sample with lowest TDS for this group was collected in the Regis shaft and it shows chemical composition similar to the samples from the shallow Danielowiec level. In the deeper part of the mine the increasing admixture of magnesium salts in the halite is responsible for the increase of the relative concentrations of magnesium (or increase of Mg/Ca ratio; fig. 5). At



Fig. 5 Relative concentrations of main ions in the mine water samples

the highest concentration of magnesium and sulfate, the calcium level is limited by solubility of gypsum, and decreases to about a few hundreds of mg/L (Table 1). The trend of the Mg/Na ratio increase resulting from halite dissolution can be also observed but it is not so clear. It occurs due to large impurity of salt and increasing admixture of magnesium and potassium evaporate salts.

Conclusions

The lowest values of the TDS have been observed in the mine water inflows to the shallow mining level of "Bochnia" mine – Danielowiec, located at the depth of about 60– 70 m. The group of the three inflows (D1, D2 and D3) with the lowest TDS between 5.6 g/L and 34.5 g/L is located close to the Regis shaft. This zone is known as possible hazard for mining galleries due to the inflow of slightly mineralized groundwater from the Quaternary aquifer, aggressive to the salt formation.

The next zone with low water TDS (inflow D5 - 57 g/L) is connected with the vicinity of the Gazaris shaft and also with the inflow of the Quaternary groundwater. Groundwater

from the Quaternary aquifer inflowing into the zone of Sutoris and Gazaris shafts and migrating to the deeper parts of "Bochnia" mine is responsible for formation of the inflows with TDS of about 260–270 g/L at the August level located at the depth of 160–170 m.

Groundwater inflowing to the "Bochnia" mine from the Cretaceous flysch formation is observed also in the southern part of the mining area. The origin of the three inflows with the TDS between 160–260 g/L, located in the Danielowiec and August levels is strictly connected with Cretaceous groundwater. Total of dissolved solids in the other water inflows in the mining galleries of the "Bochnia" mine ranges from 280 g/L to 310 g/L. The origin of these inflows is connected with percolation of the natural and also artificial water (e.g. from drilling and mining operations) in the mining galleries. Low flow of water and also contact with salt formation is responsible for the origin of saturated brines.

Analysis of the water chemistry from inflows to the "Bochnia" salt mine is an important factor in safety of mining operation. Inflow of the groundwater, especially with low TDS is potentially dangerous for stability of the ground in the vicinity of the mine (geotechnical problems). The main hazard for the "Bochnia" mine is connected with possible activation of the groundwater inflow from the Quaternary aquifer in the zone of shafts. Water chemistry analyses in the inflow are an important element of the failure preventing monitoring system.

Water chemistry of inflows in the shaft zones is relatively stable over the time. Groundwater from Quaternary aquifer dissolved some amount of evaporate minerals (halite and dolomite) in the border zone of "Bochnia" salt deposit. Small recharge of salt formation by the groundwater from Quaternary aquifer is a reason for minimizing the possible failure hazard in "Bochnia" mine.

Acknowledgements

This work was supported by research program no. 501-02-0006-0-08-B/07/0657.001 of the KGHM Cuprum R&D Centre. We thank an anonymous reviewer for useful suggestions and editorial changes, which improved the manuscript.

References

- Bezkorowajny A, Stochel B (2012) Hydrogeological conditions documentation of the "Bochnia" Salt Mine. Report (in Polish).
- Garlicki A (1968) Autochthonic salt formation within Carpathian Foredeep Miocene in the area of Skawina and Tarnów. Bull. PIG, 215 (in Polish).
- Osika R (1970) Geology and mineral resources of Poland. Wyd. PIG, Warszawa (in Polish)
- Wagner M., Bukowski K., Stochel B (2010) Petrological character of lignite (brown coal) from Badenian salts in the Bochnia Mine (Southern Poland). Geological Quarterly, 54(4):439–448.

Process sustenance in an organic carbon exhausted chemo-bioreactor by sweetmeat waste dosing

Jayanta BHATTACHARYA, Bidus Kanti DAs

Department of Mining Engineering, Indian Institute of Technology Kharagpur, India, 721302 jayantaism@gmail.com, bidus123@gmail.com

Abstract External organic carbon was added into nutrient exhausted spent mushroom compost (SMC) substrate in a reactor designed for sulfate reduction. Sweetmeat waste (SMW) supplementary was used as organic carbon dose. Tracer study established moderate dispersion in the reactor. Pulse dosing experiment showed that consistent 60 % sulfate reduction is possible even in a deficient matrix. Maintaining pH by NaHCO₃ in the reactor was found effective than using quick lime.

Keywords Compost reactor, nutrient exhaustion, external organic carbon dosing, sweetmeat waste

Introduction

Treatment of sulfate-rich waste water is a common practice in mining industries where sulfate, dissolved metals and low pH are a major concern. Passive remediation strategies have been adopted by scientists and researchers for low sludge production and cost effectiveness. Along with other microbial species, sulfate reducing bacteria (SRB) play a major role by reducing sulfate to sulfide with simultaneous alkalinity generation. Successive alkalinity producing systems (SAPS) have been remodelled as a chemo-bioreactor with a view to field application. Selection of the reactor matrix in these systems is related to the biodegradability of the material and longevity of the system. Mainly cellulosic and lingo-cellulosic waste materials have been used for their microstructure of microbial attachment and availability of readily exploitable nutrients. Plant-based waste materials have been characterized and successfully utilized (Coetser et al. 2006). These materials contain abundant lignin (10 to 28 %) with easily biodegradable substrates for biological sulfate reduction. Lignin is one of the recalcitrant substances, and its slow biodegradation by limited microbial species makes it suitable for preparation of a skeleton for biofilm development. In the reactor process, lignin present in the matrix acts as the long-term attachment site for microbes (Das *et al.* 2012), which reside where they can collect nutrients from their surroundings.

One of the limitations of using these plant waste based matrices in treatment systems is the depletion of available nutrients, especially organic carbon, after a limited period of use. Depending on the nature of waste used, available organic carbon was exhausted from these matrices after certain period of use (Coetser et al. 2006; Das et al. 2012). However, the lignin portion, which serves as the attachment site for active biofilm, remains unaltered. During operation, it is not feasible to replace the exhausted organic-carbon matrix due to the length of time required to establish an active biofilm. Introduction of an external supply of organic carbon into the reactor is a preferable engineering option to sustain the reactor.

Selection criteria for an external organic carbon source for the reactor include the biodegradability, availability and cost effectiveness of the material. Pure and synthetic materials are reported to be readily utilized by SRB (Das *et al.* 2013). However, use of pure or synthetic materials at the large scale of the reactor would be cost prohibitive. Recently, food waste has been tested as a possible alternative because it is readily available at low cost in most areas (Das *et al.* 2013).

Sweetmeat waste (SMW) is produced in high amount in the Indian subcontinent. These materials contain high sucrose along with readily SRB degradable organic acids (Das et al. 2013). Successful application of SMW has been tested in batch mode for biological sulfate reduction with suitable nitrogen supplementation. Sulfate reduction is reported to occur in a continuous reactor with sucrose as the sole source of organic carbon (Lopes et al. 2010; Bertolino et al. 2012). Sulfidogenesis and acidogenesis can take place simultaneously in sucrose fed reactor without any observed interference (Mizuno et al. 1998). However, a pH balance is always preferable to prevent the process shifting towards acidogenesis.

The objective of the study was to investigate the possibility of performance continuation in an organic carbon exhausted spent mushroom compost reactor using an external supply of sweetmeat waste as the organic carbon source. Efficacy of quick lime and NaHCO₃ as the neutralizing agent was also tested during the dosing process.

Methods

The tubular reactor (58 × 3.85 cm) used in this study was made of an acrylic sheet with steel adaptors at both ends (Fig. 1). The working volume in the acrylic sheet column was 674.868 mL. A stainless steel mesh (1 mm pore diameter) was placed in the junction for better flow dispersion. Butyl rubber tubing was used over the mesh to minimize the oxygen flux. All joints of the reactor were sealed with Teflon tape. Two ports, one for dosing and another for sampling, were situated in the adapters, closed with a removable rubber cork. Flow was regulated with a peristaltic pump. Silicone tubing with stoppers was used to connect the reservoir, column and effluent container.

The column was packed with 80 g of autoclaved spent mushroom compost, collected from a household farm after mushroom cultivation. Porosity of the reactor bed was calculated as 0.6347, leaving 428 mL of void volume with a mass density of 0.1185 g/cm³.

Tracer pulse input was used to obtain the residence time distribution (RTD) characteristics of the SMC packed column. A similar column, packed with same amount of SMC, had a porosity of 0.6293. It was washed with 50 bed volumes of Milli-Q water (conductivity of $0.33 \,\mu$ S/cm) with a hydraulic retention time (HRT) of 18 h. A conductivity tracer test was performed using a NaCl solution (3.5 g/L) injected at the bottom dosing port using a Dispovan syringe. The flow rate during tracer test was 41 mL/min, resulting in a theoretical HRT of 626.25 seconds (0.17395 h). The conductivity at the outlet was measured online using a conductivity probe in a multi-parameter water analyzer.

The inoculum was previously acclimatized with sweetmeat waste (SMW) containing media for 6 months. Inoculum used for the reactor was maintained in anaerobic water (100 mL/L reducing agent supplement and 2.1 g/L NaCl) with 1 mM bromoethane sulfonic acid containing a total cell count of 2.26×10^{11} (±8.256×10⁹)/mL, with SRB of 6.89×10^8 MPN/mL and fermentative bacteria of 1.64×10^8 MPN/mL, respectively. Reducing agent supplement (RAS) was prepared with



Fig. 1 Column reactor used in the experiment. (A) The reactor during continuous operation with dosing; (B) Dosing port; (C) Adapter with steel mesh and butyl rubber tubing; (D) Spent mushroom compost; and (E) Sweetmeat waste.

7.5 g/L of both Na-thioglycollate and ascorbic acid.

After packing, the column was purged with N_2 (99.99 %) Three bed volumes of RAS (pH 7.5) containing 7.5 g/L each of ascorbic acid and Na-thioglycollate were passed slowly through the column, with HRT maintained at 36 hours. Inoculation of the reactor was done by passing two bed volumes of inocula through the colum. To facilitate biofilm development, the reactor was covered with black paper to prevent light penetration, and maintained at batch mode for 3 weeks.

Continuous operation of the reactor was started after the static stage with an initial HRT of 36 hours, and was gradually decreased to a HRT of 18 hours after four days. Feed solution was composed of (g/L) Na₂SO₄, 2.1; FeSO₄.7H₂O, 0.025; MgCl₂.6H₂O, 0.125, and pH 7.2 \pm 0.1 was maintained by using a NaOH solution. The operation continued for 3 months, after which the operation was ended due to lack of sulfate reduction.

Dosing of SMW as an external organic carbon was initiated at that time. The reservoir solution was prepared as follows (g/L): Na₂SO₄, 2.1; FeSO₄.7H₂O, 0.025; MgCl₂.6H₂O, 0.125; trace-element solution, 10 mL; pH was maintained at 7.4 by adding 1.4 g/L NaHCO₃. This experiment continued for 30 days.

For the evaluation of an improved alkaline supplement, another 35 day experiment was performed replacing NaHCO₃ with quick lime in the reservoir sample. Exactly 0.48 g/L quick lime was required to provide the desired pH (7.4). However, a slight change in the quick lime concentration was found to result in a drastic change in solution pH; as a result, the reactor was operated with a NaHCO₃ neutralized reservoir solution for 15 days.

HRT was kept at 18 h throughout the dosing experiment, resulting in a superficial flow velocity of 1.84 cm/h. The mass SO_4^{-2} loading rate was 816±4 mg/d. In every 24 h interval, 10 mL of SMW solution was dosed into the reactor through the dosing port using a sterile Dispovan Syringe. The dosing solution was pre-

pared with filtered 1:10 (w/v) SMW solution comprised of (per litre): NH₄Cl, 17.549 g; K₂HPO₄, 1.679 g and vitamin solution, 15 mL. The dosing solution had chemical oxygen demand (COD) of 81600 mg/L, and hence, the ratio of mass COD dosing/d to mass SO_4^{-2} loading/d was maintained at 1.

Filtered (0.22 µm cellulose nitrate membrane) samples were used for analytical purposes except for pH and conductivity. Sulfate concentrations, acidity (to pH 8.3 by NaOH), alkalinity (to pH 4.5 by HCl), chemical oxygen demand (COD; spectrophotometric), dissolved sulfide (titrimetric) and total organic carbon (TOC) were the parameters analyzed in the experiment.

Results and Discussion

Hydraulic characteristics of the reactor were studied throughout the pulse input tracer test. The test was carried out in triplicate, mean values were taken and tracer response curves were prepared. Each curve was analyzed for mean residence time and variance, and the dispersion number (d) was calculated (Metcalf and Eddy 2003) to be 0.07583, indicating moderate dispersion in the reactor. Lack of dispersion might allow maximum time for substrate conversion; however, it can also inhibit bacterial activities due to high substrate concentration. On the other hand, high dispersion might result in short-circuiting. Hence, an intermediate level of mixing could be preferable.

Continuous flow was started after 3 weeks of static period. At the end of the static mode there was high alkalinity, pH, dissolved organic carbon (DOC), and dissolved sulfide present in the effluent with almost all sulfate reduced (Fig. 2).

Released DOC facilitated the biofilm development and sulfate reduction. By SRB metabolism, bicarbonate was produced that subsequently increased the alkalinity of the water. After initial inequilibrium due to flow continuation, the reactor produced enhanced performance when it was able to reduce 85 to 96 % of influent sulfate. Adequate DOC and dissolved sulfide was also observed in the effluent during this period. However, after 11th week, sulfate reduction process slowed down resembling lesser DOC content. Exhaustion of SRB degradable DOC, halted the process after some instances is a common phenomenon in SMC packed reactor reported earlier (Das *et al.* 2012).

Earlier we proposed external addition of organic carbon into an exhausted SMC reactor would sustain the process. SMW was characterized for this purpose. It contained high sucrose along with easily SRB utilizable organic acids. Adequate sulfate reduction was reported with SMW as organic carbon source in batch study (Das *et al.* 2013).

SMW media was added as pulse dose, initially into the reactor at that point of time. Theoretical HRT was set for 18 h and the dosing interval was maintained at 24 h. Sulfate loading rate was kept constant. Sulfate concentration in the effluent started to decrease gradually after the dosing experiment started (Fig. 3).

For the first 7 days of the dosing experiment, sampling was performed as follows: in each 2 h interval up to 16th hour after dosing, each 30 min interval for 16th to 21st hour and each 1 h interval from 22nd to 24th hour. Maximum sulfate reduction was achieved between 17.5 h to 20 h after dosing, peaking at the 19th hour. The sample taken during the 18.5 h to19.5 h exhibited maximum sulfate reduction.After each dosing, effluent samples were continuously taken for 24 h till the next dosing. The grab samples were taken from time to time account for other analyses. Throughout the experiment, when reservoir pH was maintained by NaHCO₃, maximum sulfate reduction was more than 60 % and overall sulfate reduction was near 60 % (Fig.3A). pH of the effluent was maintained consistently near 8.0, with high alkalinity ranging from 800 to 1100 mg/L as CaCO₃ and little acidity of 10 to 30 mg/L as CaCO₃ (Fig.4).

Sulfate reduction of 350 to 470 mg/d in average was achieved against 550 to 650 mg/d COD and 150 mg/d TOC consumption during this experiment. Dissolved sulfide in the effluent was 90 mg/L in average (Fig. 3B).

After the acceptable sulfate reduction with external SMW dosing, the reservoir solution composition was changed to observe the effect of the neutralizing compound, and NaHCO₃ was replaced with quick lime. However, during the course of the experiment, sulfate reduction did not reach the desired level, with the maximum sulfate reduction value hardly reaching 20 %, and overall sulfate reduction was around 10 % (Fig. 5A).

This observation can be explained by the buffering difference of the two reservoir sam-



Fig. 2 Effluent characteristics of the reactor without external organic carbon dosing (A) pH, acidity, alkalinity, chemical oxygen demand (COD), dissolved organic carbon (DOC) and dissolved sulfide; (B) Mass loading and effluent rate of sulfate and sulfate reduction(%).



Fig. 3 Parameters during 1−30 day of dosing experiment (pH in the reservoir maintained with NaHCO₃). (A) Mass sulfate loading and effluent rate with sulfate reduction (%) (B) Mass COD and TOC loading and effluent rate with effluent dissolved sulfide concentration

ples. In NaHCO3 supplemented reservoir solution, acidity and alkalinity content were 29.375 ±0.625 and 665.625± 5.413 mg/L as CaCO₃. These values were 1.146±0.1 and 13.958±0.21 mg/L as CaCO₃ respectively when the solution pH was maintained with quick lime. Also, bicarbonate is a better buffer in the pH range of the experiment. In sucrose and sulfate rich media, acidogenesis and sulfidogenesis occurred simultaneously. Fermentative bacteria target sucrose and produce volatile fatty acids (VFA), thereby reducing the solution



Fig. 4 Acidity, alkalinity and pH of the effluent during dosing experiment. Day 1- 30 and 81- 95, reservoir pH maintained with NaHCO₃ day 39-73, reservoir pH maintained with quick lime; day 31–38 and 74–80, reservoir filled with only 2.1 g/L Na₂SO₄ without any external dosing.

pH. Sulfidogenesis on the other hand neutralizes the pH by oxidizing these VFA and producing bicarbonate alkalinity (Bertolino et al. 2012). In the dosing experiment, initial acidity produced by fermentative bacteria was neutralized by alkalinity in form of NaHCO₃. That effectively allowed SRB to perform. However, quick lime could not counter the initial acidity production due to its low alkalinity, hence could not in any case maintain the pH near neutral (Fig. 4). SRB are reported to work in the pH range of 5 to 9 (Mizuno et al. 1998). As the pH decreased due to increasing acidity, sulfate reduction also declined gradually (Fig. 5A). Most of the consumed COD (around 600 mg/d) and TOC (around 150 mg/d) were not utilized in sulfidogenesis. Therefore, low dissolved sulfide was produced (Fig. 5B).

Confirmation of the mentioned phenomenon was tested by reintroduction of NaHCO₃ into the reservoir. When quick lime in the reservoir solution was replaced with NaHCO₃, sulfate reduction started steadily again and reached maximum. Dissolved sulfide in the effluent also increased gradually (Fig. 6).

Conclusions

SMW was tried as external organic carbon dose into a nutrient exhausted reactor treating sulfate-rich wastewater. The study revealed that



Fig. 5 Parameters during 39–73 day of dosing experiment (pH in the reservoir maintained with quick lime). (A) Mass sulfate loading and effluent rate with sulfate reduction (%) (B) Mass COD and TOC loading and effluent rate with effluent dissolved sulfide concentration

filtered SMW can be used with buffering for desired results. As a pH buffer, NaHCO₃ was found more effective than quick lime. Around 60 % sulfate reduction was observed when mass loading ratio of COD to SO_4^{-2} was set as 1. The study shows rejuvenation of ineffective SAPS is possible with external supplementary dose.

Acknowledgements

The authors thank the Council of Scientific and Industrial Research (CSIR), India for the financial support to carry out the study.



Fig. 6 Sulfate reduction (%) and dissolved sulfide concentration in the effluent when reintroduced into the reactor with NaHCO₃ buffered influent (81–93 day of dosing experiment).

References

- Bertolino SM, Rodrigues ICB, Guerra-Sa R, Aquino SF, Leao VA (2012) Implications of volatile fatty acid profile on the metabolic pathway during continuous sulfate reduction. J Environ Manage 103: 15—23
- Coetser SE, Pulles W, Heath RGM, Cloete TE (2006) Chemical characterisation of organic electron donors for sulfate reduction for potential use in acid mine drainage treatment. Biodegradation17: 169– 179
- Das BK, Gauri SS, Bhattacharya J (2013) Sweetmeat waste fractions as suitable organic carbon source for biological sulfate reduction. Int Biodeter Biodegr, http://dx.doi.org/10.1016/j.ibiod.2013.03.027
- Das BK, Mandal SM, Bhattacharya J (2012) Understanding of the biochemical events in a chemo-bioreactor during continuous acid mine drainage treatment. Environ Earth Sci 66: 607—614
- Lopes SIC, Capela MI, Lens PNL (2010) Sulfate reduction during the acidification of sucrose at pH 5 under thermophilic (55 °C) conditions. II: effect of sulfide and COD/SO₄^{2–} ratio. Bioresource Technol 101: 4278-4284
- Mizuno O, Li YY, Noike T (1998) The behavior of sulfatereducing bacteria in acidogenic phase of anaerobic digestion. Water Res 32: 1626—1634
- Tchobanoglous G, Burton FL, Stensel HD, Metcalf & Eddy, Inc (2003) Wastewater engineering, treatment and reuse. Tata McGraw-Hill, New York, p 215—301

Assessing the Reliability of an Unlined Tailings Storage Facility for Protecting Water Resources

Larry Breckenridge¹, Fred E. Bickford², Emily Luscz³

¹Global Resource Engineering Ltd., 7000 South Yosemite St., Centennial, Colorado 80112, lbreckenridge@global-resource-eng.com ²fbickford@global-resource-eng.com,³eluscz@global-resource-eng.com

Abstract Many regulatory agencies request lined Tailings Storage Facilities (TSFs) in hopes of better protecting groundwater resources. For the Corani Silver-Lead-Zinc project in Peru, lining the 160 Mt capacity TSF is not desirable. However, tailings solution containment is critical to meeting environmental requirements. To simulate containment of an unlined TSF, two models were used in tandem: a tailings consolidation model, and a groundwater flow model. The model results showed low-conductivity consolidated tailings seal the facility such that minimal seepage occurs. The modeling demonstrated that an unlined TSF can contain tailings solution equal to or better than a lined TSF.

Keywords Tailings, tailings consolidation, water resources, MODFLOW Surfact.

Introduction

The Corani epithermal silver-lead-zinc deposit in southeastern Peru will produce 160 Mt of mine tailings from its process plant over a projected mine life of 20 years. The project site is in the high Andes, 150 km southeast of Cusco, at an elevation of 5000 m above sea level (masl). The TSF will store conventional wet-tailings behind a 162 m high clay-core rock fill centerline-construction tailings dam. The TSF will require two saddle dams to reach the planned total capacity of 134 Mm³ and will cover a footprint of 2.8 km². The impoundment falls in the Amazonian watershed, and is adjacent to several sensitive watersheds. As a result, the TSF must effectively contain tailings solutions, and must be protective of adjacent water resources over the long-term. Fig. 1 shows the TSF location and the location of the adjacent drainage basins.

Due to the projected size of the impoundment, covering the surface area of the TSF with an impermeable synthetic liner is not cost-effective, and despite state-of-the-art geochemical management practices, it is unlikely that seepage from the TSF will meet water quality guidelines. However, due to the physical properties of the tailings and the geologic properties of the TSF foundation, it is possible to achieve seepage containment without a liner.

To simulate the effectiveness of TSF solution containment, two models were constructed in tandem: a large-strain tailings consolidation model (FSConsol) and a MODFLOW-Surfact groundwater flow model (MODFLOW). The FSConsol model simulated the consolidation of the tailings and the ultimate conductivity of the tailings, and the MODFLOW model predicted the seepage from the dam and to adjacent watersheds.

Methods

Site Data

GRE conducted an extensive field investigation of the geologic conditions of the TSF. Approximately 3.2 km of boreholes were drilled under the dam, the saddle dams, and the impoundment. Packer tests as well as aquifer tests were performed in all borings to quantify the hydrogeologic properties of the TSF foundation. The investigation revealed that the impoundment is underlain by a lithic tuff that



Fig. 1 Location of TSF and adjacent drainage basins at the Corani Project

contains very little primary or secondary conductivity. Isolated areas of fracturing were discovered in some boreholes, but these zones are not related to obvious geologic structures, and testing confirmed fracture zones are finite in extent and poorly connected to the surface water system. Unconsolidated sediments and bog-type organic soils (locally referred to as bofedal(es)) overlie the tuff in some portions of the TSF (Fig. 1). These bofedales host the shallow aquifer system in the TSF area. Apart from these shallow deposits which will be covered or excavated during construction, the TSF has a relatively impermeable foundation. The geomean of hydraulic conductivity from the 52 packer test intervals conducted in the TSF foundation rock is 4.6×10^{-6} cm/s.

Due to limitations in the amount of available clay, the TSF dam will be constructed with a dual material clay core with a 1×10^{-6} cm/s upstream core and a 5×10^{-5} cm/s downstream core. It has a chimney drain and a toe drain leachate collection system. The final dam also requires two saddle dams located adjacent to the Quelcaya and Jorge Chavez drainage basins (Fig. 1). The stage-mine life-volume relationship for filling the TSF was taken from the site operations plan (M3 2012).

In the latter half of mine life, the Corani

project will install a pyrite flotation system to create a de-pyritized tailings product. The depyritized tailings will be created to minimize the risk of acid rock drainage (ARD) in the tailings impoundment. These de-pyritized tailings have a slightly different consolidation behavior than the tailings produced for the first half of the mine life. This difference is considered in the consolidation model and the TSF containment model.

Consolidation Model

Tailings that are deposited subaqueously consolidate under their own weight and under the weight of subsequent tailings deposition. This results in the densification of the tailings, the creation of excess pore pressure, and a reduction in the hydraulic conductivity of the tailings over time.

The consolidation behavior was simulated using the software package FSConsol, a one-dimensional consolidation program based on finite strain consolidation theory. Finite strain consolidation theory is used to model scenarios which involve large strains and non-linear soil properties. FSConsol models simulate tailings consolidation using varying filling rates, varying pond areas, drainage conditions, and material types. The consolidation model requires material properties relating to compressibility, permeability, and initial solid content for each material type.

The compressibility of the tailings determines the relationship between void ratio (e) – defined as the ratio of the volume of voids to the volume of solids – and effective stress (σ ') – defined as the stress transmitted through a soil mass less pore pressure. This relationship is expressed in FSConsol in the following form:

$$e = A\sigma^{'B} + M \tag{1}$$

where A, B and M are constants.

FSConsol determines the hydraulic conductivity (k) as a function of the void ratio (e). This relationship is expressed in the following form:

$$k = Ce^{D}$$
 (2)

From these relationships, the FSConsol model can generate curves that relate the settling time, the tailings depth, and the conductivity of the tailings (GWP 2007).

Groundwater Flow Model

The Corani TSF was modeled using MODFLOW-Surfact (HGL 2010) and the Groundwater Vistas (Rumbaugh 2011) interface.

The steady-state version of the model was calibrated to water levels from the network of monitoring wells and vibrating wire piezometers installed during the field investigation. The calibration data set al. so included dry-season stream flow measurements, and average annual precipitation based on several years of records collected at the on-site automated weather station.

Simulating the filling of the TSF required simultaneous accounting of the changes in tailings depth, hydrostatic head, and hydraulic conductivity associated with the tailings deposition over time and space. Recent advances in MODFLOW code allow for the transient adjustment of hydrostatic head, and hydraulic

conductivity, but the code does not allow for time-variant changes in model layer thickness. Therefore, the filling of the TSF was simulated through the General Head Boundary (GHB) boundary package. The filling of the TSF was simulated by adjusting the head on the boundary condition, and the consolidation of the tailings was simulated by adjusting the conductivity in the boundary condition. This method was applied at different values for different areas of the TSF under the assumption that the deeper portions filled faster and consolidated faster than the edges of the impoundment. Ten different boundary-condition zones resembling concentric rings were used to simulate the differential filling behavior over space and time. The result was a simulation that captured the complexity of the consolidation behavior over the footprint of the TSF.

The use of GHBs to simulate the tailings cannot simulate the drain-down of the consolidated tailings after closure because the tailings are a boundary condition, not an intrinsic part of the model with defined conductivity and storage. To overcome this issue, the TSF filling and consolidation was modeled for 30 years as a boundary condition to allow consolidation time to complete. Once consolidated, the model geometry was altered to make the tailings an active model layer with a thickness equal to the depth of deposited tailings, and with the properties of the fully-consolidated tailings. Using this method, the drain-down of the tailings could be simulated after TSF closure.

Results

Consolidation Model

Over time, the Corani tailings consolidate down to as low as 3.8×10^{-7} cm/s, but much of the de-pyritized tailings located in the upper portions of the impoundment will experience considerably less consolidation and will have a final conductivity of approximately 1×10^{-5} cm/s. This decreased consolidation is due to the shallower tailings depth in the up-

land areas of the TSF, and the nature of the depyritized tailings product. Fig. 2 shows an example of the tailings consolidation and permeability curve over time and tailings depth.

This complex consolidation behavior was integrated into the MODFLOW model of the tailings solution containment.

Groundwater Flow Model

Dam seepage was evaluated by the discharge into the toe drain boundary condition located beneath the downstream toe of the tailings dam (Fig. 3). The seepage behavior showed a linear increase in seepage with an exponential decrease to steady-state after closure. The discontinuity in the seepage line at year 10 reflects the change-over to de-pyritized tailings. The maximum seepage of $\approx 100 \text{ m}^3/\text{d}$ (1.2 L/s) is modest for a 165 m high dam. Upon closure, the seepage rapidly decreases to 10 m³/d (0.12 L/s).

The Quelcaya Basin (Fig. 1) showed no significant change in seepage resulting from the TSF. In fact, the stripping of bofedal sediments during the construction of the saddle dam results in a net decrease in seepage during mining operations. The Quinimari and Jorge Chavez basins see a slight increase in groundwater flow (10–20 %), but the change is not significant in comparison to the total water balance of the area, and as discussed below, does not generate from the TSF. The project does not anticipate that the water quality of the tailings interstitial fluid will meet stringent water quality requirements due to elevated sulfate concentrations. As a result, Modpath (USGS 2000) simulations were used to determine the travel paths and travel time of any tailings fluid migration. The simulation showed that the TSF effectively captures all tailings seepage into the Collpa Mayo drainage under the tailings dam (Fig. 4). In addition, because the seepage must travel through the low-conductivity tailings and bedrock to escape the impoundment, travel times to the toe of the main dam are on the order of hundreds of years.

The total seepage of the TSF reaches a maximum of 219 m³/d (2.5 L/s) just prior to closure. This modest seepage volume is the result of the consolidated tailings working in conjunction with the low-conductivity bedrock to prevent seepage from the tailings despite considerable hydrostatic head.

No liner system is perfect, and as a result, the US EPA has created liner seepage calculations and design guidelines to predict the seepage through a synthetic liner (Giroud & Badu-Twneboah 1992; Giroud & Bonaparte 1989; EPA 1992).The EPA techniques are analytical calculations that consider the typical frequency of small liner failures and the hydrostatic head present on holes in the liner, and extrapolate the potential seepage through lin-





Fig. 3 Model simulated dam seepage through time.

60

ers covering large surface areas. This potential seepage was calculated for the Corani TSF and was compared to the MODFLOW predicted results. With all other assumptions identical to the MODFLOW model, the EPA liner seepage calculations predicted a total leakage from the TSF of \approx 470 m³/d.

Conclusions

For projects with fine-grained tailings, it is often the consolidation behavior of the tailings, and the final hydraulic conductivity, that determines the hydrogeologic behavior of the TSF. In the case of the Corani Project, large-strain consolidation testing and simulation indicate that the tailings would consolidate to a conductivity as low as 3.8×10^{-7} cm/s. This low conductivity consolidated tailing product, in conjunction with a competent-rock TSF foundation, produces a very low predicted total

seepage despite the size and depth of the TSF. As a result the TSF has modest seepage to the dam toe drain (where it can be managed if required), and no significant seepage to adjacent drainage basins. In addition, particle tracking demonstrated that the TSF successfully contains tailings solution by channeling all potential seepage to the toe drain of the dam where it can be monitored and managed.

When compared to a synthetic liner, the unlined TSF has less than half the leakage estimated from a simulated lined facility. As a result, installing a synthetically-lined TSF foundation would result in no significant improvement in environmental protection despite the great expense.

This project provides an example to mining companies and regulators that unlined tailings storage facilities are not necessarily a threat to water resources even in cases when



Fig. 4 Model simulated flow paths of tailings fluid within the TSF.

the interstitial water quality within the tailings may not meet regulatory requirements.

Acknowledgements

The authors thank Bear Creek Mining Company for permitting the results of the study to be presented at the IMWA 2013 conference.

References

- EPA (1992) Action Leakage Rates for Leak Detection Systems-Supplemental Background Document for the Final Double Liners Leak Detection Systems Rule for Hazardous Waste Landfills, Waste Piles, and Surface Impoundments. V EPA 530-R-92-004, PB92-128214. U.S. Environmental Protection Agency, Office of Solid Waste.
- Giroud J, Badu-Twneboah K (1992) Rate of Leakage through Composite Liner due to Geomembrane Defects. Geotextiles and Geomembranes, 11, 1–28.

- Giroud J, Bonaparte R (1989) Leakage through liners constructed with geomembranes — Part II: composite liners. Geotextiles and Geomembranes, 71– 111.
- GWP (2007) FS Consol Slurry Consoliation Software, Version 3. Edmonton, Alberta, CA: GWP Software Inc.
- HGL (2010) MODFLOW-Surfact. HydroGeoLogic.
- M3 (2012) NI 43–101 Report on the Corani Project. Tuscon, Arizona: M3 Engineering.
- Rumbaugh J (2012) Groundwater Vistas Version 6.29. Environmental Simulations.
- USGS (2000) MODPATH particle trackign postprocessing model for MODFLOW. Reston, VA: United States Geological Survey.

Characterising the Acid Generating Potential of Mine Wastes by means of Laboratory-scale Static and Biokinetic Tests

Jennifer L. BROADHURST¹, Christopher G. BRYAN², Megan BECKER¹, Jean-Paul Franzidis¹, Susan T.L. Harrison¹

¹Minerals to Metals, University of Cape Town, South Africa, jlb@absamail.co.za ²Environment and Sustainability Institute, University of Exeter, United Kingdom, C.G.Bryan@exeter.ac.uk

Abstract The reliable prediction of acid rock drainage risks associated with sulfide mine wastes plays an important role in planning for their disposal. This paper explores the application of a novel biokinetic test, in combination with conventional static chemical tests, for the rapid and effective characterisation of the acid generating potential of a number of mine wastes from the processing of both hard-rock ores and coal. Findings also highlight the need to consider microbial colonisation and the effects of such on the relative kinetics of the acid forming and neutral-ising reactions.

Keywords Acid rock drainage, sulfide mine waste, static tests, biokinetic tests

Introduction

Wastes from the extraction and beneficiation of sulfide-bearing hard rock ores and coal deposits may contain significant quantities of sulfide minerals, particularly pyrite, which are susceptible to oxidative dissolution in the presence of water and oxygen, giving rise to the formation of acid rock drainage (ARD). In order to be effectively managed, the long-term acid generating potential of mine wastes first need to be accurately and reliably characterised using simple, robust and precise testing procedures. Whilst the chemical oxidation of pyrite occurs at a relatively slow rate, the formation of ARD is greatly accelerated in the presence of naturally-occurring acidophilic micro-organisms (Bryan 2006, Johnson and Hallberg 2005).

Typically, predictions of the acid generating potential of mine wastes are based on static and kinetic chemical tests (INAP 2009, Smart *et al.* 2002, Price 2009). Static chemical tests, such as acid base accounting (ABA) and net acid generation (NAG), provide an indication of the absolute potential of a material to generate acid over geographical time, but do not take into account reaction kinetics. These tests are thus

mainly used as initial screening tests, whereby materials are classified in accordance with universally accepted criteria. Kinetic tests are designed to provide information on the time-related acid generating potential of a material. The most common kinetic tests include humidity cell tests and leach column tests, both of which provide long-term dynamic weathering data. A major drawback of these standard kinetic tests is the time required to generate meaningful data, which may often run into years. Furthermore, standard kinetic tests do not take microbial activity into account-this despite the fact that microbial colonisation of sulfide-bearing waste rock or tailings is inevitable (Bryan 2006). Finally, both humidity cells and leach column tests are carried out using a large particle size distribution of heterologous ore which limits reproducibility.

In an attempt to address the short-comings of standard humidity and leach column tests, a microbial shake flask test was developed by Duncan and Bruynesteyn (1979) and subsequently modified and refined in a more recent study by Hesketh *et al.* (2010a). This paper extends the application of the biokinetic shake flask tests to a range of sulfide-bearing mine wastes from different sources and origins, and demonstrates its role in both validating and enhancing the results from standard static chemical tests.

Methods

Chemical static and biokinetic shake flask tests were carried out on the following mine waste samples:

- Untreated copper sulfide tailings: Sample represented typical tailings from the flotation of porphyry-type copper sulfide ores, with the sulfide minerals comprising mainly pyrite (≈7 % by mass) and minor quantities of chalcopyrite (≈0.5 % by mass).
- Desulfurised copper sulfide tailings: Sample prepared from the untreated copper sulfide tailings in a two-stage batch desulphurization flotation process, as described in Hesketh *et al.* (2010b).
- Copper sulfide waste rock: Sample of waste rock prepared from a blend of lowgrade porphyry copper sulfide and complex base-metal sulfide ores. The sulfide minerals comprised mainly pyrite (≈ 2.6 %) and no carbonate minerals were detected by XRD.
- Nickel-pyrrhotite flotation tailings: Sample prepared from a low-grade nickel sulfide (pentlandite) ore in a laboratory-scale batch flotation cell (Chimbganda *et al.* 2013). Pyrrhotite was identified as the major sulfide mineral and calcite as the major carbonate. The ore also contained relatively reactive silicate minerals, such as olivine (≈ 4 %).
- Gold tailings: Sample prepared through the crushing and screening of a Witwatersrand gold ore. Mineralogical analysis indicated that pyrite is the major sulfide mineral (≈1%) and calcite the major carbonate mineral.
- Coal waste slurry: Two samples of fresh ultra-fine thickener underflow procured from two different coal processing plants

in the Middelburg area, South Africa. Sample 1 was screened into various size fractions, prior to further testwork. The coal slurry samples contained 25–40 % ashforming minerals, comprising mainly quartz and kaolinite with minor quantities (<5 %) of pyrite, calcite, dolomite and sulfate minerals.

- Untreated coal discard: Sample generated at a South African power station, through the destoning of a low-grade coal by means of an experimental X-ray sorter. The discard had an ash content of 56.4 %.
- Desulfurised coal discard: Sample prepared from the untreated coal discard sample in a two-stage flotation process as described by Kazadi Mbamba *et al.* (2012), using oleic acid to recover coal in the firststage float and xanthate to remove sulfide minerals in the second flotation stage. The desulfurised tailings comprised 36 % of the feed discards, and had an ash content of 82.4 %.

Static tests were conducted on all samples using both the ABA and NAG test methodologies. The ABA test measures the net acid producing potential (NAPP), which represents the balance between the maximum potential acidity (MPA) and the acid neutralising capacity (ANC). The MPA was based on the total LECO sulfur concentration in the case of the wastes from the processing of hard-rock ores, and the sulfide sulfur content (as determined by the standard ISO 157: 1996 method) in the case of coal wastes. ANC was determined empirically in accordance with the method proposed by Skousen et al. (1977). NAG tests were conducted according to the method described by Smart et al. (2002). This method measures the acid forming potential, by allowing both the acidforming and neutralising reactions to occur simultaneously, using H_2O_2 as an oxidant. The waste samples were subsequently classified using a slightly modified version of the combined ABA/NAG classification system, proposed by Smart et al. (2002).

Biokinetic tests were carried out on all waste samples in accordance with the standard batch method described in Hesketh et al. (2010a). In this test, 7.5 g of sample, with a particle size of <150 µm, is added to a basal salts medium at pH 2.0, prior to inoculation with an active, mixed microbial bioleaching culture. The prepared flasks are subsequently maintained at 37 °C on an orbital shaker at 150rpm for a period of approximately 90 days. In order to better present an open flow-through system, a dynamic (semi-continuous) version of the standard batch biokinetic test was also carried out on selected samples under circumneutral pH conditions. In these tests, the initial pH of the basalt salts medium was adjusted to a value of 6 prior to the introduction of the waste sample. This was followed by intermittent removal and replacement of 90 % of the supernatant during the course of the shake flask test.

Results

Static test results for the wastes from the processing of hard-rock ores (table 1 and fig.1) indicate that the untreated sulfide tailings and waste rock samples investigated are all classified as acid generating. The low-sulfur copper tailings sample, generated through the desulfurisation flotation of the copper sulfide tailings, is classified as non-acid forming.

The results of standard batch biokinetic tests (fig. 2) yielded the same results as the static tests in terms of classification *i.e.* all untreated mine waste samples tested were net acid generating, under conditions of microbial activity, whilst removal of the sulfide by means of flotation effectively removed the long-term ARD risk.

The biokinetic test results also show that the acid neutralising reactions occur more rapidly than pyrite oxidation, with the pyritebearing wastes becoming net acid consuming in the initial leach stages. This neutralising capacity is, however, generally short-lived (<15 days) for wastes that have not been desulfurised, and the acidification observed in the biokinetic tests thus ultimately exceeds that predicted by the static tests (final biokinetic pH values are lower than the NAG pH values). This is particularly the case for the pyrrhotite-bearing nickel sulfide tailings which, despite the

Waste description	Total S (%)	ANC (kg/t H ₂ SO ₄)	NAPP (kg/t H2SO4)	NAG pH
Untreated copper sulfide tailings	3.84	23.2	94.8	2.57
Desulfurised copper sulfide tailings	0.21	28.7	-22.3	5.71
Copper sulfide waste rock	3.39	3.39	92.8	2.63
Nickel-pyrrhotite flotation tailings	3.59	89.4	20.3	3.19
Gold tailings	1.41	16.5	24.9	2.51



Table 1 Static ARD test results for wastes from hardrock ore processing

Fig. 1 Static ARD classification plot for the wastes from hard-rock ore processing (NAF: non- acid forming, UC: uncertain, PAF: potentially acid forming and AF: acid forming)



Fig. 2 Batch biokinetic test results for wastes from the processing of hard-rock ores

relatively high ANC, exhibited acid generating behaviour after the first day. This can be attributed to the relatively rapid kinetics of pyrrhotite oxidation in comparison to that of pyrite (Janzen *et al.* 2002).

Static test results for the coal waste samples (tab.2 and fig. 3) indicate that the untreated coal discards are acid forming, the coal waste slurry 1 potentially acid forming, and the coal waste slurry 2 and the desulfurised coal discards both non-acid forming.

In accordance with Miller (2008), the standard NAG test may overestimate the acid generating potential of samples with relatively low acid generating potential (*i.e.* those falling in the PAF region of the graph), due to organic acid effects. However, biokinetic tests (fig. 4) confirmed that samples classified as either acid forming or potentially acid forming on the basis of static chemical tests are also acid generating under conditions of microbial colonisation. In agreement with the static chemical tests, biokinetic tests indicate that coal waste slurry 2 and the desulfurised coal discards are both non-acid generating. A comparison of the leach behaviour of the -75 µm fraction of coal slurry waste 1 under biotic and abiotic conditions confirms, furthermore, that microbial activity plays a significant role in acid generating behaviour. As in the case of the wastes from hard-rock ore processing, the biokinetic test results indicate that, although the samples classified as PAF and AF are initially acid consuming, this acid neutralising capacity is consumed relatively rapidly. This is of relevance when considering a tailings deposit where soluble fractions are transported away from the waste material, and thus are not

Waste description	Total S (%)	S ²⁻ (%)	ANC (kg/t H ₂ SO ₄)	NAPP (kg/t H₂SO₄)	NAG pH
Coal waste slurry 1: -75µm	2.08	1.00	27.7	2.9	2.50
Coal waste slurry 1: +212-315µm	1.03	0.64	28.2	-8.6	2.97
Coal waste slurry 2	0.82	0.50	131.9	-116.6	5.20
Untreated coal discards	5.11	3.30	55.6	101.0	2.20
Desulfurised coal discards	0.21	n/d	76.7	-70.6	5.90



Table 2 Static ARD test results for coal processing wastes

Fig. 3 Static ARD classification plot for the coal processing wastes (NAF: nonacid forming, UC: uncertain, PAF: potentially acid forming and AF: acid forming)



Fig. 4 Batch biokinetic test results for wastes from coal processing

available to neutralise acid generated through the oxidation of pyrite over the longer term.

Dynamic biokinetic leach tests on the two size fractions of coal waste slurry 1 (fig. 5) confirm that these samples eventually become net acid generating under conditions of microbial colonisation in a semi-continuous flow scenario, even when using a leach solution with a relatively mild circum-neutral pH (6). Mineralogical analysis of the leach residues indicated incomplete oxidation of pyrite over the 87 day biokinetic test period, particularly in the case of the coarser size fraction.

Conclusions

This study has demonstrated that the biokinetic test can be used to both validate and enhance the results of simple static tests, providing valuable additional information on the effect of microbial activity and the relative kinetics of the acid forming and neutralising reactions under stagnant and dynamic flow conditions. Such information provides a measure of the potential for conditions that promote bioleaching to be established and, ultimately, assists in the implementation of waste management strategies that are effective in both the short and long-term. The advantages of the biokinetic test over other conventional kinetic tests include its relatively simple and inexpensive methodology. The biokinetic test also delivers meaningful results pertaining to the long-term ARD generating potential of both fine and coarse wastes in a relatively short period of time (< 3 months for wastes from hardrock ore processing, and 4-5 months for coal processing wastes).

Acknowledgements

This work is based on research supported by the South African Research Chairs Initiative of



Fig. 5 Dynamic biokinetic test results for wastes from coal processing at circumneutral pH conditions (where A, B and C correspond to supernatant replacement intervals of 3, 8 and 14 days respectively) the Department of South Africa and Technology and National Research Foundation of South Africa (NRF). Any opinion, finding, conclusion or recommendation expressed in this material is that of the authors and the NRF does not accept any liability in this regard. The authors also acknowledge the contribution of the following post-graduate students within the Department of Chemical Engineering at the University of Cape Town: Alex Hesketh, Alex Opitz, Juarez Amaral, Lerato Kotelo, Noluntu Dyantyi and Tapiwa Chimbganda.

References

- Bryan CG (2006) A study of the microbiological populations of mine wastes, PhD thesis, School of Biological Sciences, University of Wales.
- Chimbganda T, Becker M, Broadhurst J *et al.* (2013) Comparison of pyrrhotite rejection and passivation in two Nickel ores. Minerals Engineering, 46-47:38-44.
- Duncan D, Bruynesteyn A (1979) Determination of acid production potential of waste materials. Metallurgy Society, AIME, paper A-79-29 AIME, Littleton, CO.
- Hesketh AH, Broadhurst JL, Bryan CG, van Hille RP, Harrison STL (2010a) Biokinetic test for the characterisation of AMD generation potential of sulfide mineral wastes. Hydrometallurgy 104(3):459-464.
- Hesketh AH, Broadhurst, JL, Harrison STL (2010b) Mitigating the generation of acid mine drainage from copper sulfide tailings impoundments in perpetuity: A case study for integrated management strategy. Minerals Engineering 23:225–229.

- INAP (International Network for Acid Prevention) (2009) Global Acid Rock Drainage (GARD) Guide. Available at www. gardguide.com (accessed March 2013).
- Janzen MP, Nicholson RV, Scharer JM (2000) Pyrrhotite reaction kinetics: reaction rates for oxidation by oxygen, ferric iron, and for nonoxidative dissolution. Geochimica et Cosmochimica Acta 64(9):1511-1522.
- Johnson DB, Hallberg KB (2005) Acid mine drainage remediation options: a review. Science of the Total Environment 338:3–14.
- Kazadi Mbamba C, Harrison STL, Franzidis J-P, Broadhurst J (2012) Mitigating acid rock drainage risks while recovering low-sulphur coal from ultrafine colliery wastes using froth flotation. Minerals Engineering 29: 13–21
- Miller, S (2008) Development of ARD assessment for coal process wastes (ACARP project C15034). Environmental Geochemistry International Pty Ltd, Australia.
- Price WA (2009) Prediction manual for drainage chemistry from sulphidic geological materials (MEND report 1.20.1). CANMET Mining and Mineral Science Laboratories, British Columbia, Canada.
- Skousen J, Renton J, Evans, P*et al.* (1977) Neutralization potential of overburden samples containing siderite. J. Environmental Quality 26:673–681.
- Smart R, Skinner B, Levay G *et al.* (2002) ARD Test Handbook (AMIRA project P387A: Prediction and Kinetic Control of Acid Mine Drainage), Ian Wark Research Institute and Environmental Geochemistry International, Melbourne, Australia.

Investigating the potential impact of efflorescent mineral crusts on water quality: complementing analytical techniques with geochemical modelling

Bronwyn Camden-Smith¹, Raymond H. Johnson², Robert Richardson¹, David Billing¹, Hlanganani Tutu¹

¹Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa

²Crustal Geophysics and Geochemistry Science Center, U.S. Geological Survey, Denver CO 80225 USA; bronwyn.camden-smith@students.wits.ac.za

Abstract Efflorescent crusts are a common feature forming on the surface of gold mining sites and tailings storage facilities during the dry season. Their dissolution at the start of the wet season releases an acidic pulse of water rich in metal pollutants. The composition of the crusts is indicative of the water from which they precipitated. This study aimed at assessing the crust formation and dissolution processes that result in episodic changes in receiving water quality. The approach involved characterising the composition of the crusts by analytical techniques (powder X-ray diffraction (PXRD)) and establishing compositional discrepancies by modelling the formation and dissolution processes.

Keywords geochemical modelling, efflorescent crusts, PXRD, forward modelling, reaction paths

Introduction

Since 1886, the Witwatersrand Basin has hosted more than 150 mines which have extracted over 4.5 Gt of ore at an average grade of nine grams of gold per tonne (McCarthy 2006). Waste rock dumps and tailings storage facilities (TSF), often referred to as "slimes dams," are a common sight in the region. There are more than 270 tailings storage facilities that cover an area of 400 km² in the Witwatersrand and Far West Rand (Durand 2012).

Leachates emanating from these sites have been identified as posing problems of pollution in surrounding water systems (Tutu *et al.* 2008). A common feature fingerprinting this pollution is the occurrence of efflorescent mineral crusts that are usually observed around gold mine TSFs, adjacent streams and other water bodies during the dry season. The crusts contain elevated concentrations of metals and are commonly soluble and insoluble sulphates, hydroxysulphates or hydrated oxides (Jambor *et al.* 2000). Their chemical nature varies depending on the reactions prevailing in the source water, *e.g.* acid generation and neutralisation as well as incongruent precipitation and dissolution.

This variation has been observed particularly in the form of multicoloured crusts (Naicker *et al.* 2003). For instance, white crusts usually indicate the presence of calcium (gypsum), pink indicates cobalt or manganese and green indicates nickel or iron (Naicker *et al.* 2003). Yellow salts can indicate the presence of uranium (Naicker *et al.* 2003). Mineral crusts are significantly more soluble than the primary minerals from which they are derived. The quick dissolution of these salts into surface water at the start of a rainy season leads to a spike in the metal concentration and a lower pH of discharging waters (Nordstrom 2011).

Assessing the mineralogy of these crusts and simulating their dissolution and formation helps to understand the underlying processes leading to their variable composition and subsequently, that of the water in which they dissolve. This is important in identifying and interpreting gaps existing between what analytical techniques can identify and what simulations predict, thus giving a comprehensive characterisation of the crusts. Remediation attempts and strategies can then be planned by using such information.

Materials and methods

Samples were collected from an abandoned tailings footprint during the dry season in 2012. This site hosted a TSF which was partially reprocessed in 2004. However, due to poor management, the facility was abandoned without rehabilitation. This has resulted in uncontrolled leaching of pollutants into an adjacent natural stream. Leachates drain into a pond within the facility and then seep into the stream via shallow groundwater passages (Fig. 1). Efflorescent crusts are a common feature in the capillary fringe of the pond and can also be observed where leachates seep out of the tailings material. Six samples of distinctly differently coloured efflorescent material were collected from the site (Table 1). The efflorescent material was sampled from the vertical edge of the tailings material (as seen in Fig. 1) as well as from the horizontal upper surface of the TSF.

The crusts (50 g) were dissolved in deionised water and transferred to a 1 L volumetric flask, which was then filled to the mark. Solutions were vacuum filtered using 0.1 µm Prima Pes filter paper. In a preliminary experiment, solutions were gravity filtered using a standard Whatman 11-µm pore-sized filter paper. Measurements of pH, oxidation reduction potential (Eh) and electrical conductivity (EC) were taken before and after filtration. A portion of the solution was analysed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) and chemically suppressed ion chromatography (IC). Bottles were left open and the solutions evaporated at 30 °C. Powder X-ray diffraction of the original samples and the evaporation products were



Fig. 1 The edge of an abandoned tailings storage facility with efflorescent crust on the wall

made using a Bruker D2 Phaser desktop diffractometer which was fitted with a cobalt Xray source and a LynxEye 1-D detector.

Forward geochemical and reaction path modelling using PHREEQC (Parkhurst and Appelo 1999) were applied to trace the dissolution, evaporation and selective precipitation paths of the solutions of these mineral crusts. Complementary programs used include Simile, a system dynamics, object-based modelling software and Berkely Madonna, a differential equation solver software (Muetzelfeldt & Massheder 2003; Macey *et al.* 2009).

Results

Dissolution of the crusts generated acidic solutions, with pH between 2.1 (crust 6) and 3.3 (crust 1). Solutions of crusts with a significant iron concentration had higher Eh measurements than the aluminium-dominant solutions. The highest Eh value was 676 mV (crust 6) whereas the lowest Eh value was 511 mV (crust 2). The crusts that had a significant portion of insoluble mass (crusts 3 and 5) had correspondingly lower EC values (6.4 mS and 5.7 mS). Crusts that were mostly fully dissolved had higher EC values (greater than 10 mS).

The IC results revealed that the solutions of dissolved crusts were essentially sulphate salts. Crust 2 contained a small percentage of chloride. The metal composition of the dissolved sulphate crusts after filtration through o.1-µm Prima Pes filter paper was analysed using ICP-OES (Table 1). The mole percentages were calculated as the ratio of the metal of interest to the total analysed metal content. The results are listed as mole percentages of the metal content. Crusts 1, 2, 4, and 5 are predominantly aluminium-magnesium sulphate salts. Crust 3 contained similar portions of aluminium, iron and magnesium. Crust 6, a white crust with a bright green interior, contained a high percentage of iron. Crusts with significant iron concentrations (crusts 3 and 6) correspond to the solutions with the highest Eh and lowest pH.

The preliminary experiment using coarse filter paper revealed the potential presence of trace amounts of bismuth, cerium, iridium, gallium, ruthenium, tantalum, thorium, titanium and vanadium. The quantified results for these elements will not be presented here. There have been accounts of a strong dependence of aluminium content on the pore size of filter paper used as it is possible that colloidal aluminium particles dominate an analysis in which there is actually a low portion of dissolved aluminium (Zhu & Anderson 2002). Coarse filter paper was used in the preliminary experiment, and the possibility that these metals were adsorbed on the surface of the colloidal aluminium minerals and not incorporated into the efflorescent crust must not be excluded.

Evaporation modelling of the 0.1-µm filtered solutions of dissolved crusts was undertaken using PHREEQC with the current wateq4f.dat and llnl.dat databases that are provided with the program. The activity models used in these databases are based on the theory of ion dissociation and incorporate modi-

fied Debye-Hückel equations. During evaporation, the ionic strength of the solution increases and the validity of these models decreases. The Pitzer approach, a semi empirical method which uses the theory of ion interaction, would be a more appropriate choice for calculating the activity of the concerned species given the high ionic strength of the solutions towards the end of the evaporation process (Pitzer 1973). Unfortunately, there is a lack of virial coefficients for the system under study. Accornero and Marini (2009) have evaluated the Pitzer parameters for the aluminium species: Al^{3+} , $AlOH_2^+$ or AlO^+ , with SiO_2 and CO_2 but the parameters for aluminium in an acidic, sulphate-rich system appear to be lacking. In this work, the evaporation has been only modelled up to the point in which the ion-dissociation activity model is valid (an ionic strength of approximately 1 mol kg⁻¹).

Evaporation modelling was approached in a stepwise manner. First, the charge balances and speciation of the solutions were inspected. Second, evaporation of water was modelled with no minerals defined as equilibrium species (Fig. 2). Ideally, minerals of interest should start as undersaturated or close to saturation and become oversaturated during the evaporation of the solution. In the third step, minerals that conform to this requirement are set as equilibrium minerals and are allowed to precipitate when they become oversaturated. In both the wateq4f.dat and llnl.dat databases, none of the aluminium minerals follow this ideal path. Alunite $(KAl_3(OH)_6(SO_4)_2)$ and jurbanite (Al(OH)(SO₄)) start as oversaturated whereas the other aluminium minerals remain undersaturated. Aluminium minerals.

Crust	Colour	Al Ca	a Cr	Со	Cu	Fe	К	Mg	Mn	Na	Ni	ΤI	Zn	
1	Yellow-white	56.9		0.6	0.3		0.6	39.1	1.0		0.9	0.0	0.7	
2	Beige	51.4		0.4	0.3	0.3	0.5	43.9	1.2	0.7	0.7		0.6	T-1-1- • • • •
3	Green-yellow	38.7		0.5	0.9	29.8	2.0	26.6	0.6		0.6		0.4	Table 1 Mic
4	Pink-yellow	50.4	0.1	0.5	0.7	6.6	0.6	38.7	1.0		0.8		0.6	metals c
5	Orange-brown	43.6 2.	.0	0.4	0.5	7.5	1.4	41.7	0.8		0.6	1.0	0.4	ph
6	White with bright green	14.6 0.	.1 0.1	0.2	0.3	71.9	0.5	11.4	0.3		0.2	0.3	0.1	

Table 1 Mole percentages of metals contained in sulphate crusts



such as alunogen (Al₂(SO₄)₃.17H₂O), dominate the efflorescent component as seen in the PXRD patterns (Table 2). An exact mineral match is not available in the databases and as such jurbanite and alunite were defined as equilibrium phases. Given that the solutions were exposed to the atmosphere, it was assumed that they are in equilibrium with atmospheric oxygen and carbon dioxide.

The assumption of equilibration of the solution with the atmosphere presented a problem for the crusts that possessed significant iron content. The Eh of these solutions was between 590 and 690 mV. Given the low pH of the solutions, the original iron distribution in these solutions was close to a 1:1 ratio of ferrous to ferric ions. Equilibrating the solutions with atmospheric oxygen increases the Eh and the ferric ion dominates. Ferric minerals are thus oversaturated from the beginning of the evaporation modelling. In such cases, the addition of oxygen up to atmospheric conditions was first modelled (Fig. 3) and then followed by the evaporation of water (Fig. 3). The minerals that become oversaturated during the addition of oxygen were selected as equilibrium minerals. Jarosite-H ((H₃O)Fe₃(SO₄)₂(OH)₆) was close to saturation at the start of the process and was selected as an equilibrium mineral (Fig. 3). If jarosite-H is not selected as an equilibrium mineral, then amorphous iron hydroxide (Fe(OH)₃) precipitates instead.

Cruch	Original	Evaporatio	Geochemical			
Crust	Onginal	11 µm filtering	0.1 µm filtering	Modelling		
1	Quartz, alunogen, pickeringite, (bixbyite)	Epsomite, alunogen	None (formed a resin)	Jurbanite, (epsomite close to saturation)		
2	Quartz, pickeringite	Pickeringite, alunogen	Pickeringite, alunogen, apjohnite hexahydrite,	Jurbanite, Nsutite (MnO2), Jarosite-ss (redissolves)		
3	Quartz, alunogen	Alunogen, Al ₂ (SO ₄) ₃ .14H ₂ O	None (formed a resin)	Jarosite-H, jurbanite		
4	Quartz, alunogen, pickeringite	None (formed a resin)	None (formed a resin)	Jarosite-K, jarosite-H, jurbanite, nsutite		
5	Quartz, alunogen, epsomite	Alunogen, epsomite, hexahydrite	Alunogen, hexahydrite	Gypsum, jurbanite		
6	Quartz, coquimbite, magnesiocopiapite	Ferricopiapite, coquimbite, rhomboclase	None (formed a resin)	Jarosite-H, jarosite-K, jurbanite, nsutite		

Table 2 Comparison of original, experimental and predicted mineralogy



Fig. 3 Modelled precipitation of minerals as a result of addition of oxygen followed by evaporation of dissolved crust solution of Crust 3

The relative rates of evaporation, ferrous oxidation and amorphous iron hydroxide precipitation was investigated by developing a simple systems model in Simile. In this model, a solution containing ferrous and hydronium ions was evaporated. As the solution evaporated, the concentration of the ions increased. The ferrous ions were oxidised to ferric ions. Amorphous iron hydroxide precipitated when the saturation index became positive. This model did not take into account the activity of the ions, but merely their concentration. The modelled rate of evaporation of the solution was fitted to the experimentally observed data with the use of a curve fitting exercise in Berkelv Madonna. Literature values for the rate constant of the oxidation of ferrous ions (Singer & Stumm 1970) and the rate constant of precipitation of amorphous iron hydroxide (Grundl & Delwiche 1993) were used. A oneminute time step was used. The 99 % evaporation of a solution which initially contains only ferrous ions and was at an initial pH of 3 was



Fig. 4 Simile model of precipitation of amorphous *Fe*(*OH*)₃ during evaporation of water

modelled (Fig. 4). The PHREEQC reaction models assumed equilibration between the ferrous and ferric ions. In relation to a 30 day complete evaporation, the conversion of ferrous ions to ferric ions is slow but the ferric ions quickly precipitate as amorphous $Fe(OH)_3$ and there are no free ferric ions in solution (Fig. 4). The oxidation of ferrous to ferric ions is known to be a slow process at low pH values (Singer & Stumm 1970), and this kinetic restraint in relation to the rate of evaporation will need to be investigated further for a wider range of minerals.

Table 2 summarises the mineralogy of the crust samples. Predicted minerals do not correlate well with the observed minerals, however the PXRD patterns and the modelling indicate that aluminium minerals are dominant. Thermodynamic data for the minerals observed are not present in the common databases. The geochemical modelling performed in this paper does not take into account factors such as co-precipitation and solid solutions. Both of these factors could cause a mineral to behave differently, in terms of its dissolution and precipitation, to that of the pure end members.

Conclusion

The results of the study indicate the presence of elevated metal concentrations in mineral salt crusts (making them temporary sinks). The efflorescent mineral crusts are readily soluble and mostly generate acidic solutions when dissolved. With additional rainfall and low pH conditions, these pollutants become mobile and can potentially degrade surface water quality. Geochemical modelling provided more insight into the reactions that occur during formation of the crusts; for instance, the modelling revealed the complexity posed by Eh that causes jarosite precipitation. This complexity derives from the kinetics of Fe precipitation and may help explain why jarosite is predicted to precipitate in geochemical models, but is not observed in the PXRD patterns. However, coquimbite and ferricopiapite were detected in the PXRD patterns and these minerals are paragenetically linked to jarosite. Further, evidence of the need to update most geochemical databases in order to model some of the components became more apparent; for instance, although Al and sulphate appear to be most important, modelling of processes involving them presented a challenge due to the inadequacies of most common databases. Discrepancies between minerals determined analytically and through modelling highlighted the need to use these techniques in a complementary fashion.

Acknowledgements

The authors thank the South African National Research Foundation for funding; the USGS Crustal Geophysics and Geochemistry Science Center for their assistance; the USGS reviewers for their valuable input and the anonymous IMWA reviewer for their helpful comments. Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

References

- Accornero M, Marini L (2009) Empirical prediction of the Pitzer's interaction parameters for cationic Al species with both SiO₂(aq) and CO₂(aq): Implications for the geochemical modelling of very saline solutions, Applied Geochemistry 24(5), 747–759.
- Durand JF (2012) The impact of gold mining on the Witwatersrand on the rivers and karst system of Gauteng and North West Province, South Africa, Journal of African Earth Sciences 68, 24–43.
- Grundl T, Delwiche J (1993) Kinetics of ferric oxyhydroxide precipitation, Journal of Contaminant Hy-

drology 14, 71–97.

- Jambor JL, Nordstrom DK, Alpers, CN (2000) Metal-sulfate Salts from Sulfide Mineral Oxidation, Reviews in Mineralogy and Geochemistry 40(1), 303–350.
- Macey R, Oster, G, Zahnley T (2009) Berkeley Madonna User's Guide, Department of Molecular and Cellular Biology, University of California, www.berkeleymadonna.com.
- McCarthy TS (2006) The Witwatersrand Supergroup, in The Geology of South Africa, Geological Society of South Africa and Council for Geoscience, Johannesburg.
- Muetzelfeldt RI, Massheder J (2003) The Simile visual modelling environment, European Journal of Agronomy 18, 345–358.
- Naicker K, Cukrowska E, McCarthy TS (2003) Acid mine drainage arising from gold mining activity in Johannesburg, South Africa and environs, Environmental Pollution, 29–40.
- Nordstrom DK (2011) Hydrogeochemical processes governing the origin, transport and fate of major and trace elements from mine wastes and mineralized rock to surface waters, Applied Geochemistry 26, 1777–1791.
- Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC (Version2)—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water-Resources Investigations Report 99–4259, 310 p.
- Pitzer KS (1973) Thermodynamics of electrolytes. Part I: Theoretical basis and general equations., J. Phys. Chem. 77(2), 268–277.
- Singer PC, Stumm W (1970) Acidic mine drainage: The rate determining step, Science 167(3921), 1121–1123
- Tutu H, McCarthy TS, Cukrowska E (2008) The chemical characteristics of acid mine drainage with particular reference to sources, distribution and remediation: The Witwatersrand Basin, South Africa as a case study, Applied Geochemistry 23(12), 3666–3684.
- Zhu C, Anderson G (2002) Environmental Applications of Geochemical Modeling, The Press Syndicate of the University of Cambridge, Cambridge, United Kingdom.

Characterization and Remediation of Iron(III) Oxide-rich Scale in a Pipeline Carrying Acid Mine Drainage at Iron Mountain Mine, California, USA

Kate M. CAMPBELL¹, Charles N. Alpers², D. Kirk Nordstrom³, Alex E. Blum⁴, Amy Williams⁵

¹U.S. Geological Survey, Boulder, Colorado, USA, kcampbell@usgs.gov
²U.S. Geological Survey, Sacramento, California, USA, cnalpers@usgs.gov
³U.S. Geological Survey, Boulder, Colorado, USA, dkn@usgs.gov
⁴U.S. Geological Survey, Boulder, Colorado, USA, aeblum@usgs.gov
⁵University of California, Davis, California, USA, amywill@ucdavis.edu

Abstract A 3.4 km pipeline carrying acid mine drainage to a treatment plant at the Iron Mountain Mine Superfund Site (California, USA) develops substantial scaling, resulting in occasional spillage and requiring periodic, costly clean-out. Samples of scale and water were collected from four points along the pipeline and water was collected from the mine portal influent. Mineralogy of the scale samples consisted of primarily hydrous ferric oxides including schwertmannite and goethite based on powder X-ray diffraction, wet chemical extractions, and scanning electron microscopy. Laboratory batch experiments with fresh, unfiltered water from the site showed that the scale was formed by microbial Fe(II) oxidation and precipitation of Fe(III) phases. A remediation strategy of lowering the pH of the influent water from 2.7 to 2.0-2.3 was tested using a geochemical model and laboratory batch experiments. Decreasing the pH did not substantially retard the rate of Fe(II) oxidation, but prevented precipitation of Fe(III) phases, suggesting that mixing the pipeline water with low pH water (pH \approx 1) from the Richmond mine portal may prevent scale formation.

Keywords Acid mine drainage, microbial iron oxidation, geochemical modeling, pipeline scaling

Introduction

Acid mine drainage (AMD) is a major environmental concern because it can degrade water quality with elevated concentrations of acidity, sulfate, iron, and other associated trace metals and metalloids. The biogeochemistry that produces AMD is complex, but can be summarized generally as the oxidation of pyrite by oxygen, facilitated by Fe(II)-oxidizing microorganisms, resulting in dissolved Fe²⁺, several potentially toxic trace metals, sulfate, and acidity (e.g. Nordstrom 2011). As the acidic water is transported away from the pyrite source, oxidation of dissolved Fe(II) to Fe(III) becomes an important process that can lead to precipitation of various Fe(III) phases. Abiotic oxidation of Fe(II) at low pH is slow, but Fe(III) can be generated rapidly by chemoautotrophic microorganisms (Nordstrom 2003 and references therein). Although precipitation of Fe(III) minerals can lead to attenuation of Fe and other elements of concern in AMD, it can also cause costly management problems when excessive precipitation interferes with treatment efforts by clogging pipelines or other treatment structures.

An example of treatment complications arising from Fe(III) precipitation occurs in a pipeline at the Iron Mountain Mine Superfund Site (California, USA), located near Redding in northern California. Mining activity at Iron Mountain began around 1879 and the site was mined intermittently through 1962. The mine produced gold, copper, zinc and pyrite. Acid

waters enriched in copper had been causing fish kills since at least 1899 and several successive studies recommended remedial measures. In 1983, the site was one of the first listed on the U.S. Environmental Protection Agency's National Priority List as part of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or "Superfund"). Its ranking was the third most hazardous site in the State of California (E.P.A. 2006). The ore bodies are massive sulfides, primarily pyrite (≈ 95 %) with lesser amounts of chalcopyrite, quartz, sphalerite, pyrrhotite, and galena (Kinkel et al. 1956, Nordstrom et al. 2000). Water draining the site is acidic (pH 0.5 to 3) and contains high concentrations of dissolved Fe(II) and other metals. As part of site remediation, a water treatment plant has been in operation to treat the AMD for acidity and metals; contaminated water is transported from the mine portals to the treatment plant through underground pipelines. There are two main pipelines: one with water pumped from the "Old Mine #8" (OM8) workings (pump station PW3, typical pH 2.5 to 3) and the other draining the Richmond and Hornet portals (Richmond, typical pH 0.5 to 1). The PW3 pipeline has developed substantial scaling over its 13-year history, resulting in occasional clogging and spillage of AMD. The scaling problem requires costly clean-out which has been done approximately every 2 to 4 years. The scaling occurs over a 3.4 km length of the PW3 pipeline. The objectives of this study are: (1) to characterize the pipe scale composition along the length of the pipeline, (2) to identify the biogeochemical processes leading to its formation, and (3) to identify and bench-test possible strategies to prevent or retard scale formation in the pipeline.

Methods

The PW3 pipeline was sampled for water and scale along a 2.1 km reach from service saddles that allowed direct access to the interior of the pipe. Water samples were collected under a low flow condition (approximately 380 L/min), al-

though there are substantial variations in flow depending on season and weather conditions. The pipe was not completely filled with AMD at the time of sampling. Scale samples were collected by physically removing the scale with a clean chisel, then placing a representative sample (≈ 0.5 kg) into an acid-washed glass jar and storing on ice until refrigerated in the laboratory. Four scale samples were collected: (1) SS12, an upper service saddle 180 m from the start of the pipe; (2) SS10, 646 m downstream of SS12; (3) SS8, 665 m downstream of SS10; and (4) SS6, 588 m downstream of SS8. In the laboratory, a subsample of each scale sample was homogenized and either air dried or gently washed with deionized water and methanol before air drying. Once dry, the sample was gently ground with an agate mortar and pestle. Samples for microscopy were dissected into 1 cm³ subsamples and mounted on aluminum specimen mounts as wet samples or air-dried before analysis.

Water samples were pumped from the pipe using a peristaltic pump and filtered (0.45 µm) into pre-washed sample bottles. Separate water splits were collected and preserved for analyses: 125 mL acidified to 1 % HCl for Fe(II)/Fe(III) determination, 125 mL acidified to 1 % HNO3 for cation analysis, and 125 mL filtered, unacidified water for anion analysis. All samples were stored on ice and shipped to the laboratory for analysis. Iron redox species were determined using the FerroZine colorimetric method (Stookey 1970), in which Fe(II) and total Fe (Fe(T)) were measured and Fe(III) was calculated by difference. Cations were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) on a Perkin-Elmer 7300DV. Anions were measured by ion chromatography on a Dionex LC20 with an AS18 column. Additional water samples were collected from a valve at the OM8 mine portal (PW3) and at the Richmond portal grit chamber (Richmond). A large volume (≈ 20 L), unfiltered water sample was collected from PW3 for Fe oxidation experiments (below). Under some conditions, water from a more dilute
source, the Slickrock Creek Retention Reservoir (SCRR) mixes with PW3 water in the pipeline. However, for the purpose of this study, PW3 water was the only influent to the pipeline.

Mineralogy of the scale was determined by X-ray diffraction (XRD), a series of wet chemical extractions, and scanning electron microscopy (SEM). Chemical extractions were performed on 2 g aliquots of the water/ methanol-rinsed scale samples. Each extraction was performed three times on the same scale aliquot at a solid to solution ratio of 50 g/L; the mass of each element extracted was summed over the three extractions and normalized to the starting mass of scale. The four extraction conditions were (1) deionized water, (2) 0.2 M ammonium oxalate, (3) 0.5 M HCl, and (4) 0.5 M HCl with 0.5 M hydroxylammonium hydrochloride. Pure phases of goethite and schwertmannite were synthesized according to Schwertmann and Cornell (1991) and extracted for comparison. XRD was performed on air-dried and ground scale samples mounted on a silicon wafer and analyzed on a Siemens D500 spectrometer with a Cu K-alpha radiation source. SEM was performed using a Hitachi TM3000 tabletop SEM for wet samples or a Philips XL30S field emission gun SEM with an energy-dispersive x-ray spectroscope (EDAX) Phoenix amplifier EDS system with a SUTW Si (Li) detector for dried samples. Carbon and nitrogen composition was determined on washed, air-dried scale samples on an Exeter CE-440 elemental analyzer. Biomass content was determined with a phosphate buffer (1X PBS) extraction with acridine orange cell straining to estimate solid-phase associated cell numbers.

Microbiological processes affecting Fe(II) oxidation and Fe(III) scale formation were investigated in laboratory batch experiments with unfiltered and filtered PW3 water. Three conditions were tested: (1) unfiltered water, (2) unfiltered water with scale, and (3) filtered water (0.1 μ m) as an abiotic control. Conditions (1) and (2) were performed in triplicate, and

condition (3) was performed in duplicate. A 700 mL aliquot was placed in a sterile, closed, 1L, acid-washed Teflon® bottle, bubbled with sterile air, and incubated on an orbital mixer at room temperature. Condition (2) contained 100 g of wet, homogenized composite scale from SS6 and SS10. Samples were collected periodically for analysis of Fe redox species, and pH, temperature, and E_h were routinely monitored with a pH electrode (Orion Ross), temperature probe (Orion), and platinum redox electrode (Orion), respectively.

The potential viability of mixing PW3 water with Richmond water to prevent scale formation was tested using a geochemical model and batch-scale experiments. The model used the geochemical code PHREEQC (Parkhurst and Appelo 1999) and an amended WATEQ4F database (Ball and Nordstrom 1991, with additional constants from Bigham et al. 1996 for schwertmannite and Baron and Palmer 1996 for jarosite). The precipitation of schwertmannite, goethite, jarosite, and ferrihydrite was calculated when PW3 and Richmond waters were mixed at various ratios with variable Fe(II):Fe(III) composition. The results were then used to guide bench-scale tests of mixing PW3 water with Richmond water in proportions of 99:1, 95:5, and 90:10. Filtered water was mixed at the appropriate ratio, then inoculated with a fresh culture of Iron Mountain Fe(II) oxidizing microorganisms grown in PW3 water. The effect of pre-existing scale also was tested by amending another set of bottles with composite air-dried scale (20 g/L) and mixtures of PW3 and Richmond waters at the same ratios as above. For comparison, composite scale also was mixed with 100 % Richmond water (20 g/L). Each condition was performed in duplicate. Samples were collected periodically for analysis of Fe redox species and pH was routinely monitored.

Results

Selected results from water samples collected from the OM8 portal valve (PW3) and from sampling sites along the pipeline are presented in Table 1. Iron was initially present as \geq 97 % Fe(II) (PW3 and SS12), but became progressively oxidized as the water flowed through the pipeline, containing 22 % Fe(III) at SS6. In addition, the total amount of Fe in solution decreased along the pipeline, consistent with precipitation of hydrous Fe(III) oxides. Other elements, such as Al, K, and Zn, also showed small but measureable decreases in aqueous concentration along the pipeline. The pH increased slightly, consistent with proton consumption during Fe(II) oxidation by dissolved oxygen (Equation 1).

$$4 \operatorname{Fe}^{2+} + \operatorname{O}_2 + 4 \operatorname{H}^+ \to 4 \operatorname{Fe}^{3+} + 2 \operatorname{H}_2 \operatorname{O}$$
 (1)

The travel time along this reach of the pipeline is less than one hour, and the water experiences turbulent flow along the pipeline because the water does not completely fill the pipe.

Mineralogical characterization of the scale indicated that the dominant phase is schwertmannite [ideal composition: $Fe_8O_8(OH)_6SO_4$], with poorly ordered goethite (FeOOH) and trace amounts of jarosite [MFe₃(OH)₆(SO₄)₂, where M is a cation, most commonly K⁺]. The powder XRD patterns showed the broad peaks associated with schwertmannite and some peaks characteristic of goethite, and the XRD patterns were similar between all four scale samples. The amounts of Fe and S measured in the chemical extractions of the scale samples were similar to the schwertmannite reference compound, and the composition indicated a hydrated schwertmannite as well as schwertmannite with goethite, consistent with the XRD results. Mineral textures characterized in SEM are consistent with documented schwertmannite textures (Cornell and Schwertmann 2003), and observed EDS spectra indicate a S peak associated with the schwertmannite. The bulk of the pipe scale is composed of agglomerations of schwertmannite mineral spheres 1.5 to 7 µm in diameter, with a sporadic distribution of filamentous schwertmannite mineral structures (diameter $\approx 2.2 \text{ }\mu\text{m}$) and bare putative microbial filaments (diameter ~ 0.7 µm).

Results of wet chemical extraction and XRD indicate very little bulk mineralogical difference between the four scale samples. The extractions show, however, that several trace elements (Al, Cu, Zn, Ca, Co, Mg, and Sr) decrease in concentration from SS12 to SS6, with preferential accumulation upstream in the pipeline, where the scale is softer and has a higher water content. Concentrations of total

Site name	рН	E _h SC	Fe(T)	Fe(II)	Fe(III)	Sulfate	Al	Cu	К	Zn
Richmond	0.84	0.63 76200	12590	12460	130	57500	772	130	86.4	1030
PW3	2.62	0.60 7250	1460	1440	nd	6890	465	85.8	0.64	36.5
SS12	2.63	0.60 6900	1400	1400	nd	6690	452	84.6	0.55	34.3
SS10	2.71	0.62 6600	1390	1320	70	6480	420	78.3	0.53	32.6
SS8	2.73	0.62 6440	1360	1040	320	6820	453	83.7	0.52	33.8
SS6	2.74	0.62 6340	1360	1060	300	6770	453	84.7	0.52	33.3

Table 1 Selected water chemistry for samples collected from OM8 portal valve (PW3), Richmond portal, and four service saddles (SS) along the PW3 pipeline. SS12 is closest to the OM8 portal and SS6 is the farthest downstream. All values reported in mg/L except for pH, Eh (reported in V), and specific conductance (SC, reported as μS/cm). Because Fe(III) is calculated by difference between Fe(T) and Fe(II), any Fe(III) value less than 3 % of Fe(T) is considered not detectable (nd). carbon and nitrogen in the scale also decrease along the flow path from SS12 to SS6, indicating a higher biomass content in the upstream scale. This is consistent with a phosphate buffer extraction to estimate solid-phase associated cell numbers, in which the most upstream site (SS12) had 100 times more cells than the most downstream site (SS6). Microbial community analysis of the scale samples is ongoing.

Results from bench Fe(II) oxidation experiments with filtered PW3 water, unfiltered PW3 water, and unfiltered PW3 water with composite scale are shown in Fig. 1. Oxidation of Fe(II) occurred in the unfiltered experiments, whereas no oxidation occurred in the filtered control, indicating that the Fe(II) oxidation in the unfiltered experiments was driven by microbial processes. The shapes of the Fe(II) oxidation curves are typical of substrate consumption caused by microbial growth. The presence of scale increased the initial rate of Fe(II) oxidation, but the fastest instantaneous rate occurred without the scale. In general, the rates of Fe(II) oxidation observed in these experiments are consistent with experiments utilizing synthetic AMD media (pH 2.5) and a

pure culture of *Acidithiobacillus ferrooxidans* (Campbell *et al.* 2012). Microbial community analysis of the Iron Mountain batch experiments is underway. The precipitate formed during the batch experiments was primarily schwertmannite, as identified by XRD, and is similar to the pipe scale.

One of the most promising options to reduce costs associated with the pipe scale problem at Iron Mountain is to prevent scale formation by lowering the pH. The scale was composed of primarily schwertmannite and goethite, and pH is an important control in the solubility of these phases. Calculations using the PHREEQC code with the PW3 water composition showed that a relatively small decrease in pH from 2.6 to 2.3 may be enough to prevent schwertmannite from forming upon oxidation of Fe(II). A second set of calculations determined that the theoretical proportion of Richmond water (pH 0.84) needed to decrease the pH and prevent Fe(III) precipitation was about 5 % Richmond water mixed with 95 % PW3 water. These calculations were used to design a bench-scale experiment in which PW3 water was mixed with 1 %, 5 % or 10 % Richmond water; each condition was performed



with and without composite scale added. The water from the site had been filtered, so it was necessary to inoculate the solution with a microbial culture that had been grown in PW3 water.

In all cases, the Fe(II) was oxidized to Fe(III) within 140 hours, and oxidation was complete sooner in bottles containing scale, similar to the biotic oxidation experiment, as described above. Higher proportions of Richmond water resulted in higher initial starting concentrations of dissolved Fe(II) (data not shown) and lower initial pH (Fig. 2). In bottles without added scale, the pH increased because of Fe(II) oxidation, then decreased in the 99 % PW3/1 % Richmond condition because of Fe(III) precipitation. No precipitation was observed in the 5 % and 10 % Richmond conditions, which is corroborated by the lack of a decrease in pH (Fig. 2A), and is consistent with the PHREEQC calculations. In the bottles with scale, however, the scale acts as a pH buffer, causing the 1 %, 5 % and 10 % conditions to cluster around a pH of approximately 2.2 (Fig. 2B). In addition, the total amount of Fe is higher as some of the scale dissolved, then reprecipitated as Fe(II) started oxidizing after approximately 50 hours (data not shown), causing the pH to decrease slightly with time (Fig. 2B). These results suggest that once scale is formed in the pipeline, it can act as a pH buffer in the system, decreasing the effectiveness of reducing pH by mixing PW3 water with Richmond water. When 100 % Richmond water was mixed with scale, approximately 60 % of the scale dissolved. Not surprisingly, the pipeline delivering Richmond water to the treatment plant has never had a scaling problem, consistent with the geochemical model that indicates undersaturation with respect to hydrous Fe(III) oxides at pH <1. It may also be possible to periodically flush the PW3 pipeline with Richmond water to partially dissolve the scale, but the success of that approach may depend upon the buffering capacity of the scale and the rate of dissolution.

Conclusions

Scaling in the PW3 pipeline at Iron Mountain Mine is the result of microbial Fe(II) oxidation, which causes the precipitation of primarily schwertmannite with some goethite. Dissolved Fe(II) in the pipeline was measurably oxidized along the flow path, even though the travel time was less than 1 hour. Bulk mineralogy of the scale was similar among four scale samples taken from the pipeline, but there is a higher concentration of biomass, carbon, nitrogen, and other trace elements associated with the upstream site (SS12), with concentrations decreasing along the pipeline. Geochemical modeling and bench tests indicate that a potential management strategy for the site would be to lower the pH of the pipeline water



Fig. 2 Changes in pH during batch experiments with 1 %, 5 % or 10 % Richmond water (balance PW3 water); (A) without scale and (B) with scale.

by mixing it with Richmond water after the pipeline has been cleaned of currently existing scale, preventing schwertmannite from precipitating even when Fe(II) becomes completely oxidized. To inhibit Fe(III) precipitation on a continuous basis, Richmond water would need to be added to the PW3 pipeline at approximately 5–10 % of the flow volume.

Acknowledgements

Funding for this work was provided by the U.S. Environmental Protection Agency (EPA). The authors thank James Sickles and Lily Tavassoli of EPA for project management, and Rudy Carver, Theron Elbe, and Don Odean of Iron Mountain Operations for field support and for discussions regarding remediation options. The authors also thank Gary Campbell (USGS Volunteer for Science), JoAnna Barrell (Colorado School of Mines), David Metge (USGS), and Deb Repert (USGS). Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the US Government.

References

- Ball JW, Nordstrom DK (1991) WATEQ4F user's manual with revised thermodynamic database and test cases for calculating speciation of major, trace and redox elements in natural waters. U.S. Geological Survey Open-File Report 91–183, 188 pp.
- Baron D, Palmer CD (1996) Solubility of jarosite at 4-35 °C. Geochimica et Cosmochimica Acta 60:185– 195.
- Bigham JM, Schwertmann U, Traina SJ, Winland RL, Wolf M (1996) Schwertmannite and the chemical modeling of iron in acid sulfate waters. Geochimica et Cosmochimica Acta 60: 2111–2121.

- Campbell KM, Hay MB, Nordstrom DK (2012) Kinetic modelling of microbial Fe(II) oxidation, Fe(III) hydrolysis, and As(III) oxidation in acid waters. In: Ng JC, Noller BN, Naidu R, Bundschuh J, Bhattacharya P (Eds), As 2012: Understanding the geological and medical interface of arsenic, CRC Press, p 479–480.
- Cornell RM, Schwertmann U (2003) The iron oxides: Structure, properties, reactions, occurrences and uses, VCH, Weinheim, Germany, 664 pp.
- Environmental Protection Agency (2006) Abandoned mine lands case study: Iron mountain mine. http://www.epa.gov/aml/tech/imm.pdf.
- Kinkel AR, Hall WE, Albers JP (1956) Geology and basemetal deposits of west Shasta copper-zinc district Shasta county, California. U.S. Geological Survey Professional Paper 285, 156 pp.
- Nordstrom DK, Alpers CN, Ptacek CJ, Blowes DW (2000) Negative pH and extremely acidic mine waters from Iron Mountain, California. Environmental Science and Technology 34: 254–258.
- Nordstrom DK (2003) Effects of microbiological and geochemical interactions in mine drainage. In: Jambor JL, Blowes DW, Ritchie AIM (Eds), Environmental Aspects of Mine Wastes, Mineral Association of Canada, 227–238.
- Nordstrom DK (2011) Mine waters: acidic to circumneutral. Elements 7: 393–398.
- Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC (version 2): A computer program for speciation, batch reaction, one-dimensional transport, and inverse geochemical calculations. USGS Water Resources Investigation Report 99–4259, 327 pp.
- Schwertmann U, Cornell RM (1991) Iron oxides in the laboratory. VCH, Weinheim, Germany, 137 pp.
- Stookey LL (1970) FerroZine a new spectrophotometric reagent for iron. Analytical Chemistry 42: 779– 781.

MiniSipper: A New, High-capacity, Long-duration, Automated In Situ Water Sampler for Acid Mine Drainage Monitoring

Thomas CHAPIN¹, Christina PROGESS², Andrew TODD¹

¹USGS, Box 25046, MS 964D, Denver Federal Center, Denver, CO 80225, tchapin@usgs.gov, atodd@usgs.gov ²EPA, 1595 Wynkoop St, Denver, CO80202, Progess.Christina@epa.gov

Abstract The US Geological Survey (USGS) has developed the MiniSipper, a low-cost, automated, *in situ* water sampler to provide high-resolution, year-round, sampling for acid mine drainage monitoring at remote sites. The MiniSipper typically collects 250 five mL acid preserved water samples and operates unattended for 8–12 months for over-winter and snowmelt runoff sampling. Year-round, high-resolution metal data from two different abandoned mines in CO, USA document opposite water quality responses to snowmelt runoff and demonstrate the advantages of MiniSipper technology in difficult sampling environments.

Keywords high-resolution sampling, acid mine drainage, seasonal variations, *in situ* water sampler

Introduction

Abandoned mines are often located in remote, high-elevation areas that are very challenging to sample, especially during the inaccessible 7-8 month winter period. Hand-collected 'grab' samples are the most common type of water sampling in remote areas and grab sampling typically collects a few samples per year at times when the site is easily accessible. Grab sampling can be very labor intensive and expensive, with significant costs for personnel salary, field vehicles and sampling equipment. Thus high-resolution grab sampling in remote as well as snowbound areas is usually not feasible nor affordable. Automated samplers could provide water sampling at these remote, difficult to access. or snowbound sites. but currently available automated samplers are typically large, heavy, collect 24 1 L samples, and are not well suited for operation in freezing conditions.

The US Environmental Protection Agency (EPA) is currently evaluating remediation options at the abandoned Pennsylvania Mine near Keystone, CO, USA and the abandoned Standard Mine near Crested Butte, CO, USA (Fig. 1). Both mines are situated in high alpine watersheds at \approx 3300 m above sea level and are snowbound for 7–8 months/a. The Pennsylvania and Standard Mines have large metal sulfide ore deposits and are significant point sources of acid mine drainage and toxic metals to streams that have both water supply and recreational use classifications. Local, state



Fig. 1 Location maps of the Pennsylvania and Standard Mines, CO, USA.

and federal agencies are examining clean up options for the Pennsylvania and Standard Mines but their remediation designs are hampered by the limited amount of water quality data, especially metal data from major runoff events such as spring snowmelt runoff and large rainstorms. In order to better understand the effects of major runoff events, the EPA has contracted with the USGS to provide high-resolution water sampling at the Pennsylvania Mine and Standard Mine over the entire water year. The USGS has developed the MiniSipper; a small, lightweight, low-cost, high-capacity water sampler to address the limitations of current automated water samplers. This paper will discuss year-round highresolution metal data collected by MiniSippers from the Pennsylvania and Standard Mines

Methods

MiniSipper methods and analytical details can be found in Chapin and Todd (2012) and only a brief overview is presented here. The MiniSipper is a battery powered, automated, *in situ* water sampler that uses micro-pumps to inject filtered water samples, acid preservative, and a gas separation bubble into a long sample coil (Fig. 2). The MiniSipper typically collects 250 5 mL samples with <5 % carryover between samples. Sample volume, timing and number are adjustable and up to five hundred 2.5 mL samples can be collected. Sample filtration is provided by a 10 µm polyethylene filter which closely tracks 0.45 µm grab samples. After recovery, samples are analyzed by standard USGS ICP-MS methods for 44 elements (Lamothe *et al.* 2002). Total cost for MiniSipper parts is \approx \$3,000 USD. The small size, low power requirement, and *in situ* operation of the MiniSipper enable 8–12 month deployments and the MiniSipper operates in water under surface ice/snow for over-winter and snowmelt runoff sampling.

MiniSippers were deployed at the Pennsylvania and Standard Mine adits and sampled acid mine discharge every 3-7 days during winter and daily from spring to fall. Over-winter hand-collected grab sampling by USGS personnel required snow machine access and backcountry skiing to reach the Pennsylvania and Standard Mines from November through June. Comparison of MiniSipper results with hand-collected grab samples is an important validation check and MiniSipper results were typically within 10 % of grab sample results. Data gaps were caused by instrument failures or MiniSipper redeployments. Instrument reliability has improved and the MiniSipper now routinely operates for 8-12 months unattended

Results and Discussion

The following discussion will focus on Cu, Mn, and Zn results as these toxic metals are representative of different geochemical responses to hydrologic events observed at both the Pennsylvania Mine and Standard Mine. We have high resolution annual data from 2009 through 2012 at both the Pennsylvania and Standard Mines and will examine subsets of this data.



Fig. 2 Schematic layout and photo of MiniSipper.

Pennsylvania Mine

Metal concentrations at the Pennsylvania Mine site showed a consistent annual pattern with the lowest metal concentrations during the low-flow winter period and the highest metal concentrations during snowmelt runoff (Fig. 3). During snowmelt runoff, metal concentrations at the Pennsylvania Mine adit increased 2-15 times over late winter low-flow metal concentrations. After peak metal concentrations in mid-June, metal concentrations at the Pennsylvania Mine gradually declined over the next 6 months to low-flow winter (baseline) metal concentrations (Fig. 3). The gradual decrease in metal concentrations after snowmelt runoff can be interrupted if large summer thunderstorms lead to a second metal concentration and conductivity peak as observed in 2010 (Fig. 3). These secondary latesummer conductivity and metal peaks were not observed in 2009 (Fig. 3) or 2011-2012 (not shown).

Significant thunderstorms were observed in summer 2010 and led to dramatic changes in water quality flowing out of the Pennsylvania Mine. Fig. 4 shows the Zn concentration, flow and conductivity response to snowmelt runoff during June and large rainstorms at the end of July and beginning of summer of 2010 was similar to metal increases observed during the snowmelt runoff in June 2010 (Fig. 4). Metals concentrations declined slowly after the large late summer rain event, taking over a month to return to pre-rain metal concentrations (Fig. 4). Late summer increases in metal concentrations were not recorded in 2009. 2011, or 2012. High metal concentrations associated with high runoff at the Pennsylvania Mine likely indicate that a rising water table comes into contact with efflorescent salts or isolated mine pools which increases metal concentrations in the mine runoff (Butler et al. 2008, Nordstrom 2009, Chapin and Todd 2012).

Standard Mine

In contrast to the Pennsylvania Mine, most metals at the Standard Mine (*e.g.* Mn) showed a dilution signature with lowest metal concentrations during maximum snowmelt runoff and highest metal concentrations during the low-flow winter period (Fig. 5). Zinc concentrations were high during the winter low-flow period, increased during the initial snowmelt runoff in April and May, and were lowest during maximum snowmelt runoff (Fig. 5). The Zn



Fig. 3 Two years of conductivity and Cu (a), Mn (b) and Zn (c) concentrations at the Pennsylvania Mine (n=400). Large blue symbols represent hand-collected grab samples (n=17)



pattern suggest that initial snowmelt runoff pushed elevated Zn waters out of the mine workings and then Zn concentrations were diluted during maximum snowmelt runoff. Metals sensitive to pH changes (*e.g.* Cu) showed very different behavior at the Standard Mine, with lowest values during the winter low-flow period and transient high concentration spikes during initial snowmelt runoff (Fig. 5).

Fig. 6 shows the water quality details during snowmelt runoff in 2010 at the Standard Mine and we observed some interesting responses for pH sensitive metals. During the November-April low-flow winter period, Cu concentrations were low (<0.1 mg/L), pH was above pH 6, and conductivity was steady. In mid-April temperatures warmed and initial snowmelt led to an increase in flow from the Standard Mine and a decrease in conductivity (Fig. 6). The initial snowmelt pulse caused a drop in pH (pH >6 to pH 3) and a large spike in Cu concentrations (<0.1 to 1.25 mg/L, Fig. 6). Initial snowmelt runoff pH and metal spikes have been observed in other snowpack dominated acid mine drainage sites(Sondergaard et al. 2008). An early May snowstorm dropped temperatures and refroze the snowpack. This resulted in a decrease in flow, increase in pH (pH 3 to pH5), and decreased Cu concentrations to ≈ 0.3 mg/L for a few weeks (Fig. 6). In late May 2010, the area warmed again and snowmelt runoff resumed, resulting in an increase in flow, decrease in pH, and increase in Cu concentrations (Fig. 6). During maximum snowmelt runoff in mid-June, waters issuing from the Standard Mine had pH values between 3-4 and relatively high Cu concentrations (0.6-1.0 mg/L). After peak snowmelt runoff, Cu concentrations decreased during summer and remained low through the fall and winter. Other pH sensitive metals (Al and



Pb) displayed the same pattern as Cu (not shown). MiniSipper results were confirmed by fortuitously-timed USGS grab sampling which required snow mobile and backcountry ski access to the Standard Mine at two week intervals from late March through June 2010 (blue diamond symbols, Manning *et al.* 2011). This early snowmelt pattern was observed again in 2011 so the early pulses in pH and pH sensitive metals may be a common response at the Standard Mine (not shown).

Metal-Conductivity Correlations

Toxic metals such as Cu and Zn were highly correlated with conductivity at the Pennsylvania Mine (R^2 > 0.9, Fig. 7), but were poorly correlated with conductivity at the Standard Mine

 $(R^2 < 0.4, Fig 7)$. High-resolution conductivity data is relatively easy and inexpensive to collect and conductivity could be used as a proxy for metal concentrations where metals are highly correlated to conductivity. This opens up the potential for low-cost, real-time metal flux estimates using real-time conductivity and flow data. Conductivity based metal estimates would be a valid approach at the Pennsylvania Mine but not at the Standard Mine. Robust conductivity-metal correlations require high-resolution metal and conductivity data throughout the entire water year. One of the greatest advantages of MiniSipper technology is the ability to inexpensively collect water samples during the entire year, especially during inaccessible periods.



Fig. 7 Conductivity-metal correlations for the Pennsylvania and Standard Mines.

Conclusions

MiniSippers provide low-cost, high-resolution water sampling for year-round monitoring of acid mine drainage systems. We observed excellent agreement between hand-collected grab samples and MiniSipper results at both the Pennsylvania and Standard Mines. MiniSipper sampling provided a detailed look at metal responses to hydrologic events that had not been previously documented.

The MiniSipper is a very flexible platform and is easily adapted to other sampling challenges. MiniSippers have been used in tracer studies; in high-resolution monitoring of watersheds impacted by wildfires; and deployed underground for year-long, high-resolution monitoring of acid mine drainage sites. Other MiniSipper applications currently undergoing field-testing are the Borehole MiniSipper and the Event Response MiniSipper. The Borehole MiniSipper is a smaller instrument that fits down a 5 cm borehole and collects 52 water samples over an entire year. The Event Response MiniSipper has a depth-sensitive trigger that puts the MiniSipper into a faster sampling mode to capture the details of fast transient events such as flash flood events

Acknowledgements

The authors thank USGS and EPA personnel for providing grab sample data and C. Mills (USGS) for reviewing the manuscript.

References

- Butler BA, Ranville J, Ross PE (2008) Observed and modeled seasonal trends in dissolved and particulate Cu, Fe, Mn, and Zn in a mining-impacted stream. Water Research, 42: 3135–3145.
- Chapin TP, Todd AS (2012) MiniSipper: A new *in situ* water sampler for high-resolution, long-duration acid mine drainage monitoring. Sci Total Environ, 439:343–353.
- Lamothe PJ, Meier A, Wilson S (2002) The determination of forty-four elements in aqueous samples by inductively coupled plasma, mass spectrometry. USGS Open-File Report 2002–0223.
- Manning AH, Verplanck PL, Mast MA, Marsik, J, Mc-Cleskey RB (2011) Spring runoff water-chemistry data from the Standard Mine and Elk Creek, Gunnison County, Colorado 2010: USGS Open-File Report 2011–1159, 20 p.
- Nordstrom DK (2009) Acid rock drainage and climate change. J Geochem Exploration, 100:97–104.
- Sondergaard J, Elberline B, Asmund G (2008)Metal speciation and bioavailability in acid mine drainage from a high Arctic coal mine waste rock pile: Temporal variations assessed through high-resolution water sampling, geochemical modelling and DGT.Cold Regions Sci Tech, 54:89–96.
- Disclaimer: Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Acid Rock Drainage Challenges and a Path Forward

Terrence CHATWIN¹, Dean WILLIAMS², Mike CREEK³

¹INAP, 2105 Oneida Street, Salt Lake City, UT 84109, USA, tchatwin@inap.com.au ²Kinross Gold, 5370 Kietzke Lane, Suite 102, Reno, NV 89511, USA, dean.williams@kinross.com ³Newmont Mining, 1393 Royal Crest, Elko, NV 89801, USA, mike.creek@newmont.com

Abstract Acid Rock Drainage (ARD) is one of the most serious and long-lasting environmental problems of the mining industry. To address these problems, INAP, a network of international mining companies, has prepared the GARD Guide, a best practices guide for the prevention of ARD. This guide is found on the internet at www.GARDGuide.com, and is free for use by all mining stakeholders. INAP's approach to meeting this challenge is through teaming with partners across the globe and adapting the GARD Guide to meet the specific needs of all stakeholders. Finally, INAP plans to publish case studies of current mining practice that demonstrate ARD prevention.

Keywords ARD, GARD Guide, best practices, internet based, ARD prevention, case studies

Introduction

Acid rock drainage (ARD) is one of the most serious and potentially enduring environmental problems of the mining industry. While most mines do not have an ARD problem, the few that do represent a significant liability for their owners as indicated in many of their financial disclosures. Unchecked, ARD can result in such extensive water quality impacts that it could well be this industry's most harmful legacy. Effectively preventing acid drainage is a formidable challenge for which applying best management practices early in the mining process has demonstrated success.

While not every old mining site has ARD, the Global legacy mining sites where ARD is an issue have created a difficult public image problem for the mining industry. To overcome this image the mining industry needs to differentiate between the mining companies of the present with those of the past. We need to continue to enhance and standardize our methods to characterize mining wastes and strengthen our models and tools to predict the potential generation of ARD. With this information, we can assure that appropriate mitigation measures are applied to potential acid generating (PAG) wastes. With relevant monitoring we can continue to measure and improve our methods to prevent ARD.

In 2009, INAP published a best practices guide (INAP 2009) designed to prevent ARD. This guide is located on the internet at www.gardguide.com; it includes a discussion of the chemistry and physics of ARD formation and current characterization, prediction, prevention, mitigation, treatment and monitoring methods to help in the prevention of ARD. It is available for use by all.

We need to demonstrate that not only do we have the methods and resources to mine in a manner that mine wastes do not generate ARD, but that we are committed to achieving this goal. INAP believes that the mining industry has the best practices as set forth in the GARD Guide to demonstrate ARD prevention. Consequently, we need to develop a large compendium of case histories to justify this claim. This compendium of case studies will be one of INAP's upcoming projects. Each of these acts INAP performs is based on joint commitment of its members to the sustainable development of the mining industry. We believe that mining not only creates resources for the world economy and value for the companies and its stakeholders, but it can create value for all if it is done in a sustainable manner.

What is INAP?

The International Network for Acid Prevention (INAP) is an industry-led network created to help meet this challenge. INAP fills the need for an international body to mobilize information, experience and resources to prevent and address ARD. The network was created in 1998 to coordinate and facilitate global research on the management of mine wastes and the prevention of acid drainage. Since then, INAP has become a proactive, global leader in this field.

Two primary approaches that INAP uses to meet this objective are

- **1.** planning and implementing cost-effective collaborative research to develop solutions for ARD issues and
- **2.** information and knowledge transfer to all mining industry stakeholders across the globe.

INAP has been very effective in directing and funding applied research relating to ARD prevention. While INAP funding support is limited, we do have tools that make INAP research support extremely effective. The collaborative nature of INAP ARD research is key, based on the review and vetting of INAP research projects by multiple mining companies, whose experience, understanding and research needs are very broad. In this network, each research project has a project champion, typically from the INAP Operating Committee, who is responsible to assure that project stays on schedule and meets project objectives. In addition, we have many potential demonstration sites whose characteristics can fit research project needs. Because of the INAP network knowledge and understanding, our seed funding can be very effective in generating collaborative funding. Other funding agencies know that INAP's strong technical presence, our commitment of company champions and our review and vetting of project plans, design and progress enhances the potential for program success. INAP member companies and partners are pleased with the successes of our research program.

Global Alliance

To expand local engagement in the diverse mining regions across the globe INAP has supported the formation of the Global Alliance (GA). This is a network of regional organizations whose expressed purpose is to mitigate and prevent ARD. Currently, the GA is composed of eight regional groups located in:

- Australia SMIKT, Sustainable Mining Institute – Knowledge Transfer
- Canada MEND, Mine Environment Neutral Drainage
- China CNAMD, Chinese Network for Acid and Metalliferous Drainage
- Europe PADRE, Partnership for Acid Drainage Remediation in Europe
- Indonesia INAD, Indonesian Network for Acid Drainage
- South Africa WRC, Water Research Commission
- South America– SANAP, South American Network for Acid Prevention
- United States ADTI. Acid Drainage Technology Initiative

Other regions and countries have expressed interest in participating in the GA.

ICARD

Since its founding, INAP has acted as the virtual home of the International Conference for Acid Rock Drainage (ICARD). The most recent ICARD was held in Ottawa, Canada and was extremely successful with over 500 people in attendance for the courses, presentations and tours. In addition, INAP held a Path Forward Symposium to share innovative technical developments and concepts that related to the mitigation of ARD and its effects. Over 90 ARD practitioners participated in the symposium. Seventeen innovative technologies and ideas were presented in a plenary session. Four focused discussion groups on (Biogeochemistry, Waste cover design, Innovative treatment technologies and Stakeholder engagement) and two additional plenary sessions were held to vet and expand the ideas presented. Results were forwarded to INAP for its consideration. A summary of the Path Forward was distributed to all attendees.

GARD Guide

In 2009, INAP commissioned and published a best practice guide (INAP 2009) aimed at the identification and avoidance of potential ARD as well as addressing its management and treatment, which is found on the internet at www.gardguide.comand is available free to all mining industry stakeholders. Since the publication of the GARD Guide, the eleven chapters of the GARD Guide have received over 700,000 total hits, for which a very focused and technical document; it has exceeded INAP's expectations. More details on the GARD Guide are found in a paper published in Mine Water and the Environment (Verburg et al. 2009). When INAP published the GARD Guide our purpose was to engage as many mining industry stakeholders as partners in its application and promotion. We were extremely pleased when the Global Alliance members volunteered to organize and teach short courses on the GARD Guide. Since that time, we have had numerous short courses and presentation on the GARD Guide in the USA, Australia, Canada, Brazil, Chile, Germany, Sweden, Indonesia, China, South Africa and Turkey, with most of the organization and instruction being performed by GA members.

Global Alliance members have also been instrumental in the translations of sections of the GARD Guide into relevant languages of their regions. The GARD Guide executive summary was translated into Spanish by Patrick Williamson, of SRK and ADTI, and into French by Gilles Tremblay, of MEND. Golder Associates and others in Turkey are presently translating the GARD Guide executive summary into Turkish and are planning to seek membership in the GA.

Beside the Global Alliance, other partners are assisting INAP to promote the GARD Guide. The US Environmental Protection Agency (EPA) has borrowed a large section of the GARD Guide and translated it into Spanish and attached the translation as an appendix to the mining guidance document they prepared for Central America under the Central American Free Trade Act (CAFTA; EPA 2012). EPA also sponsored a webinar focused on technical resources relating to mitigating environmental issues caused by mining. A section of this webinar covered the GARD Guide and was presented on June 13, 2012 by Carol Russell, of EPA and ADTI.

In discussions with International Finance Corporation (IFC), INAP has learned that IFC will be referencing the GARD Guide in their future mining guidance for projects funded by their organization. In the past, INAP has reviewed and commented on IFC mining guidance documents, and we are pleased with this development. INAP is currently in discussions with the US Forest Service (USFS) concerning how INAP might assist the USFS in their training relating to mines on Forest Service land.

In addition, the GARD Guide is also being taught on the internet by EduMine. Over the past two years, the GARD Guide course has been taken by over 300 students. INAP is also discussing with the University of British Columbia and the University of Arizona the possibility that the GARD Guide internet course be included in their mining certificate programs.

Path Forward

INAP is pleased with the reception the on-line GARD Guide has received, but we recognize the need for broader adoption of the practices within the GARD Guide. Our outreach efforts are focused on two diverse populations. First, we want to increase the awareness of the GARD Guide among technical disciplines in

the mining industry. Second, we want to improve the level of understanding in this issue by external stakeholders, such as community leaders, who are interested and concerned about the mine plans and issues but may not have the technical training necessary to fully comprehend the GARD Guide.

Broader technical engagement

INAP wants broader technical engagement and understanding of the GARD Guide by geologists, materials handling designers, mining engineers and planners. The better engineers, designers and planners understand the GARD Guide and the ARD management plan – the more effectively ARD prevention will be implemented, The ARD management plan, which isthe keystone of effective ARD prevention and application of the GARD Guide, is often based on the work of the mine planner.

During exploration, determining the volume, grade and location of the ore are critical, but characterization of the waste is also important. While ore is the first priority, wastes also need to be sampled and available for early characterization to determine potentially acid generating (PAG) materials. During the mine planning and design phase, the mine plan should address how any potentially acid generating (PAG) waste will be managed to mitigate the potential of ARD formation. This should be an integral part of the mine planning activity. It is also important that the costs of ARD management are fully captured in the mine operating budget and continually updated as the mine plan progresses. One suggestion from the GARD Guide is to develop a mine block model including PAG characterization as well as ore grade. In Chapter 9 of the GARD Guide, an illustration, of how this block model was prepared at the Mt. Milligan project, was used as an example.

As well as, geologist, mine planners and engineers, it is important for all mining and mineral processing disciplines to be engaged in addressing ARD issues. Additional processing of waste streams both solid and liquid can result in reduction of current and future acid and metalliferous drainage. This practice can also have the added advantage of recovering saleable bi-products to mitigate the cost of sulfide waste management.

For the ARD management to be effective, full buy in by the mine operation management and staff is required. This means that during mine operations, the ARD management plan is fully implemented and integrated into the mine operations and the mine wastes are fully characterized. If this buy in occurs, it is unlikely that unidentified PAG wastes and ARD seeps are discovered during mine closure or post closure, when resources are limited and remobilization is very expensive. This situation has occurred at some of the previously closed mine sites with resulting major cost over-runs and long-lasting management commitments. An even more significant problem is that once ARD is observed it is almost assured that there will be a long-lasting and potentially perpetual water treatment effort, unsignificant waste re-handling less and reclamation efforts are implemented.

Business Case for ARD Prevention

Often, we hear complaints that net present value drives the postponement of the ARD preventative measures until closure because they are cost intensive and not value producing. In response, we need a stronger argument to show that less expensive preventative options could be available if they are integrated into mine operations during early planning and design. As these mitigation options are postponed some of the more effective and less costly options become no longer viable because of prior operational actions.

The ARD Management Plan and preventative actions are site specific to the operation. Hence, each business case for ARD prevention is site specific. Thus we need a general document like the GARD Guide that addresses the concerns of accountants, written so they also grasp the importance of mitigating corporate risk through ARD prevention and understanding the trade offs in early waste characterization and ARD management planning. We also need to engage mine planners to develop computer programs and tools to design the mine plan not only to generate the highest net present value, but do it in a manner that also has the lowest risk profile.

Community engagement

We understand that the technical issues surrounding ARD can be daunting and misinformation difficult to overcome. For these reasons we are focused on the development of communications and guidance aimed at demystifying ARD for the lay public. We believe that it is important to have a short, simplified version of the GARD Guide that is designed for these stakeholders that explains the issues and actions in terms that are understandable to all regardless of their education or background. INAP is in the process of working with partners to design and publish a guide as described.

Since the publication and success of the GARD Guide, INAP has focused on information and knowledge transfer to match of the momentum of the GARD Guide success. In the immediate future, INAP is planning to prepare GARD Guide supplements to focus on applying its principles to relevant mining planning functions and to enhance its understanding to lay stakeholders. We will also focus on developing a compendium of ARD preventions case studies. Results of a recent strategic planning meeting propose to continue information and knowledge and to expand INAP's collaborative research efforts relating to ARD prevention.

Case Study Compendia

Generating this compendium of case history requires time as well as the consistent use of best practices by companies to mine sulfide ore bodies. The GARD Guide has only been published for four years and many of these best practices included in that document have only been developed in the past two decades. For a case study of ARD prevention to be considered of sufficient value, a demonstration of at least 10 years would be expected (Wisconsin 1997). Hence, we are presently at the point where some mining operations are demonstrating ARD prevention of this duration.

Consequently, the mining industry must continue to maintain this highly focused effort to assure that future mining does not result ARD discharges, and publish case studies of these successful operations to demonstrate that this best practice is the common practice of the industry. In addition, it is important to recognize that ARD discharge is limited to mines where potentially acid producing wastes (PAG) are generated. Hence, an ARD management plan is required only in these cases where ARD could be potentially generated and is not a uniform requirement for all mining sites. Most mines do not generate ARD discharges; hence, an ARD management plan is not required

Collaborative Research

Resulting from INAP's recent strategic planning meeting, our next research project will focus on mine waste cover design. At recent meetings including the Australian AMD Workshop in Darwin in 2011 (SMIKT 2011), the EPA Hard Rock Mining Conference in Denver in April 2012 (EPA 2012), the ICARD in Ottawa in May 2012 and the Path Forward Symposium in May 2012, there was much discussion of on the design of waste covers. A recent publication by MEND addresses waste covers in arctic regions (MEND 2012). This wealth of discussion and thought demonstrates the intense interest in cover design and stability.

Conclusions

By broadening the awareness and application of the GARD Guide across the mining industry, INAP believes that the industry will be able to demonstrate ARD management, thus lowering the risk of ARD formation and its accompanying impacts. ARD management needs the engagement and commitment of all company technical and financial disciplines for its success. By preparing case studies that illustrate successful ARD prevention, we believe that we will be able to help counteract the negative image with which the mining industry has saddled. But this effort will require consistent and committed action by the entire industry. We also believe that a successful ARD prevention plan requires the full engagement of all industry stakeholders. INAP will continue to pursue the involvement of all disciplines and stakeholders by broadening and promoting the principles of ARD prevention presented in the GARD Guide. As stated in the beginning INAP and its members embrace sustainable development. The actions of INAP are designed not only to prevent ARD, but as part of our commitment to sustainable and responsible mining for the benefit of all of our stakeholders

References

- Environmental Protection Agency (EPA) (2012) Vol 1 EIA Technical Review Guideline: Non-metal and metal mining, regional doc prep under CAFTA App (E):93-114
- Environmental Protection Agency (EPA) (2012) Hardrock Mining Advancing Solutions for a New Legacy, April 3–5, 2012, Denver, CO.
- International Network of Acid Prevention (INAP) (2009) The Global Acid Rock Drainage Guide. http://www.gardguide.com is the web address
- Mining Environmental Neutral Drainage (MEND) (2012) Cold Regions Cover System Design Tech Guidance Doc, MEND Report 1.61.5c
- Verburg R, Bezuidenhout N, Chatwin T, Ferguson K (2009) The Global Acid Rock Drainage Guide (GARD Guide), Mine Water Environ 28(4):305-310
- Wisconsin Department of Natural Resources (WDNR) (1997) Wis. Stat. §293.50

Interactions between dolomite and acid mine drainage in the Witwatersrand – Results of field and laboratory studies and the implications for natural attenuation in the West Rand Goldfield

Henk Coetzee¹, Mpho Kotoane¹, Maria Atanasova¹, Freddie Roelofse²

¹Council for Geoscience, Pretoria, South Africa, henkc@geoscience.org.za ²Department of Geology, University of the Free State, Bloemfontein, South Africa

Abstract Since 2002, acid mine drainage (AMD) has discharged from the West Rand Goldfield of the Witwatersrand into nearby streams and through subsurface flow into the adjacent dolomitic aquifer. Surface discharge has also been shown to recharge the dolomitic aquifer. This has led to fears of increased dissolution of the dolomite which, it has been proposed, could lead to land subsidence in the affected area. Laboratory investigations show that precipitation of resistant mineral coatings on reactive carbonate surfaces limit the potential for dissolution of dolomite and the potential for natural attenuation.

Keywords Acid mine drainage, natural attenuation, precipitation, laboratory simulation

Introduction

Gold has been mined in South Africa's West Rand Gold Field since the late 19th Century. The gold occurs in conglomerate layers within an Achaean volcano-sedimentary basin, overlain by dolomites of the Proterozoic Transvaal Supergroup (Toens and Griffiths 1964). The mineralised conglomerates contain appreciable quantities of pyrite, leading to the generation of acid mine drainage when these are disturbed by mining (Coetzee *et al.* 2005). Fig. 1 shows the spatial relationship of the West, Central and East Rand Gold Fields to the outcrop of the Malmani Dolomite.



Fig. 1 Location of the West, Central and East Rand Goldfields relative to the City of Johannesburg and surrounding urban areas and the outcrop of the Malmani Dolomite (Ramontja et al. 2011).

Concern has been expressed relating to the possibility of acid mine drainage generated in the Witwatersrand contaminating valuable groundwater resources contained within the dolomite (Hobbs and Cobbing 2007), while Krige (2006) proposes that acidic water entering dolomitic aquifers could lead to accelerated dissolution of dolomite and the formation of sinkholes. Krige's (2006) study identifies the possibility of iron and sulphaterich precipitates forming in the reactions between dolomite and both AMD and sulphuric acid and uses results derived from consideration of the reaction with HCl. as would be used in an acid base accounting test (Sobek et al. 1978), to determine the potential dissolution of dolomite. This study aims to examine the potential impacts of acid mine drainage from the Witwatersrand entering the groundwater in the adjacent dolomitic areas.

Experimental studies Initial batch experiment

Shortly after the discharge of acid mine drainage commenced in the West Rand in 2002, a qualitative experiment was undertaken to assess the potential use of dolomite in the neutralisation of AMD. Dolomite chips were added to a sample of AMD from the West Rand and shaken overnight. This was found to only slightly raise the pH, while an orange precipitate was observed on the surface of the dolomite. This was not pursued further as it was assumed that the iron in the AMD was precipitating as a hydroxide mineral and armouring the dolomite surface, preventing neutralisation reactions from taking place.

Batch study with petrographic and mineralogical investigation

Polished thin sections were cut from a dolomite sample and investigated petrographically. Following the initial investigation, these were exposed to AMD from a shaft where water decants from the old Randfontein Estates Gold Mine. The thin sections were placed in beakers which were then filled to the brim with AMD from the shaft and sealed in an attempt to avoid additional oxygen entering the beakers. These were returned to the laboratory and agitated slowly for a period of one week to allow constant flow of AMD over the dolomite surface. Following the week of immersion in AMD the thin sections were removed and air dried to allow re-investigation to determine the effects of AMD exposure. The pre- and post-leaching chemical parameters of the AMD are presented on Table 1.

These results indicate a drop in pH during the week of leaching, most likely due to the oxidation of Fe^{2+} to Fe^{3+} with the concomitant lowering of pH, characteristic of acid mine drainage from this mine (Coetzee *et al.* 2007). This was also indicated by the precipitation of Fe^{3+} hydroxide phases observed on the samples. No neutralisation effects are seen in these data however this could be expected due to the extremely small volume of dolomite contained in a single thin section.

Petrographic investigation (Roelofse 2010) shows an exaggeration of grain boundaries and microfractures within the dolomite (Fig. 2). In some cases and the deposition of a brown coloured opaque precipitate can be seen along grain boundaries. These effects suggest etch-

Sample	pH- Initial	EC-Initial (mS/m)	ORP - Initial (mV)	pH-Post Leaching	EC-Post Leaching (mS/m)	ORP Post- Leaching (mV)	
Dolomite (a)	5.44	548	-57	4.405	514	113	
Dolomite (b)	5.44	548	-57	4.312	510	110	Table 1 Chemical parame
Blank (a)	5.44	548	-57	4.498	517	85	ters of AMD pre and post
Blank (b)	5.44	548	-57	3.898	558	119	leaching of dolomite thin sections



Fig. 2 Photomicrographs (PPL) of dolomite before (a) and after (b) leaching with AMD collected the West Rand Gold Field (the dark line in the images is a line scribed in the polished thin section to allow the identification of the same area before and after leaching).

ing of the dolomite surface by partial dissolution of the dolomite as well as the precipitation of new minerals, presumably iron hydroxide minerals, in the etched areas.

The precipitate identified on the samples was further investigated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) on the same polished thin sections and on crushed dolomite exposed to the same AMD as the polished thin sections, allowing the identification of the mineral precipitates formed (Fig. 3).

The precipitates formed were shown to comprise largely gypsum (CaSO₄) and goethite (FeO(OH)), which are the products expected to form due to the neutralisation of typical acid mine drainage by a calcium-rich carbonate mineral.

Column tests using synthetic AMD

Following the batch tests, a column test was designed to simulate the flow of acid mine drainage through a dolomitic aquifer. A synthetic acid mine drainage mixture (Coetzee *et al.* 2011)was prepared which aimed to simulate acid mine drainage sampled from the West Rand Goldfield, with the chemistry modified to allow iron to remain in solution to avoid rapid armoring of the dolomite with iron minerals. This was allowed to flow through vertical columns packed with different size fractions of dolomite at a constant liquid to solid ratio of around 0.1 L/kg/d. This experiment was allowed to run for a period of 5 months, with frequent measurements of pH and EC and monthly chemical analyses of the produced leachate. The results are summarised in Table 2.

During the course of this experiment, a precipitate consisting of a mixture of a white and and orange coloured mineral began to



Fig. 3 Typical SEM image of the precipitate phases in the leached dolomite samples

Analyte	Input solution	Column leachate range	Comments						
	range								
pH	3.6	7.5-8.5	Dolomite proved effective at neutralising the synthetic AMD						
			solution during the period of the experiment.						
Fe (mg/l)	1.5-13	< 0.05	Iron was precipitated during the course of the experiment.						
Al (mg/l)	16-21	< 0.025-0.5	Aluminum was strongly attenuated by the interactions with						
			dolomite.						
SO_4	730-920	630-920	Sulphate was hardly attenuated in the interactions with						
			dolomite.						
Ca	8-21	60-100	Calcium was dissolved from the dolomite during the						
			experiment.						
Mg	65-77	94-131	Some magnesium was dissolved.						

Table 2 Summary of the results of the column test using synthetic AMD

form at the bottom of each of the columns (Fig. 4). SEM investigation of this material, using EDS, shows the development of a crys-



Fig. 4 Precipitate forming at the bottom of a column due to the reaction between synthetic AMD and dolomite.

talline and amorphous (botryoidal) mineral containing Al, O and S (Fig. 5).

These results illustrate the ability of dolomite to neutralise AMD. However it was felt that the low iron content of the synthetic AMD used was not realistic and that a more realistic experiment using AMD generated in the lab via the reaction of the relevant sulphidic rock material, oxygen and water would produce more realistic results.

Column test using lab-generated AMD

In order to produce a more realistic simulation of the reaction between dolomite and acid



Fig. 5 SEM image o the amorphous and crystalline precipitate generated in the reaction between synthetic AMD and dolomite.

mine drainage for the West Rand Gold Field, a similar kinetic experiment was initiated, replacing the synthetic AMD solution with leachate generated in a column where Witwatersrand ore is exposed to water and oxygen, generating an acidic solution, as described by Tlowana et al. (2013). This method typically produces a leachate with an iron concentration of the order of 20-200 mg/L which is similar to measured values from the West Rand. In this experiment, neutralization was less effective and a red, iron rich precipitate formed rapidly (Fig. 6). In physical appearance, this is similar to precipitates observed in the field where AMD reacts with dolomitic material on the surface.

Conclusions

This study used a series of laboratory experiments to assess the potential impact of acid mine drainage from the West Rand Gold Field flowing into dolomitic aquifers. Batch and kinetic experiments were undertaken and the resulting reactions characterised via analysis of the produced solutions and mineralogical investigation of the precipitates generated. The generation of precipitates on reactive dolomite surfaces will tend to armour the dolomite and prevent further reactions from taking place, potentially mitigating the risk that interactions between AMD and dolomite will lead to an increased risk of sinkhole formation. This will also stop beneficial reactions between dolomite and groundwater from occurring. This could also limit the potential of natural attenuation of AMD using locally occurring dolomitic material.

This work has been limited to the laboratory investigation of a conceptual geochemical model. The experimental studies undertaken in this study emphasise the importance of realistic laboratory simulations of natural systems. Experimental methods which aimed to limit the potential of AMD to coat reactive rock surfaces with precipitates tended to overestimate the risk of sinkhole formation and the potential of dolomite to neutralise AMD.



Fig. 6 Iron-rich precipitate in a dolomite-filled column fed with lab-generated AMD

Field measurements to determine the range of pH and redox conditions and rock and solute compositions will be required to identify the specific reactions which are likely in different parts of the affected area. This will also require a good understanding of the local hydrogeology. Sampling of rocks and precipitates would also assist in determining which reactions have taken place.

References

- Coetzee, H., Croukamp, L., Venter, J. and de Wet, L. (2005) Contamination of the Tweelopiesspruit and environs by water from the Western Basin decant point on Harmony Gold's property., Council for Geoscience, Report No. 2005–0148, Pretoria: 28p.
- Coetzee, H., van Tonder, D., Wade, P., Esterhuyse, S., van Wyk, N., Ndengu, S., Venter, J. and Kotoane, M. (2007) Acid mine drainage in the Witwatersrand, Council for Geoscience, Pretoria: 80p.
- Coetzee, H., Wade, P. W., Kotoane, M., Atanasova, M. and Roelofse, F. (2011) Experimental investigation of the effects of influent acid mine drainage on dolomitic aquifers, Council for Geoscience, Council for Geoscience Report No. 2011–0069, Pretoria: 24p.
- Hobbs, P. J. and Cobbing, J. E. (2007) A hydrogeological assessment of acid mine drainage impacts in the West Rand Basin, Gauteng Province, CSIR/THRIP, CSIR/NRE/WR/ER/2007/0097/C, Pretoria: 59p.
- Krige, W. G. (2006) Hydrological/chemical aspects of the Tweelopie/Riet/Blaauwbankspruit, with specific

reference to the impact water, decanting from the Western Basin mine void has on this system, African Environmental Development, Mogale City: 71p.

- Ramontja, T., Coetzee, H., Hobbs, P. J., Burgess, J. E., Thomas, A., Keet, M., Yibas, B., van Tonder, D., Netili, F., Rust, U. A., Wade, P. and Maree, J. (2011) Mine Water Management in the Witwatersrand Gold Fields With Special Emphasis on Acid Mine Drainage Inter-Ministerial-Committee on Acid Mine Drainage, Pretoria: 146p.
- Roelofse, F. (2010) Comparative petrography of dolomite samples before and after exposure to acid mine drainage (AMD), Petrographic Laboratory, Council for Geoscience, 09/886(b), Pretoria: 11p.

- Sobek, A. A., Schuller, W. A. and Freeman, J. R. (1978) Field and Laboratory Methods Applicable to Overburdens and Minesoils, United States Environmental Protection Agency, EPA-600/2-78-054: 203p.
- Tlowana, S., Coetzee, H. and Makgae, M. (2013) Realistic simulation of acid mine drainage generation in the gold mines of the Witwatersrand, South Africa. IMWA 2013: Reliable Mine Water Technology. Colorado School of Mines, International Mine Water Association.
- Toens, P. D. and Griffiths, G. H. (1964) The Geology of the West Rand. in The geology of some ore deposits of Southern Africa. S. H. Haughton. Johannesburg, Geological Society of South Africa. 1: 283–322.

Availability of trace elements in the abandoned Freixeda gold mine area, NE Portugal

M. R. Costa¹²; P. Ávila³; A. Ferreira³; E. Ferreira da Silva²

¹Dep. de Geologia. Universidade de Trás-os-Montes e Alto Douro, Apartado 1013, 5001–801 Vila Real, Portugal, rosariomc@utad.pt

²GeoBioTec – Geobiosciences, Geotechnologies and Geoengineering Research Center, Dep. de Geociências. Universidade de Aveiro, Campus de Santiago, 3810–193 Aveiro, Portugal, eafsilva@ua.pt

³LNEG – Laboratório Nacional de Energia e Geologia, Lab. S. Mamede de Infesta, Rua da Amieira, Apartado 1089, 4466–901 S. Mamede de Infesta, Portugal, paula.avila@lneg.pt; adelaide.ferreira@lneg.pt

Abstract Selected geochemical results are presented from Freixeda gold mine area. The purpose was to establish the geochemical patterns of trace elements, which are useful for predicting their release ability into the aquatic environment for the assessment of pollution extension on surface waters along the Freixeda stream. Stream sediment and water samples were found to be contaminated for a considerable distance downstream. Based on chemical sequential extraction the distribution of trace elements in sediments, in particular As, is linked to exchangeable and acid-soluble species, upon which desorption and ion-exchange reactions may originate the release of these readily mobile and available phases.

Keywords Abandoned mines, selective chemical extraction, availability, trace metals, arsenic

Introduction

Freixeda mine is located in NE Portugal and was exploited for Au, Ag and Pb until 1955. The mine was closed after 1995, where more than 0.5 Mt of tailings remained exposed to erosion for more than 50 years. Several studies on soils, sediments, surface water and groundwater were carried out in the last 15 years (Montes *et al.* 2007; Pereira *et al.* 2007, 2008) in order to evaluate the environmental impact of Freixeda mine in the surrounding region.

The objective of the present study was (a) to study the geochemical patterns of As, Cu, Fe, Mn, Pb, and Zn; (b) predicting their availability to the aquatic environment and (c) the assessment of pollution extension along the Freixeda stream till the mouth in Tua river, a source of public water supply.

Geological and environmental setting of the study area

Freixeda Mine is part of the Gold-Silver Metalogenetic Province of Iberian Peninsula. These Au-Ag deposits are usually associated with Paleozoic quartzites and black schists and not so often they are intragranite. Gold ocurrences are associated with veins in metamorphic metasediments, affected by Variscan Orogeny (Almeida and Noronha 1988). According to Montes et al. (2007) the Freixeda quartz veins are composed by silicate minerals (mainly quartz and chlorite) and sulfide minerals (such as arsenopyrite, pyrite, sphalerite, galena, chalcopyrite and As, Pb, Fe and Sb sulphosalts). Arsenopyrite is the most representative mineral. In this mineral some As was replaced by Sb. Pyrite has some As in its composition reaching 1.74 % (Montes et al. 2007). Studies carried out by Cogema (1988) showed that soils presents higher As (6 to 7663 mg kg⁻¹) and Pb concentrations (18 to 1000 mg kg⁻¹). According the same study soils were classified as inappropriate for agriculture. Pereira et al. (2008) showed AMD impacted stream that the has 3.5 <pH< 4.2 and the water samples are classified as Mg-SO₄ type with high concentration



Fig. 1 Sampling locations of waters and sediment samples in the Freixeda study area.

of Al (1.01 mg L^{-1}), Fe (5.22 mg L^{-1}), Mn (10.1 mg L^{-1}) and low As concentration (18 µg L^{-1}). Main environmental problems in the region are related to As concentration in groundwater and in surface water.

Materials and Methods

In order to assess the dynamics of leaching, transport, and accumulation of some selected trace elements, stream surface waters (A) and sediments (S) were sampled (Fig. 1).

Sampling and analysis of water samples

Thirteen water samples were collected (Fig. 1). Sample A-1 represents the adit outflow, A-2 from a deep well, A-3: samples collected in Macedinho stream; A-4: sample collected outside the Freixeda mine influence, representing the local geochemical background; A-5 to A-13 samples collected in the Freixeda stream from the adit confluence to the Tua river. Water samples were filtered *in situ* by filling a 60 mL syringe, rinsed three times with the water, and forcing the water passing through a 25 mm disposable disk filter of cellulose acetate membrane with a pore size of 0.20 μ m. After filtration into 100 mL polyethylene bottles, samples were immediately acidified at 2 % HCl for the analysis of major cations and trace metals by ICP-OES or AAS. For the analysis of major anions and alkalinity, samples were collected into 1-L polyethylene bottles and filtered through a 0.45 μ m acetate cellulose membrane only in the moment of the sample analyze preparation. Field blanks for assessing possible contaminations were prepared with de-ionised water in the field.

Temperature, pH, and electric conductivity (EC) of the waters samples were recorded at each site. The pH was measured using a HI 8424 microcomputer pH meter and EC using a HI 8633 microcomputer electric conductivity meter. All EC measurements are referenced to 25 °C.

Water sample analysis was carried out in the Laboratory of the LNEG an accredited lab by the Portuguese official authority of Quality IPAC. At least, 20 % of the samples were analyzed in duplicate and some tests of recuperation were also performed. Quality control was

assessed for accuracy by analysing a reference water sample (AQUACHECK) and also for accuracy and precision by analysing an internal control standard solution. The analyzed elements include major anions (HCO₃⁻, Cl⁻, NO₃⁻ and SO_4^{2-}), major cations (Na, K, Mg and Ca), as well a suite of dissolved trace elements (Ag, Al, As, Bi, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb, S, Sb, and Zn). Chloride, NO_3^- and SO_4^{2-} on filtered unacidified samples were analyzed using a Dionex 1000i ion chromatography (IC) Work33 station. Bicarbonate was determined by titration on filtered unacidified samples. The concentrations of major cations and trace elements in acidified waters were determined using mass inductive plasma spectrometry (ICP-MS).

Stream Sediments Sampling and Analysis

In order to evaluate the extent of contamination, 11 stream sediments samples (composite samples of 3 sub-samples collected from several places at the sample site) were collected (Fig. 1). Sample S-1 was collected upstream AMD inflow to Freixeda stream; samples S-2 and S-3 were collected in a different watershed. Sample S-3 represents the local geochemical background; samples S-5 to S-11 were collected in Freixeda stream; and sample S-4 was sampled in the Tua river.

Stream sediments for chemical analysis were oven dried at 40 °C before dry sieving, mixed, homogenized, and sieved through a 200 mesh screen for chemical analyses. The homogenized stream sediments were analyzed also in the Laboratory of the LNEG. For trace metal analyses, a 0.5-g split was leached in hot (95 °C) aqua regia (HCl–HNO₃–H₂O) for 1 h. After dilution to 10 mL with deionized water, the solutions were analyzed for Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Mn, Mo, Nb, Ni, P, Pb, Sb, V, Y, and Zn by conductive plasma emission spectrometry.

Selective Chemical Extraction Procedure

Aiming to establish the geochemical patterns of selected trace elements (As, Cu, Fe, Mn, Pb,

and Zn), which are useful for predicting their release ability into the aquatic environment and into the ecosystem, the elements were analytically partitioned into labile and residual fractions using a selective sequential extraction (SCE) procedure proposed by Cardoso Fonseca and Ferreira da Silva (1998). According to Cardoso Fonseca (1982), the extractable fractions were obtained with different solutions: (a) F1 – ammonium acetate (1M NH₄Ac, pH 4.5) for extraction of water soluble and dissolved exchangeable ions, specifically adsorbed and carbonate-bound; (b) F2 – hydroxylamine hydrochloride (0.1M NH₄OH.HCl, pH 2) for elements adsorbed by Mn oxyhydroxides; (c) F3oxalate (dark) ammonium (0.175M $(NH_4)_2C_2O_4-0.1MH_2C_2O_4$, pH 3.3 in darkness) for elements linked to amorphous Fe oxides; (d) $F_4 - H_2O_2$ 35 % to extract elements associated with organic matter (on this step sulfidebound as primary sulfide minerals could not be totally leached out according to Rapin and Forstner (1983) and Khebonian and Bauer (1987)); (e) F5 – ammonium oxalate (UV) (0.175M (NH₄)₂C₂O₄-0.1M H₂C₂O₄, pH 3.3 under UV radiation for extract ions associated with crystalline Fe oxides; (f) F6 - mixed acid (HCl+HNO₃+HF) where metals strongly associated with crystalline structures of minerals (such as the remaining silicates) will be decomposed (they are therefore unlikely to be released). In this study the SCE was carried out on 1 g of selected samples that were previously air dried at room temperature in order to not disturb the original metal distribution (as suggested by Quevauviller et al. 1994). Samples were sieved to obtain the appropriate particle size distribution (Filgueras et al. 2002). After each reaction timing the solutions were centrifuged and filtered. Metal analyses were carried out by AAS (for Cu, Pb, Zn, Fe) and by hydride generation combined with AAS (for As). The accuracy of the sequential treatment, considered as a whole, may be estimated by the comparison of the total sum of the amounts obtained after each sequential extraction step with the total amount obtained after hot

mixed-acid attack of the same sample. The overall recovery rates ranged from 77 % to 112 %.

Results and Discussion

Results of water chemical analyses are presented in Table 1. Mine gallery outflow (A-1) results classifies this sample as AMD: low pH (4.1) and high Fe, SO_4^{2-} , and Al, Cd, Cu, Mn and Zn concentrations. Groundwater from a deep well (A-2) shows near neutral pH (6.5) and high As (745 µg L⁻¹) and Fe (6.6 mg L⁻¹) concentrations. This well is overflowing during all the year,. During driest years Freixeda stream is dried and it was possible to identify points of discharge from the aquifer into the stream from the left margin (Pereira *et al.* 2008).

Surface water A-3, is from a different watershed (Macedinho stream) shows influence from sulfides mineralization associated with Pedra Luz and Macedinho mining works. Sample A-4 is representative of local geochemical background values (pH 8.0, low SO_4^{2-} (13 mg L⁻¹), As (12 µg L⁻¹) and trace metal concentrations below the detection limits of the method. After the confluence of AMD with Freixeda stream (A-13), SO_4^{2-} reaches 127 mg L⁻¹, and trace element concentrations increase to As = 326, Zn = 515, and Mn = 207 (μ g L⁻¹). Composition of surface water downstream sample A-13 is characterized by samples A-12 to A-5 (distance of about 6 km), being A-5 the sample collected at the confluence of Freixeda stream with Tua River. Cadmium, Cu and Pb are bellow detection limit in all samples. Manganese and Zn concentrations decrease below detection limits about 1 and 3 km distance, respectively. Sulfate and As decrease to background values at Tua River (A-5) but As keeps in solution with high concentration for longuer distance that other trace elements (Fig. 2).

Table 2 presents the analytical results from 11 stream sediment samples. Background values are represented by sample S-3 (in mg kg⁻¹): As = 32; Cu = 21; Mn = 558; Pb < 32; Zn < 12 and Fe = 4.53 %. It can be observed that some of the stream sediments are seriously contaminated compared to local geochemical background values, despite some mitigation after the confluence with the Tua River. Comparing the concentrations obtained in the Freixeda stream samples (S-11 to S-5) with background values, it is clear that they are moderately to strongly enriched (As – 3.4 to 35 times;

Sample ID	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9	A-10	A-11	A-12	A-13
Temp. (°C)	18.2	17.3	20.4	26.2	25	21.7	26.6	26.7	29.2	23.9	23.0	22.3	23.3
pН	4.1	6.5	6.5	8.1	6.9	6.4	6.6	6.6	6.8	5.9	5.9	6.0	6.6
EC (µS cm ⁻¹)	624	695	145	110	53	124	146	123	153	266	267	315	350
AI (mg L ⁻¹)	2.04	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.13	< 0.1	0.32	0.83
Ca (mg L ⁻¹)	59.6	57.2	10.5	7.13	4.0	8.6	9.6	8.1	11.1	21.9	21.9	25.5	30.0
Mg (mg L ⁻¹)	48.6	47.6	5.4	4.47	2.2	4.9	5.5	4.7	6.1	13.2	13.5	16.7	15.9
Na (mg L ⁻¹)	16.4	69	14.5	11.3	5.4	13.0	13.4	12.9	14.2	20.4	20.5	22.9	21.5
K (mg L ⁻¹)	5.3	3.90	3.04	1.48	0.75	1.42	1.72	1.62	1.94	7.4	7.3	9.9	20
Sr (mg L ⁻¹)	0.25	0.94	0.07	0.05	0.02	0.07	0.07	0.06	0.07	0.14	0.14	0.16	0.17
SO ₄ (mg L ⁻¹)	405	345	13.8	13.4	2.9	16.3	17.4	12.6	24.2	73	71	118	127
$HCO_3 (mg L^{-1})$	1.2	157.8	52.9	38.2	25.7	46.8	51.5	44.3	55.7	65.3	67.9	53.4	55.2
Cl (mg L^{-1})	4.7	8.4	14.3	10.3	4.5	11.1	11.0	12.2	10.1	15.6	15.7	14.4	12.8
$NO_3 (mg L^{-1})$	4.81	< 1.1	3.88	1.31	0.98	< 0.3	< 0.3	< 0.3	< 0.3	5.07	5.84	< 0.5	5.26
Fe (mg L ⁻¹)	1.12	6.6	0.66	< 0.02	0.06	< 0.02	0.05	< 0.02	< 0.02	< 0.02	< 0.02	0.03	0.10
Mn (mg L ⁻¹)	9.36	1.98	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.45	0.21
Cu (µg L ⁻¹)	47	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25
Zn (μg L ⁻¹)	4820	20	< 15	< 15	< 15	< 15	< 15	< 15	< 15	35	18	330	515
Cd (µg L ⁻¹)	37	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8	< 8
Pb (µg L ⁻¹)	< 200	< 200	< 200	< 200	< 200	< 200	< 200	< 200	< 200	< 200	< 200	< 200	< 200
As (µg L ^{−1})	< 5	745	185	14	12	62	75	96	24	46	50	171	326

A-1: AMD sample outflow from the adit; A-2: deep well, A-3 Macedinho stream; A-4: sample collected outside Freixeda mine influence and representing the local geochemical background; A-5: Tua river near the mouth of Freixeda stream; A-6 to A-13: Freixeda stream.

Table 1 Chemical composition of water samples from Freixeda study area.



Fig. 2 Variations in sulfate, As and Zn concentrations from surface water of Freixeda stream downstream Freixeda mine adit until discharge in Tua River (A-5).

Pb - 2 to 17 times; Zn - 6 to 100 times). Given the toxicity of these elements, this represents a potentially harmful situation.

In areas exposed to AMD, stream sediment samples usually consist of a complex mixture of geochemical bearing phases containing potentially toxic metals. It is well known that the availability of such hazardous metals strongly depends on their specific chemical forms and binding capabilities, rather than on the total element concentrations. Table 3 shows the geochemical partitioning of some selected elements in those metal bearing phases for each selected sample.

According to the SCE results (Table 3) Fe is mostly extracted in the fraction linked to amorphous Fe oxyhydroxides (25 to 52 %). A considerable proportion of Fe (36 to 43 %) appears to be also accumulated in the residual fraction associated to the primary sulfides. It must be pointed out that the easily extractable Fe, in the sediments, still reached around 30 %.

Copper and Pb show high and similar partitioning pattern with ammonium oxalate (dark) (34.3 to 42 % for Cu and 32.9 to 36.3 % for Pb) suggesting that Pb may also be linked, to some extent, to amorphous Fe oxides. Moreover, part of extracted Pb was obtained with ammonium acetate indicating that the exchangeable/carbonate fraction is probably a preferential sink for Pb.

High extraction percentages of As (20.8 to 36.5 %), Zn (9.8 to 53 %), and Mn (8.2 to 61.7 %) were also extracted by ammonium acetate, probably related with secondary minerals and sulphosalts dissolution. Arsenic concentration values extracted in F1 ranges from 13 μ g L⁻¹ to 441 μ g L⁻¹. Nevertheless these elements also show considerable extraction in ammonium oxalate (dark) fraction (As 42.3 to 57.4 %, Zn 17.8 to 19.8 %, and Mn 11 to 18.8 %) suggesting sorption onto amorphous Fe oxi-hydroxides.

Sample ID	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9	S-10	S-11
As (mg kg ⁻¹)	118	385	32	65	108	139	115	418	140	271	1129
Cu (mg kg ⁻¹)	35	33	21	19	24	26	21	34	22	45	55
Fe (%)	3.97	3.09	4.53	2.66	3.02	3.45	3.49	3.58	3.49	3.55	2.61
Mn (mg kg⁻¹)	862	743	558	496	805	746	734	1051	854	1042	534
Pb (mg kg ⁻¹)	38	47	<32	<32	<32	<32	<32	55	33	64	273
Zn (mg kg ⁻¹)	645	37	<12	<12	80	80	104	46	314	880	636

Table 2 Concentrations of As, Cu, Fe, Mn, Pb and Zn in Freixeda stream sediment samples.

1: Freixeda stream, near AMD outflow; S-2 Macedinho stream; S-3: sample collected outside Freixeda mine influence and representing the local geochemical background; S-4: Tua river, near the confluence with Freixeda stream; S-5 to S-11 Freixeda stream.

	S-11						S-6						S-4					
	F1	F2	F3	F4	F5	F6	F1	F2	F3	F4	F5	F6	F1	F2	F3	F4	F5	F6
As	36.5	3.7	42.3	1.4	1.4	0.9	24.9	1.4	47.1	0.4	24.4	2.1	20.8	2.3	57.4	0.5	14.4	5.2
Cu	29.8	0.0	42.0	0.0	0.0	20.9	0.0	0.0	34.3	0.0	23.3	42.1	0.0	0.0	41.0	0.0	21.3	37.7
Fe	18.5	3.7	32.7	0.5	0.5	36.0	8.9	3.0	24.7	0.2	20.4	42.8	33.8	10.9	51.9	0.6	37.6	42.6
Mn	61.7	7.5	18.8	1.6	1.6	4.0	49.3	12.4	18.8	0.6	12.4	6.5	8.2	3.8	11.0	0.0	13.2	63.7
Pb	37.9	0.0	32.9	3.7	3.7	14.3	18.6	0.0	36.3	0.0	24.5	20.4	18.2	0.0	33.9	0.0	22.1	25.7
Zn	53.0	12.3	19.8	1.0	1.0	8.0	15.0	8.3	20.8	0.0	24.3	31.6	9.8	4.5	17.8	0.0	29.1	39.0

Table 3 Relative extraction ratio (%) of As, Cu, Fe, Mn, Pb and Zn of each step of the SCE procedure. The percentage of extraction associated to the 3 initial steps of the sequential extraction reaches values of 34.3 to 71.8 % for Cu, 44.1 to 85.1 % for Zn and 73.4 to 82.5 % for As, revealing that these elements are bioavailable and may be easily mobilized to the ecosystem through the modification of pH and Eh conditions. This interpretation is supported mainly by high As concentrations measured in water samples.

Conclusions

In this study it was intended to investigate and quantify the impact of the former Freixeda mine in the surrounding environment, with a basis on geochemical analysis of stream sediments and waters.

Obtained data allowed a better understanding of the chemical dynamic, between stream sediments and surface water, of As, Cu, Fe, Mn, Pb, and Zn and their environmental relevance. The geochemical results obtained indicate that the Freixeda stream sediments are contaminated in As, Cu and Zn. Iron is mostly extracted in the fraction linked to amorphous Fe oxy-hydroxides, but about 30 % is easily extractable Fe. High percentages of As and Zn were also extracted by ammonium acetate, probably from secondary minerals and sulphosalts dissolution. Nevertheless these elements also show considerable extraction in ammonium oxalate (dark) fraction suggesting sorption onto Fe oxi-hydroxides.

The approach based on chemical sequential extraction demonstrates that the distribution/accumulation of As, is mainly linked to exchangeable and acid-soluble species upon which desorption and ion-exchange reactions may originate the release of this readily mobile and available metalloid into surface waters.

References

- Almeida A, Noronha F (1988) Fluids associated with W and Ag-Au deposits of Mirandela area, NE Portugal: an example of peri-granitic zoning. Bull. Minéral. 111
- Cardoso Fonseca E (1982) Emploi de l'extraction chimique sélective séquentielle et détermination des phases-support du Pb et du Zn en milieu silico-alumineux lors de l'altération supérgene du prospect de Sanguinheiro (SE Aveiro-Portugal). Comunicacões Serviços Geológicos Portugal 68: 267–283
- Cardoso Fonseca E, Ferreira da Silva E (1998) Application of selective extraction in metal-bearing phases identification: a South European case study. Journal of Geochemical Exploration 6: 203–212
- Filgueiras AV, Lavilla I, Bendicho C (2002) Chemical sequential extraction for metal partitioning in environmental solid samples. J. Environ. Monit., 2002, Issue 4, p 823–857
- Montes R, Gomes ME, Pereira MR (2007) Mineralogia e Geoquímica dos Filões Mineralizados e das Escombreiras da Mina de Freixeda. In E. Gomes e A. Alencoão (coord), Actas da XV Semana de Geoquímica e VI Congresso Ibérico de Geoquímica. Vila Real: UTAD, p 333–336
- Pereira MR, Gomes MEP, Montes R (2007) Hydrogeochemistry of water resources from abandoned Freixeda gold mine (NE Portugal)". Goldschmidt Conference Abstract. Geoch. et Cosmoch. Acta, Volume 71, Issue 15, Suppl. 1, A778
- Pereira MR, Montes R, Gomes E, Ferreira A, Ávila P (2008) Geochemistry of Soils and Waters from the Abandoned Freixeda Gold Mine, Northeast Portugal. Rev. da Soc. Española de Mineralogía y Universidad de Sevilla, MACLA 10: 136–137
- Quevauviller P, Rauret G, Muntau H, Ure AM, Rubio R, López-Sánchez JF, Fiedler HD, Griepink B (1994) Evaluation of a sequential extraction procedure for the determination of extractable trace metal contents in sediments. Fresenius J Anal Chem. 349, p 808– 814

Apparent Rates of Fe(II) Oxidation and Associated Hydrogeochemical Interactions in an Extensively Mined Watershed, Pennsylvania, USA

Charles A. CRAVOTTA III

U.S. Geological Survey Pennsylvania Water Science Center, New Cumberland, PA 17070, cravotta@usgs.gov

Abstract Baseflow in the West Branch Schuylkill River, which drains a 61.8 km² watershed in eastern Pennsylvania, consists of coal-mine drainage (CMD) from two large outfalls. During 2005–12, the CMD had elevated Fe(II) concentrations but was net alkaline with near-neutral pH (5.3–7.3). Along a 4,950 m flow path downstream of the outfalls, pH increased by as much as 1 unit and Fe concentrations decreased by 30 to 95 % because of CO₂ degassing and Fe(II) oxidation, respectively. Iron attenuation was greatest during low flows when transport times, pH, and temperature were greatest. Fe(II) oxidation was consistent with the Singer-Stumm abiotic, homogeneous rate model.

Keywords abandoned mines; acid mine drainage; iron oxidation rate

Introduction

The Schuylkill River in eastern Pennsylvania, USA, has its headwaters in uplands of the Southern Anthracite Coalfield and its mouth 208 km downstream, on the Delaware River at Philadelphia (Fig. 1). Because of extensive infiltration to abandoned underground mines, streams in the headwaters frequently lose water and may stop flowing, while perennial streamflow is sustained downstream by coal mine drainage (CMD). The Pine Knot Tunnel (PKN), a very large CMD source ($0.25 - 1.59 \text{ m}^3$ /s), and the Oak Hill Boreholes (OAK), a smaller CMD source ($0.096 - 0.48 \text{ m}^3$ /s) near the midpoint length of the West Branch Schuylkill River (Fig. 1), account for one-third of the contaminant loading by several dozen CMD sources to the upper Schuylkill River



Fig. 1 Drainage basins, un*derground mines (colored* polygons), and hydrological monitoring sites in the upper Schuylkill River basin, Southern Anthracite Coalfield, Pennsylvania. Descriptions of the mines and monitoring sites are given by Cravotta et al. (2013). Adjacent mines with same color are hydrologically connected. For example, the Pine Knot mine complex comprises five adjoining mines.

(Cravotta et al. 2013). The discharge of PKN responds rapidly to recharge but has a prolonged recession compared to the West Branch Schuylkill River and other nearby streams, consistent with a conceptual model of rapid infiltration of surface water and slow release of groundwater from the underground mine complex. During seasonal low-flow conditions when the streams in the headwaters lose all flow to the underground mines, these CMD sources constitute the entire streamflow from the 61.8 km² watershed of the West Branch Schuylkill River. In contrast, during high-flow conditions, streamflow from the headwaters area frequently exceeds the combined flows of the CMD sources (Cravotta et al. 2013). This paper evaluates hydrogeochemical interactions that account for the temporal and spatial variations in the concentrations and transport of iron and associated solutes from CMD sources at downstream sites in this extensively mined watershed.

Methods

Data on flow rate, pH, alkalinity, acidity, and concentrations of total and dissolved elements (0.45-µm pore-size, 45 mm diameter nitrocellulose membrane filter) were collected over a range of hydrologic conditions during 2005-12 at the PKN and OAK outfalls and associated upstream and downstream sites on the West Branch Schuylkill River (Fig. 1). When samples were collected, temperature, pH, specific conductance (SC), dissolved oxygen (DO), and redox potential (Eh) were measured with a submersible sonde that was calibrated daily. Values for Eh were corrected to 25 °C relative to the standard hydrogen electrode and used to compute the activities of Fe(II) and Fe(III) species from dissolved iron (Nordstrom 1977, 2004). The geochemical program PHREEQC (Parkhurst and Appelo 1999) with WATEQ4F database (Ball and Nordstrom 1991) was used to evaluate the equilibrium partial pressure of carbon dioxide (Pco₂), the saturation index values for various minerals, and mass-balance reactions to explain the composition of (1)

downstream water from mixtures of upstream waters and (2) high-flow water from base flow plus runoff. Apparent first-order Fe(II) oxidation rates within the West Branch were estimated based on the decrease in dissolved iron concentration along a 4,950 m flow path from station WB2 downstream of the two CMD outfalls to station WB3 near the mouth of the West Branch watershed (Fig. 1). Transport times, calculated as reach distance divided by velocity at the downstream gaging station (WB3), were estimated on the basis of empirical relations among the average velocity measured by current meter across the channel, associated discharge rate, and stream stage at the time of sampling. The stream channel between WB2 and WB3 has relatively uniform shape and slope. Apparent first-order Fe(II) oxidation rates were computed on the basis of the estimated transport time and also considering data on pH, DO, and temperature.

Results and Discussion

CMD a PKN and OAK was net alkaline (acidity < 0) with near-neutral pH (5.3 to 7.3), elevated concentrations of sulfate, iron, and manganese, and relatively low concentrations of aluminum (Fig. 2). Streamwater quality of the West Branch above PKN (WB1) varied from net acidic to alkaline (pH 3.9 to 6.8; acidity 210 to -9.1 mg/L); however, streamwater at sites downstream of the CMD sources (WB2 and WB3) consistently was net alkaline with nearneutral pH (Fig. 2). The pH and concentrations of dissolved iron in CMD at PKN decreased with increased flow rate (Spearman's r; r_{S} = -0.69 and -0.63, respectively; P < 0.001; Fig. 2). Likewise, dissolved iron concentration was inversely correlated with CMD flow rate at the Oak Hill Boreholes ($r_{\rm S}$ = -0.64; P < 0.001). At sites on the West Branch upstream (WB1) and downstream (WB2 and WB3) of the CMD outfalls, pH, SC, sulfate, and other major ion concentrations decreased with increased flow rate: however, dissolved iron concentrations did not vary with flow rate at sites WB1 and WB3 (Fig. 2).



Fig. 2 Discharge rate and water quality of CMD from the Pine Knot Tunnel (PKN) and Oak Hill Boreholes (OAK), and associated stream water from West Branch above PKN (WB1), and West Branch below PKN and OAK at intermediate (WB2) and downstream (WB3) sites, July 2005–July 2012.

During high-flow conditions, the CMD and stream waters exhibited increased acidity with decreased pH and smaller changes in iron concentrations and pH along downstream flow paths (Figs. 2 and 3). These water-quality characteristics at the downstream sampling point WB3 were modeled by starting with the water quality at WB2 below the CMD outfalls and considering geochemical reactions, with or without dilution by runoff. For the low-flow end members (sampled 2008/09/24) when flows at WB2 and WB3 were comparable, geochemical mass-balance reactions, alone were indicated, including ingassing of O₂, degassing of CO₂, dissolution of halite, and precipitation of ferrihydrite and Al(OH)₃. For the high-flow end members (sampled 2010/03/16), the flow at WB3 (4.33 m^3 /s) was larger than that at WB2 (3.51 m³/s). Thus, flow-weighted fractions of 0.81 WB2 and 0.19 "runoff" having low pH and low ionic strength were mixed, and the indicated mass-balance reactions included degassing of CO₂, dissolution of halite, calcite, and chlorite, plus precipitation of $Al(OH)_3$ and ferrihydrite. The degassing of CO_2 and the precipitation of $Al(OH)_3$ and ferrihydrite in lowflow and high-flow models is consistent with the attenuation of the metals from CMD in conjunction with pH increases over the range of flow conditions (Fig. 2). The indicated dissolution of halite and calcite is consistent with the addition of road-deicing salts and limestone aggregate that are used in the urbanized area downstream of WB2 (Minersville, Pottsville; Fig. 1).

At WB2, dissolved and total iron concentrations ranged from 3.2 to 10 mg/L and 3.9 to 11 mg/L, respectively, pH ranged from 5.9 to 6.8, and Pco₂ ranged from $10^{-2.2}$ to $10^{-1.1}$ atm. Along the 4,950-m flow path from WB2 to WB3, dissolved iron concentrations decreased by 30 to 95 % whereas total iron decreased by 3 to 70 %, pH increased by as much as 1 unit, Pco₂ decreased by 40 to 80 %, and sulfate and manganese concentrations were largely unchanged (Fig. 3). Sulfate and manganese



Fig. 3 Attenuation of dissolved iron and associated constituents along 4,950 m flow path from WB2 to WB3 on West Branch Schuylkill River, July 2005-July 2012. A, Comparison of streamflow and water quality at WB2 and WB3; B, streamflow, average flow velocity, and computed time to travel from WB2 to WB3; C-F, change in dissolved iron concentration as a function of travel time, temperature, *pH, and* $[H^+]^{-2}$. Low-flow and high-flow end members considered in geochemical models highlighted by red outline.

(Mn(II)) were transported conservatively because these solutes were undersaturated with respect to secondary minerals. The attenuation of dissolved iron resulted from the gradual oxidation of ferrous iron (Fe(II)) to ferric iron (Fe(III)) and the rapid precipitation of hydrous Fe(III) oxides such as ferrihydrite, which was saturated or supersaturated (Cravotta *et al.* 2013). Because of the low solubility of Fe(III) at near-neutral pH, nearly all the dissolved iron was Fe(II). The pH increased downstream because of degassing of CO_2 as observed for other iron-bearing, net-alkaline waters exposed to the atmosphere (Cravotta 2007; Kirby *et al.* 2009; Geroni *et al.* 2012).

Attenuation of dissolved iron downstream of CMD sources was greatest during low-flow conditions when transport times, water temperatures, and pH values were greatest (Fig. 3). These trends indicate a kinetically limited process and are consistent with the abiotic homogeneous oxidation rate model of Singer and Stumm (1970) as presented by Stumm and Morgan (1996, 683–685):

 $-d[Fe(II)]/dt = k_{\rm H} \cdot [O_2] \cdot [H^+]^{-2} \cdot [Fe(II)]$ (1)

where at pH > 5 and 20 °C, $k_{\rm H}$ = 3×10^{-12} mol/L/min (1.8×10^{-10} mol/L/h). The second-order dependence on [H⁺] indicates a change in pH of 1 unit results in a 100-fold change in the oxidation rate. At a given pH, the rate increases by a factor of 10 for a 15 °C increase. By using the activation energy of 23 kcal/mol reported by Stumm and Morgan (1996, p. 684) with the Arrhenius equation (Langmuir 1997, p. 62), the rate can be adjusted to different temperatures.

Fig. 4A illustrates the apparent first-order rate of change in dissolved iron concentration from WB2 to WB3, without temperature correction, as a function of $[O_2][H^+]^{-2}$ per Eq. 1. The simple first-order rate (Y-axis) ranges from 0.22 to 0.60/h with a median of 0.34/h at average temperature of 10.83 °C. The slope in Fig. 4A, 9.14 × 10⁻¹² mol/L/h at 10.83 °C, is one-fifth



Fig. 4 A, Apparent first-order rate of Fe(II) oxidation without temperature correction is indicated by median value of 0.34/h, or as a function of $[O_2][H^+]^{-2}$ based on Eq. 1, in which case k_H^* is indicated as the ratio of the rate value to $[O_2][H^+]^{-2}$ (5.46 × 10⁻¹¹ mol/L/h at 10.83 °C) or the slope; B, measured and predicted dissolved iron concentration at WB3 on the basis of dissolved iron concentration at WB2, travel time, average temperature, average dissolved O₂, and average $[H^+]^{-2}$ for WB2 to WB3. Circles indicate predicted values considering median first-order rate of 0.34/h and blue diamonds indicate predicted values considering Eq. 1 with temperature-corrected median apparent rate constant, $k_H = 1.95 \times 10^{-10} \text{ mol/L/h} (3.26 \times 10^{-12} \text{ mol/L/min})$ at 20 °C.

of the reference value of k_H for Eq. 1 given by Stumm and Morgan after temperature adjustment to 20 °C. The median ratio of the firstorder rate to $[O_2][H^+]^{-2}$ (5.46 × 10⁻¹¹ mol/L/h at 10.83 °C) adjusts to kн* 3.26×10^{-12} mol/L/min at 20 °C, which is equivalent to the reference value of $k_{\rm H}$ for Eq. 1. The median ratio using the flow-weighted concentration (mass change) is similar. 2.29×10^{-12} mol/L/min at 20 °C.

Fig. 4B shows the predicted concentration of dissolved iron at WB3 based on the concentration at WB2 and estimated travel time to WB3 by using (1) the median first order decay rate of 0.34/h, without temperature or pH adjustment, and (2) the homogeneous oxidation rate model of Eq. 1 with the median apparent rate constant of k_{H}^* = 3.26 × 10⁻¹² mol/L/min at 20 °C adjusted for sample temperature. Despite consideration of variable temperature, pH, and dissolved O₂, the estimate with Eq.1 does not yield significant improvement over the simple first-order estimate. A constant first-order rate may apply because of the relatively narrow range of temperature $(10 \pm 4 \degree C)$ and pH (6.6 \pm 0.2) for most samples and their correlation with flow rate. Kirby *et al.* (1999) demonstrated that abiotic Fe(II) oxidation predominates over microbial catalysis at pH values greater than 5 and that pH increases above 6.4 had little to no effect on Fe(II) oxidation rate.

Conclusions

Observed water-quality and discharge relations for CMD and downstream sites on the West Branch Schuylkill River indicate decreased attenuation of iron with decreased transport time, decreased temperature, and decreased pH. These trends are consistent with kinetic control of Fe(II) oxidation, consistent with the Singer-Stumm abiotic, homogeneous rate model. The inverse relations between flow rate and pH can result from mixing of nearneutral CMD with low-pH runoff or recharge derived from acidic rainfall. Given kinetically controlled, pH-dependent iron attenuation, potential decreases in pH (< 6.4) during highflow events should be considered with strategies to decrease iron loads. Specifically, if aerobic ponds or wetlands are used for treatment of marginally net alkaline CMD, a supplemental source of alkalinity may be needed to maintain or increase pH during high flow conditions as well as additional storage capacity may be needed to increase retention time.

References

- Ball JW, Nordstrom DK (1991) User's manual for WATEQ4F with revised data base. U.S. Geol. Surv. Open-File Report 91–183, 189 p
- Cravotta CA III (2007) Passive aerobic treatment of netalkaline, iron laden drainage from a flooded underground anthracite mine, Pennsylvania, USA. Mine Water Environ. 26, 128–149
- Cravotta CA III, Goode DJ, Bartles MD, Risser DW, Galeone, DG (2013) Surface-water and groundwater interactions in an extensively mine watershed, upper Schuylkill River, Pennsylvania, USA. Hydrol. Proc. doi: 10.1002/hyp.9885
- Geroni JN, Cravotta CA III, Sapsford DJ (2012) Evolution of the chemistry of Fe bearing waters during CO_2 degassing. Appl. Geochem. 27: 2335–2347
- Kirby CS, Dennis A, Kahler A (2009) Aeration to degas CO₂, increase pH, and increase iron oxidation rates for efficient treatment of net alkaline mine drainage. Appl. Geochem. 24, 1175–1184

- Kirby CS, Thomas HM, Southam G, Donald R (1999) Relative contributions of abiotic and biological factors in Fe(II) oxidation in mine drainage. Appl. Geochem. 14, 511–530
- Langmuir D (1997) Aqueous environmental geochemistry. Prentice Hall, New Jersey, USA, 600 p
- Nordstrom DK (1977) Thermochemical redox equilibria of Zobell's solution. Geochim. Cosmochim. Acta 41, 1835–1841
- Nordstrom DK (2004) Modeling low-temperature geochemical processes. In Drever JI. (ed.) Surface and Ground Water, Weathering, and Soils. Elsevier, Treatise on Geochemistry 5, 37–72.

Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC (Version 2)—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geol. Surv. Water-Resour. Inv. Re99–4259, 310 p

- Singer PC, Stumm W (1970) Acidic mine drainage: the rate-determining step. Science 167, 121–123
- Stumm W, Morgan JJ (1996) Aquatic chemistry—chemical equilibria and rates in natural waters (3rd). New York, Wiley-Interscience 1022 p
Use of marine extract as nitrogen rich growth substrate for sulfate reducing bacteria

Subhabrata Dev, Aditya Kumar Patra, Jayanta Bhattacharya

Department of Mining Engineering, Indian Institute of Technology, Kharagpur, India-721302, subhabrata4@gmail.com, jayantaism@gmail.com

Abstract Marine waste extract was tested as nitrogen rich growth substrate for Sulfate Reducing Bacteria (SRB). A liquid extract was prepared from marine waste and characterized. The extract contained 14.541 g L⁻¹ of nitrogen, 12.345 g L⁻¹ of total organic carbon, 90.322 g L⁻¹ of protein and 1.48 mg L⁻¹ of magnesium. The extract supplemented medium exhibited improved performance as compared to Postgate B medium for their ability to promote the growth of SRB. It supported 95 % sulfate reduction at a rate upto 21 mg L⁻¹ h⁻¹ and 1.21×10¹³ cells/ml of SRB population. This indicates that the potential exists for the use of marine waste extract as growth substrate for SRB.

Keywords Nitrogen rich growth substrate, Sulfate reducing bacteria, sulfate reduction, bacterial growth

Introduction

Sulfate Reducing Bacteria (SRB) is group of prokaryotes which belongs to the several genera like *Desulfovibrio*, *Desulfotomaculum*, *Desulfosporosinus*, *Thermodesulfobium*. As a part of energy metabolism SRB utilizes the sulfate as electron acceptor and reduce it to sulfide. This characteristic made the SRB useful for the bioremediation of sulfate rich wastewater especially in acid mine drainage (AMD) environment.

Biological treatment of sulfate rich wastewater is mainly carried out using sulfidogenic bioreactor (Pol *et al.* 1998; Sarti and Zaiat 2011). Generation of adequate SRB biomass is necessary for the efficient reduction of sulfate. To produce high SRB biomass growth substrate should contain sufficient quantity of nutrient especially in the form of carbon and nitrogen (Bayoumy *et al.* 1999; Daubert and Brennan 2007, Newcombe and Brennan 2010).

Several studies are being conducted on different carbon sources and their effect on the growth of SRB (Costa *et al.* 2009; Das *et al.* 2013). Substances like trinitrotoluene (Boopathy and Kulpa 1992) taurine (Lie *et al.* 1999), urea (Neculita and Zagury 2008), nitrocellulose (Petrova *et al.* 2002), corn steep liquor (White and Gadd 1996), amino acids (Rees *et al.* 1998) are reported to be utilized as nitrogen source by SRB. Most of these substances have not been tested for their efficiency particularly as nitrogen source in terms of promoting the efficiency of sulfate reduction and SRB growth.

In most of cases the nitrogen source supplied for the growth of SRB inside sulfidogenic bioreactors include NH₄Cl (Kaksonen *et al.* 2003). Commercial growth media for SRB generally contains NH₄Cl (Postgate 1984), $(NH_4)_2$ HPO₄ (Kuo and Shu 2004), NH₄HCO₃ (Mizuno *et al.* 1998) as nitrogen source. These types of nitrogen sources are expensive. Therefore, use of them is impractical during the large scale and long term treatment of sulfate rich wastewater in terms of cost effectiveness. These nitrogen sources may be substituted with the one which is available, cost effective and easily utilizable.

Wastes generated from marine fishing activities are mainly composed of the shells of crab, shrimp, mussel. These shells substances generally contain high concentration of protein, chitin and minerals (Gildberg and Stenberd 2001, Xu *et al.* 2008). The protein rich fraction has good nutritional quality and was utilized as nitrogen source in growth medium for microorganisms (Solano *et al.* 2009). As this protein rich fraction is easily obtained from the marine waste, it can be used as a nitrogen rich nutrient to grow SRB.

The objective of this study included the utilization of marine waste extract to grow SRB. To perform this, the waste was deproteinized and protein rich fraction was extracted. The growth medium supplemented with this liquid extract was compared with Postgate B medium and evaluated as an alternative to the latter one.

Methods

Mixed SRB culture was previously acclimatized for 6 months in Postgate B medium (Postgate 1984) with the following composition: KH_2PO_4 0.5 g L⁻¹, NH₄Cl 1 g L⁻¹, CaSO₄ 1 g L⁻¹, MgSO₄.7H₂O 2 g L⁻¹, sodium lactate 3.5 g L⁻¹, ascorbic acid 0.1 g L⁻¹, thioglycolic acid 0.1 g L⁻¹ and FeSO₄.7H₂O 0.5 g L⁻¹. pH of the medium was kept to 7.0-7.2 using.

Marine waste was collected from the seashore area of Digha (West Bengal, India). The waste was manly composed of shells of crabs, mussel, prawn, shrimp, tails and exoskeletons of fishes. The waste was sun dried and milled. The powdered form was added as 10 % (w/v) to 1000 mL of deionized water. The suspension was kept to alkaline condition by adjusting pH to 11.5 using 2(N) NaOH and boiled at 70 °C for 2h with constant stirring. Protein rich liquid extract was separated by centrifugation at $6440 \times g$ for 15 minutes followed by filtration through 0.2 µm polycarbonate membrane filter (Millipore).

The extract was analyzed for total kjeldahl nitorogen (TKN), total organic carbon (TOC), protein content and magnesium.

Batch experiment was carried out to compare growth in medium supplemented with marine waste extract as nitrogen source, with that of the commercial growth medium like Postgate B containing NH₄Cl as nitrogen source.

Growth of study SRB mixed culture was carried out in a batch mode using 250 mL of conical flasks. Growth medium supplemented with the liquid extract was termed as marine waste extract (MWE) medium. The MWE medium had the following composition: sodium lactate, 3.5 g L^{-1} , KH₂PO₄, 0.5 g L^{-1} , CaSO₄, 1 g L⁻¹, MgSO₄.7H₂O, 2 g L⁻¹, marine waste extract, 10.322 % (v/v). To compare MWE with Postgate B, the media were added individually to different conical flasks. The Media were prepared with deionized water, boiled and cooled under continuous flow of nitrogen gas to remove dissolved oxygen and autoclaved at 121 °C temperature under 15 lbs cm⁻² pressures for 15 minutes. Subsequently the growth media were inoculated with 10 % (v/v) SRB inoculum and incubated at 35 °C. MWE medium without added inoculum was considered as control. The growth study was carried out for 192 hours and samples were collected during every 24 hours intervals. Efficiency of SRB growth was analyzed in terms of SRB population, efficiency and rate of sulfate reduction, increase in pH and the growth media were compared accordingly. Inoculation, incubation, periodic transfer of inoculum and sampling were done inside anaerobic system (Thermo Scientific, Model 1029).

Result and Discussion

Marine waste extract exhibited TKN value of 14.541 g L⁻¹ and C:N ratio of 0.854 which indicated it as a nitrogen rich substrate. TOC value of the extract was 12.345 g L⁻¹. It also contained 90.322 g L⁻¹ of protein and 1.48 mg L⁻¹ of magnesium. The value of protein, nitrogen, carbon and magnesium indicated the extract as substrate with balanced nutritional quality.

In the growth study the residual sulfate concentration in MWE medium was 130 mg L⁻¹ and exhibited 95 % sulfate reduction. In Post-gate B medium the values were 570 mg L⁻¹ with 79 %. The highest rate of sulfate reduction observed in MWE and Postgate B medium

were 21 mg L^{-1} h⁻¹ and 18 mg L^{-1} h⁻¹ respectively. The efficiency and rate of sulfate reduction in MWE medium was always higher than that of Postgate B medium (Fig. 1). Higher efficiency and rate of sulfate reduction were mainly due to the supposedly higher activity of SRB in MWE compared to the Postgate B medium.

Number of bacterial cells in MWE medium increased from approximately 7.43×10^{11} cells/mL to about 1.21×10^{13} cells/mL. Similarly, in Posgate B medium the number increased from 3.17×10^{11} cells/mL to approximately 9.02×10^{12} cells/mL.

The population of SRB in MWE medium was always higher than Postgate B medium throughout the experiment (Fig.2). The lag phase of SRB growth in MWE medium was 24 hours whereas in Postgate B medium it was 72 hours. Short lag phase in MWE medium may be due to the rapid supply of nutrient at the initial stage of the experiment (Robinson-Lora and Brennan 2009). This result was much similar to that observed in the experiment of Robinson-Lora and Brennan (2009) who used crab shell chitin as nitrogen source for SRB.

The ability of MWE medium to promote higher biomass and sulfate reduction efficiency was found superior to Postgate B. The presence of marine waste extract in MWE made it comparatively improved growth medium to support SRB growth than Postgate B. Besides providing efficient source of nitrogen the liquid extract was also the source of high organic carbon, protein and trace quantity of magnesium. The protein rich fraction could also be degraded to short chain organic electron donor and NH₄⁺ (Neculita *et al.* 2007, Robinson-Lora and Brennan 2010). NH₄⁺ was thought to be utilized directly. Therefore the presence of several electron donors in addition to nitrogen, carbon, magnesium promoted improved growth and sulfate reduction in MWE than Postgate B.

In MWE and Postgate B medium, pH was increased gradually throughout the course of the experiment (Fig. 3). The final pH in MWE and Postgate B medium was pH 7.35 and pH 7.32 respectively. After 24 hour there was a reduction of pH value. This was mainly due to the generation of several volatile fatty acids which lowered the pH. The change in pH with respect to time was similar in both the growth medium. As a part metabolism SRB generated alkalinity which increased pH during the course of incubation (Bilek and Wagner 2012).

The experiment showed that marine waste extract acted primarily as nitrogen source which developed both SRB population and thereby sulfate reduction efficiency. Similar behavior was observed on the effect of corn steep liquor as nitrogen source for SRB (White



Fig. 1 Comparison of (left) Sulfate reduction (%), (right) Sulfate reduction rate (mg $L^{-1}h^{-1}$)



Fig. 2 Log (Cell number/ml) as a function of time following the SRB population

and Gadd 1999). The authors reported that corn steep liquor enhanced both the SRB population as well as sulfate reduction performance.

The rate of sulfate reduction and SRB growth was much better than that reported by Neculita and Zagury (2008) who used urea as nitrogen source for the growth of SRB. (Boopathy and Kulpa 1992) used trinitrotoluene as nitrogen source for SRB. In our experiment MWE medium exhibited much lower lag phase than that reported by the authors. SRB population grew in MWE medium was much higher than that reported by Chockalingam *et al.* (2005) who studied husk filtrate as nutrient source for SRB. Along with rice husk the authors added ferrous ammonium sulfate which could be used as nitrogen source.

In our experiment the liquid extract exhibited 14.541 g L⁻¹ of nitrogen and C:N ratio of 0.854 which indicated very high concentration of nitrogen. However, successful sulfate reduction of 95 % with the growth of SRB population upto 1.21×10^{13} cells/mL was obtained using the extract. Substrate with C:N ratio more than 45 is reported to inhibit the growth of SRB due to unavailable nitrogen source (Gibert *et al.* 2004; Robinson-Lora and Brennan 2009). El Bayoumy *et al.* (1999) mentioned about the toxic-



Fig. 3 Changes in pH as a function time during the growth of SRB in MWE and Postgate's B medium.

ity effect of nitrogen on SRB growth above the value of 500 mg L⁻¹. Several complex substrates have been studied for their efficiency to promote sulfate reduction activity in both batch and continuous scale reactors. These substrates have not been reported to have effect on SRB growth as nitrogen source. But these substrates contained different quantities of nitrogen content and vary in C:N ratio (Tab. 1).

Marine waste extract was proved to be a nitrogen rich growth substrate which can promote the growth of SRB in an efficient manner. MWE medium used in this study can be effectively used as a substitute for commercial growth medium like Postgate B to cultivate SRB. Moreover, the expenditure of operational process to treat sulfate rich wastewater can be reduced by substituting the expensive nitrogen sources like NH₄Cl, (NH₄)₂HPO₄, NH₄HCO₃. with marine waste extract. Thus the extract prepared from marine waste serves as available, cost effective and suitable source of nitrogen for SRB.

Conclusions

• Slow rate and inefficient sulfate reduction during the long term treatment of sulfate rich wastewater is mainly due the absence

"Reliable Mine Water Technology"

SI No.	Name of the Substrate	Nitrogen (%)	C:N ratio	References	
1	Sheep manure	1.98 ± 0.07	19.52 ± 2.66	Gibert et al. 2004	
2	Compost	1.26 ± 0.05	21.58 ± 2.91		
3	Poultry Manure	1.61 ± 0.07	16.94 ± 1.58		
4	Mushroom compost	2.47	10	Neculita et al. 2011	
5	Cow Manure	2.15	18		Table A Nitro con content
6	Rice straw	0.71	54		Tuble I Mitrogen content
7	Poultry manure	5.80 ± 0.30	3.3	Zagury et al. 2006	and C/N ratio of several sub-
8	Chitin	2.85	6.42	Rbinson-Lora and Brennan 2010	
9	Urea	46.62	0.428	Neculita and Zagury 2008	strates usea for the treat-
10	NH ₄ Cl	26.17	-	Kuo and Shu 2004	ment of AMD
11	(NH ₄) ₂ HPO ₄	10.6	-		ment of mine

of nutrient specifically in the form of nitrogen source required for the growth of SRB.

- Protein rich fraction extracted from marine waste may serve as suitable nitrogen source for SRB.
- The liquid extract promoted better growth and sulfate reduction efficiency to SRB than the Postgate B medium and other growth substrates containing nitrogen.
- The extract can be used as suitable and available source of nitrogen for SRB. The costly nitrogen source used in commercial growth medium can be substituted with this liquid extract.

Acknowledgements

The authors thank Indian Institute of Technology, Kharagpur, India for the financial support to carry out the study.

References

- Bayoumy MAE, Bewtra JK, Ali HI, Biswas N (1999) Sulfide production by sulfate reducing bacteria with lactate as feed in an upflow anaerobic fixed film reactor. Water Air Soil Poll 112: 67–84
- Bilek F, Wagner S (2012) Long term performance of an AMD treatment bioreactor using chemolithoautotrophic sulfate reduction and ferrous iron precipitation under *in situ* groundwater condition. Bioresource Technol 104: 221–227
- Boopathy R, Kulpa CF (1992) Trinitrotoluene (TNT) as a sole nitrogen source for a sulfate reducing bacterium *Desulfivibrio* sp. (B strain) isolated from anaerobic digester. Current Mircrobiology 25: 235– 241

- Chockalingam E, Sivapriya K, Subramanian S, Chandrasekaran S (2005) Rice husk filtrate as a nutrient medium for the growth of *Desulfotomaculum nigrificans*: characterization and sulfate reduction studies. Bioresource Technol 96: 1880–1888
- Costa MC, Santos ES, Barros RJ, Pires C, Martins M (2009) Wine waste as carbon source for biological treatment of acid mine drainage. Chemosphere 75: 831–836
- Das BK, Gauri SS, Bhattacharya J (2013) Sweetmeat waste fractions as suitable organic carbon source for biological sulfate reduction. Int Biodeter Biodegr, doi:10.1016/j.ibiod.2013.03.027
- Daubert LN, Brennan RA (2007) Passive remediation of acid mine drainage using crab shell chitin. Environ Eng Sci 24: 1475–1480
- El Bayoumy MA, Bewtra JK, Ali HI, Biswas N (1998) Sulfide production by sulfate reducing bacteria with lactate as feed in an upflow anaerobic fixed film reactor. Water Air and Soil Poll 112: 67–84
- Gibert O, Pablo JD, Cortina JL, Ayora C (2004) Chemical characterization of natural organic substrates for biological mitigation of acid mine drainage. Water res 38: 4186–4196
- Hallberg KB (2010) New perspectives in acid mine drainage microbiology. Hydrometallurgy 104: 448– 453
- Johnson DB, Hallberg KB (2005) Acid mine drainage remediation options: a review. Sci Total Environ 338: 3–14
- Kaksonen AH, Riekkola-Vanhanen ML, Puhakka JA (2003) Optimization of metal sulfide precipitation in fluidized-bed treatment of acidic wastewater. Water Res. 37: 255–266
- Kuo WC, Shu TY (2004) Biological pre-treatment of wastewater containing sulfate using anaerobic immobilized cells. J Hazard Mater B113: 147–155

- Lie TJ, Clawson L, Godchaux W, Leadbetter ER (1999) Sulfidogenesis from 2-Aminoethanesulfonate (Taurine) fermentation by a morphologically unusual sulfate reducing bacterium, *Desulforhopalus singaporensis* sp. Nov. Appl Environ Microb 65: 3328–3334
- Mizuno O, Li YY, Noike T (1998) The behavior of sulfatereducing bacteria in acidogenic phase of anaerobic digestion. Water Res 32: 1626–1634
- Neculita CM, Zagury GJ (2008) Biological treatment of highly contaminated acid mine drainage in batch reactors: long-term treatment and reactive mixture characterization. J Hazard Mater 157: 358–366
- Newcombe CE, Brennan RA (2010) Improved passive treatment of acid mine drainage in mushroom compost amended with crab-shell chitin. J Environ Eng-ASCE 136: 616–626
- Petrova OE, Tarasova NB, Davydova MN (2002) biotechnological potential of sulfate-reducing bacteria for transformation of nitrocellulose. Anaerobe 8: 315– 317
- Pol LWH, Lens PNL, Stams AJM, Lettinga G (1998) Anaerobic treatment of sulfate-rich wastewaters. Biodegradation 9: 213–224.
- Postgate J.R. (1984) The Sulfate-Reducing Bacteria, second ed. Cambridge University Press, Cambridge
- Rees GN, Harfoot CG, sheeshy AJ (1998) Amino acid degredation by the mesophilic sulfate-reducing bac-

terium *Desulfobacterium vacuolatum*. Arch Microbiol 169: 76–80

- Robinson-Lora MA, Brennan RA (2009) Efficient metal removal and neutralization of acid mine drainage by crab-shell chitin under batch and continuousflow conditions. Bioresource Technol 100: 5063– 5071
- Robinson-Lora MA, Brennan RA (2010) Chitin complex for the remediation of mine impacted water: Geochemistry of metal removal and comparison with other common substrates. Appl Geochem 25: 336– 344
- Solano C, Cervantes J, Baypoli ON, García R, Bante NP, Machado DI (2009) Chemical and biological characteristics of protein hydrolysates from fermented shrimp by-products. Food Chem 112: 671–675
- Vieira GHF, Vieira RHSF, Macrae A, Sousa OV (2005) Peptone preparation from fishing by-products. J Sci Food Agric 85: 1235–1237
- White C, Gadd GM (1996) A comparison of carbon/energy and complex nitrogen sources for bacterial sulfate-reduction: potential applications to bioprecipitation of toxic metals as sulphides. J Ind Microbiol 17: 116–123
- Xu Y, Gallert C, Winter J (2008) Chitin purification from shrimp wastes by microbial deproteination and decalcification. Appl Microbiol Biotechnol 79: 687–697

Mine Waste Geochemistry Assessment, Corani Project, Puno, Peru

Robert Dorey¹, Larry Breckenridge²

¹Global Resource Engineering and Dorey & Associates, rdorey@attglobal.net ²Global Resource Engineering, LTD, 7000 S. Yosemite St., Suite 201, Centennial, Colorado 80112, USA lbreckenridge@global-resource-eng.com

Abstract The Corani project is located in southeastern Peru at elevations ranging from 4800 m to 5200 m. The open pit mining will produce approximately 256 Mt of waste rock, a significant portion of which will contain sulfide mineralization. A geochemical test program was performed on the waste rock to be mined. Static testing of waste rock showed neutralizing potential at essentially zero. Acid-Base-Accounting (ABA) testing was augmented using a LECO furnace. Kinetic testing using a barrel test method was performed. The results of the testing programs were used to prescribe mine waste management methods for the project.

Keywords Mine waste geochemistry, kinetic cells, static testing, acid rock drainage

Introduction

The Corani Project is a base metal and silver mine development project owned by Bear Creek Mining Company (BCMC). Surface water analyses show widespread acid rock drainage (ARD) conditions from two primary sources: naturally-occurring sulfide oxidation resulting from surficial formations high in sulfide, and sulfide oxidation augmented by prior mining activities. In summary, three different water quality groups are present in the project area:

- Clean water up-gradient from mineralized areas with a circumneutral pH (≈ 6.2), total dissolved solids of <10 mg/L, low alkalinity (≈3 mg/L CaCO3) and low dissolved metals concentrations.
- Naturally-occurring ARD with a pH at 4.2, TDS of 29 mg/L and slightly elevated dissolved metals concentrations (aluminum, cadmium, lead)
- ARD from historic areas of mining disturbance with an acidic pH (≈ 2.5), high TDS at 3180 mg/L (mostly from 2170 mg/L of sulfate), high total acidity at 2100 mg/L, and elevated levels of arsenic, lead, zinc, and cadmium.

All streams that drain the project site have water quality similar to, or more acidic than, the ARD conditions of the "naturally-occurring ARD" described above. The geochemical waste characterization program was designed on the premise that sulfide oxidation will continue to occur and would require specific management techniques for mine wastes throughout the mine's life cycle.

Methods

The approach to the geochemistry characterization is based on the following industry-standard references, recommendations, and guidelines:

- The Global Acid Rock Drainage (GARD) Guide ;
- ASTM E1915-09 : Standard Test Methods for Analysis of Metal Bearing Ores and Related Materials for Carbon, Sulfur, and Acid-Base Characteristics ; and
- ASTM D5744: Standard Test Method for Laboratory Weathering of Solid Materials

Using a Humidity Cell

It is important to note that these guidelines recognize there is a high amount of variability

in conditions from site to site, and therefore, there is no globally prescribed approach outlined in the guidelines. Rather, the guidelines encourage careful site by site consideration that gives the required flexibility to combine various tools and available data to adequately characterize a site — there is no one standard that can be applied. Fig. 1 shows a flow chart of the geochemical characterization approach that is based upon and closely follows the GARD Guidelines.

Geochemical Characterization of Waste Rock

The ore reserve modeling for the project defined several Geological and Metallurgical Types (GeoMet types). The following defines the types and gives the percentage of total waste rock in parentheses. The most important include: PM: mineralized lithic tuff with pyrite and marcasite (18 %); FBS: lithic tuff with fine black sulfides (25 %): PMT: post-mineral lithic tuff (41 %); FeO: oxidized PM or FBS (11 %): QSB: a quartzite/barite-based mineral (2 %); PG: Plumbogummite, a lead phosphate mineral (2 %). The Pre-Feasibility Study (PFS) for the project contained a screening-level geochemical characterization (23 samples) of the waste rock and confirmed that portions of the waste rock was Potentially Acid Generating (PAG). During the Feasibility Level Study (FLS),23 static tests (ABA, SPLP, Whole Rock), 194 LECO Furnace total sulfur and total carbon analyses and, 23 on-site kinetic cell tests were performed. Most of the PMT is removed in the early years of mining as this barren, non-mineralized overburden material is stripped prior to the development of the resource. The proportions of waste by GeoMet type are important to the waste characterization as specific types (FBS and PM) will dominate the geochemistry of the mine waste rock piles.

Static Results

Acid Base Accounting (ABA) indicator tests provide a simple assessment of the waste characteristics and based on industry standards for the neutralizing potential to acid generating potential (NP:AP) ratio and net neutralizing potential (NNP) values provide some measure of the potential geochemical behavior of the waste. The ABA results show that the PM and FBS and PG contain up to 4.5, 2.1 and 0.2 % sulfide sulfur, respectively, while the remaining GeoMet types have relatively low sulfide sulfur



Fig. 1 Geochemical Characterization Approach



Fig. 2 Waste Rock Acid-Base Accounting

values. Universally, all GeoMet types are bereft of NP, and where present, are assigned to clay minerals with availability only at low pH values. Fig. 2 shows the combined ABA results on a scatter plot, based on acid generating potential and GeoMet type. Throughout the development of the management plan it has been assumed that all GeoMet types, with the exception of PMT, have zero NP and are PAG.

LECO Carbon and Sulfur Assays

ASTM E1915-09 states: "In the absence of sulfate forms of sulfur. total sulfur may be used to estimate the sulfide sulfur concentration." The acid potential (AP) in the Corani Mine waste samples comes primarily from the oxidation of pyrite and other metal sulfides. As a result, an approach was adopted using total sulfur as a substitute for acid potential and by correlating total sulfur to sulfide sulfur by comparing ABA data to total sulfur data. Total sulfur (total S) analyses do not account for the effects of barite (BaSO₄) which reports as total sulfur in the LECO furnace results, but does not contribute to AP. Analysis results for barium and barite contained in the various waste rock types show that relatively high levels of barite exist in the MnO (0.1 % as S), PG (0.12 % as S), FeO (up to 0.2 % as S), QSB (0.1 % as S) and FBS (0.1 % as S). With the exception of the FBS waste rock, which forms 25 % of the overall waste rock tonnages, the remaining waste rock



Fig. 3 AP to LECO Calibration (PM

types comprise a relatively minor quantity of the waste rock produced (+/-7 %). Although the barite content is recognized to result in a conservative overestimate of the total sulfur, and thereby the AP values, application of a correction for barite would not significantly change the assessment of the PAG characteristics of these waste rock types or the total quantity of material indicated to be PAG. Fig. 3 shows an example of the calibration of Total S *vs.* ABA data for the PM GeoMet type. R² values for PM, FBS and the remaining GeoMet types are 0.99. 0.99 and 0.90 respectively, suggesting that an accurate prediction of AP can be developed from Total S LECO data with the application of a calibration equation (see PM equation in Fig. 3).

Whole Rock Analysis (WRA)

The results of the WRA show many metals at above crustal averages, typical for epithermal mineralized deposits. While many metals existed above crustal averages, the key leachable metals that could become present with respect to ARD generation at Corani are: As, Cd, Cu, Pb, Ni, Hg and Zn. The FBS and PM GeoMet type have consistently elevated As levels. Elevated Cd levels exist, particularly in the FBS GeoMet group. Cu is present at levels of up to 500 ppm. The concentrations of Pb in the rock samples show widespread lead mineralization with measured levels reaching 10,000 ppm associated with the lead sulfides in the PM and FBS and as plumbogummite in the PG GeoMet types. Similarly, Zn occurrence, related to sphalerite, reaches levels similar to Pb, particularly in the PM and FSB GeoMet types.

Synthetic Precipitation Leaching Procedure (SPLP)

The SPLP was performed to assess the readily available leachable metals in comparison to the WRA contained levels. Elevated levels of dissolved metals are present in the majority of the leachates. However, the leachability of the PM and FBS GeoMet types shows the highest levels. These results confirm that water and waste management will be critical for the waste rock dumps.

On-Site Kinetic Cells

The decision to perform on-site kinetic cell tests of the waste rock was made due to the unique site conditions at Corani that cannot be replicated in a laboratory environment. The on-site testing allowed for the samples to be exposed to ambient climate conditions, varieties and concentrations of catalyzing microorganisms that are site-specific and to test larger sample particles. The climate at Corani is defined by the project's high elevation which creates high evaporation rates (in excess of 2000 mm/a) and unique humidity and wind conditions. Snow, ice, and rain fall intermittently through the year with higher precipitation in the wet season. Freezing conditions occur almost on all nights. Laboratory cells cannot duplicate how this unique climate condition may impact ARD kinetics. Recent studies of cold climate effects on ARD also show that the kinetics is significantly slower than expected under laboratory conditions (Sartz 2011). The presence of bacterial catalysts greatly changes the kinetics of ARD reactions. Surface area is also a significant factor in reaction kinetics. The ASTM-standard laboratory humidity cell requires a sample be crushed to less than $\frac{1}{4}$ inch size. In the ASTM guidelines, however. it states that:

Caution: Recent laboratory-weathering studies of run-of mine waste rock from metal mines demonstrate that crushing bulk sample so it passes the 0.25 inch screen may change the character of the sample by artificially increasing the liberation and consequent surface areas of acid producing and acid-consuming minerals."

For this reason, the choice was made to use large particle size material in the on-site kinetic cells.

Kinetic Cell Test Procedures

Samples of the various waste rock types were obtained from drill core stored at the project. The initial steps in sample selection were based on the identification of waste types from borehole logs, photographs, and geological cross sections. The number of samples of each rock type was selected based upon the percentage of the projected quantity of waste rock predicted by the mine model for the pits with a weighting of the number of samples to the higher quantity rock types. Where possible, a range of sulfide contents representative of the individual waste rock type was selected. Samples did not cross lithologic boundaries and no blending or mixing of the samples was performed. A subsample of each sample selected for kinetic testing was subsequently subjected to static testing. The samples consisted of the equivalent of a core box. Core was broken into sections with a maximum individual core length of 100mm and all fines and intermediate particles were included in the test. No crushing or additional material preparation was performed.

Barrel Tests

The test apparatus consisted of 20 L (5.5 gal) plastic barrels fitted with a sampling tube. Initially, each sampling tube was fitted with a sampling valve; however, these tended to freeze overnight and were removed and replaced with a gravity drainage system. Once

the core was placed in the barrel, an initial wetting of the sample was performed by sprinkling 5 L of water over the surface of the core. The water was obtained from residual snow banks in and around the project and from snow melt runoff from areas outside of the known mineralized zone related to the project. After the introduction of the water, the water was allowed to drain from the core and collected. Testing of this sample for pH, dissolved oxygen, oxidation-reduction potential (ORP), conductivity and temperature was performed and formed the baseline for comparison with future samples. The barrels were not covered and were left exposed to direct precipitation. On a weekly basis each barrel was inspected. Prior to the inspection, the ambient air temperature at the test site was measured and recorded and the barrel checked for free moisture. Free moisture drained from the barrel was tested for temperature, field pH, dissolved oxygen and conductivity using portable meters. Additional observations were recorded as to whether there was a characteristic odor associated with acid generation/sulfide oxidation emanating from the barrel, whether there was formation of salts/crystals on the barrel surface, and whether the barrel was warmer or colder than the ambient air temperature. In the event that odor, salts/crystals and elevated temperature were measured, the procedure used to obtain a water sample during setup of the barrels was performed. The samples were filtered and tested for field parameters, and a solution sample was collected for laboratory testing. Based upon the field tests parameters, all barrels which showed one or more of the following were selected for additional laboratory testing: pH < 5.0, conductivity > 200 µS/cm, decrease in pH < 2 units in 2 weeks, or an increase in conductivity of 50 % in 2 weeks

Two conditions were adopted under which a specific barrel test was terminated. First, if the barrel showed low conductivity (<100 μ S/cm) and stable and neutral pH over an annual cycle, the test was terminated. Second, if depressed pH (< 3 standard units) and

elevated conductivity (> 1000 $\mu S/cm)$ was shown the barrel was terminated.

Kinetic Cell Field Results

After more than a year of leaching, FeO, MnO, QSB, and PG samples were resistant to acidification despite a negative NNP in some of these samples. The magnitude of negative NNP appears to be a strong indicator of acidification in FBS and PM samples. All FBS and PM samples with positive NNP values did not produce acidity and samples with an NNP less than -12 all turned acidic. The weekly field readings of water quality parameters indicate that the reaction rates are variable within rock types which makes characterization challenging. Overall, the field parameters indicate that the minor waste rock types (MnO/PG/QSB) are not likely to be acid generating. This is supported by their relatively high NNP values. FeO samples also have relatively high NNP values with the exception of one sample which has relatively slow reaction kinetics. The ABA results show that this sample group has at least one sample with anomalously high AP, and therefore could be a potentially acid generating; however, the potential for this waste rock type to generate acid is not as pervasive or rapid as FBS or PM. On the other end of the spectrum, PM is the most consistently acid generating. These samples have the highest overall AP and lowest NNP. This group has a high amount of variability with regards to AP, and there are a few samples in this group that have not turned acidic. This is reflected in their AP values which have the greatest range of AP results and a large number of outliers. However, this waste rock type seems to be a consistent acid generator. The FBS sample shows mixed behavior. While none of the samples immediately turned acidic, there are some that are showing signs of ARD. These samples had a lower NNP than the PM samples which is reflected in the slower reaction kinetics of these samples.

Kinetic Cell Laboratory Results

In addition to the field parameters, samples were collected from most of the cells on a monthly schedule and were sent for laboratory analysis. Most metals were elevated in the PM and FBS cells that are acid generating. From the kinetic cell data, it is clear that metals leaching will occur, especially for PM and FBS rock types. The behavior of metals in the FeO cells is variable. There were no significant issues for PG and MnO rock types except for lead and iron which were elevated in most samples. This is a result of the stable pH observed for these cells. The QSB rock type had no issues.

Waste Management Procedures (WMPs)

The waste rock characterization has provided an extensive understanding of the geochemical behavior of the various waste rock types to be mined. This understanding has led to the adoption of specific waste management procedures for the waste rock, mineralized material left in the pit walls, and, from the related tailings characterization, for the projects tailings management facility. Provision of a rigorous surface water management system is an intrinsic part of the operational phases and closure/post closure management of the mine. Separation of "contact" from "non-contact" water and the consumptive use of the water in the process circuit will be performed with zero discharge of contact water. Longterm water treatment has also been included in the feasibility study to manage closure and post closure water sources. The geochemical prediction of long-term water quality following closure and water treatment requirements has been made possible based on the data generated by the characterization work. Also, intrinsic to the WMPs is the conservative assumption that all waste rock containing mineralization should be treated as PAG material. Considering the mining will result in a mixture of the mineralized materials, this assumption was deemed to be appropriate. The mine plan has been tailored to produce nonmineralized (PMT) and PAG materials at a ratio and on a schedule sufficient to allow the placement of PMT in the waste rock dumps concurrent with PAG material to create a buffer zone on the floor, walls and, ultimately, the top of the dump as a cover. These zones will also drain shallow seepage from natural ground and groundwater emerging beneath the dump for collection. Segregation of the waste rock types will also be performed to consolidate all PAG waste rock in a single dump and the remaining PMT not used for the buffer zone will be placed in a separate, non-PAG dump. During operation of the mine the rate of material placement in the waste rock dump is such that increases in the waste rock's water content is not sufficient to reach the field moisture content at which percolation and leachate generation will occur. All contact water leaving the dump as seepage from the toe of the dump will be collected for consumptive use or for treatment. Placement of the final surface cover will be performed to create an evapotranspiration cover that is designed to reduce flux of precipitation into the dump to deminimis levels.

Acknowledgements

The authors thank Bear Creek Mining Company for support in publishing this work.

References

- ASTM D5744-07e1 (2007) Standard Test Method for Laboratory Weathering of Solid Materials Using a Humidity Cell. American Socitey of Testing and Materials.
- ASTM E1915-09 (2009) Standard Test Method for Analysis of Metal Bearing Ores and Related Materials for Carbon, Sulfur, and Acid-Base Characteristics. American Society for Testing and Materials.
- INAP (2009) Global Acid Rock Drainage Guide. International Network on Acid Prevention.
- Sartz L (2011) Weathering of Waste Rock in Differenct Climatic Conditions-A Kinetic Freeze/Thaw Humidity Cell Experiment. International Mine Water Association Congress. Aachen, Germany.

Use of a Biological Polishing Step to Improve Bioassay Test Results

James Fricke, Daniel Dean

Resource Environmental Management Consultants, Inc., 8138 S. State St., Suite 2A, Midvale, Utah 84047, USA, jim@rmc-ut.com, dan@rmc-ut.com

Abstract The Clean Water Act requires point source dischargers to determine toxicity of facility effluent using Whole Effluent Toxicity (WET) tests. At a permitted facility in Missouri where the primary contaminants are metals, wastewater treatment plant effluent meets stringent numerical discharge limits but periodically fails WET tests. Previous investigations indicated low alkalinity in the WWTP effluent was causing WET toxicity. Use of a biological polishing treatment step to increase alkalinity and improve WET results was examined. Effluent from an anaerobic biocell and aerobic limestone tank were submitted to a laboratory for chronic WET testing. Only effluent from the anaerobic biocell improved alkalinity and passed a chronic WET test.

Keywords Whole Effluent Toxicity, WET, biotreatment, alkalinity, wastewater treatment, Missouri

Introduction

The Clean Water Act requires point source dischargers to determine toxicity of facility effluent using Whole Effluent Toxicity (WET) tests. At a permitted facility in Missouri where the primary contaminants are metals, effluent from the facility's wastewater treatment plant (WWTP) meets stringent numerical discharge limits for metals and semi-metals, typically by large margins, but periodically fails WET tests. Previous toxicity investigations indicated that low alkalinity and subsequently poor buffering capacity in the WWTP effluent is the source of the toxicity.

Anaerobic biotreatment technology was selected in the pilot program. Anaerobic biotreatment utilizes sulfate-reducing bacteria in an anaerobic organic substrate to remove metals from wastewater via sulfide precipitation (Gusek 2009). A by-product of the sulfate reduction reaction is the generation of bicarbonate which increases an effluent's alkalinity. Sulfate-reducing bacteria (SRB) are obligate anaerobes that use sulfate to decompose simple organic compounds. The dominant species of SRB are in the genera Desulfotomaculum and Desulfovibrio. The reactions as presented by Gusek (2009) are as follows:

$$2 \text{ CH}_2\text{O} + \text{SO4}^{2-} \rightarrow \text{S}^{2-} + 2 \text{ CO}_2 + 2 \text{ H}_2\text{O}$$
 (1)

$$S^{2-} + 2 CO_2 + 2 H_2O \rightarrow H_2S + 2 HCO_3^{-}$$
 (2)

The goal of this project was to obtain sitespecific pilot test data demonstrating that an anaerobic biotreatment polishing step could increase alkalinity at the facility's WWTP effluent sufficiently enough to consistently pass chronic WET tests (USEPA 2002). Anaerobic biotreatment is a low-cost, low-energy and low-maintenance technology relative to traditional chemical water treatment. If shown to be viable, the addition of an anaerobic biotreatment system to generate alkalinity in WWTP effluent could enable the operator to consistently pass chronic WET tests and potentially result in significant cost savings to the operator compared to modification of the WWTP.

Methods and Materials

An anaerobic biotreatment pilot cell (anaerobic biocell) was constructed using a 5.7 m³ tank (Fig. 1). An organic substrate consisting of



Fig. 1 Anaerobic Biocell Schematic

2.3 m³ of sawdust was installed in the anaerobic biocell. The organic substrate was underlain by a 30 cm sand layer and 15 cm gravel plenum for drainage. Effluent from the anaerobic biocell flowed to an aerating cascade constructed from a series of 19 L buckets. The aerating cascade oxidized residual sulfide present in the anaerobic biocell effluent and restored dissolved oxygen concentrations. Water flowed through the anaerobic biocell in a downflow configuration and water level was controlled with a P-trap. Following construction, the anaerobic biocell was filled with water. inoculated with sulfate-reducing bacteria, and allowed to incubate for two weeks prior to the start of operation. Following the incubation period, the anaerobic biocell was operated at a flow rate of approximately 2 L/min.

In addition to the anaerobic biocell, an aerobic limestone tank was installed to test if simple dissolution of limestone could generate sufficient alkalinity to pass chronic WET tests. This was considered unlikely because WWTP effluent pH is required to be >7.5 and limestone solubility is poor at pH >7.0 (Oates 1998). However, it was deemed worth investigating due to ease and low cost of set up and would avoid the secondary aeration step required with an anaerobic system to remove residual sulfide and restore dissolved oxygen. The aerobic limestone tank was constructed from a 380 L tank filled with approximately 57 L of limestone gravel and a flow rate of approximately 2 L/min (Fig. 2). Water flowed through the aerobic limestone tank in a downflow configuration and water level was controlled with a P-trap.

The anaerobic biocell and aerobic limestone tank began operating in late September 2012. A maturation period of approximately six weeks was required for the anaerobic biocell to reach optimum operating conditions. Chronic WET tests were not conducted until early December 2012 due to scheduling conflicts with WWTP operations and the analytical laboratory. A total of three chronic WET tests were conducted using effluent from the WWTP, the anaerobic biocell and the aerobic limestone tank.

The following analytical parameters were analyzed during the pilot test.

Laboratory Parameters

- Total cadmium;
- Total lead;
- Total thallium;
- Sulfide;
- Alkalinity;



Fig. 2 Aerobic Limestone Tank Schematic

- Acidity;
- Total suspended solids (TSS); and
- Chronic Whole Effluent Toxicity

Field Parameters

- pH;
- Temperature;
- Conductivity;
- Oxidation-reduction potential;
- Dissolved oxygen;
- Flow; and
- Alkalinity (field reagent kit).

Results

Total cadmium, total lead and total thallium were not detected in WWTP effluent. Total cadmium, total lead and total thallium were not detected in effluent from the aerobic limestone tank. Total cadmium and total thallium were not detected in effluent from the anaerobic biocell. Total lead was detected in the effluent from the anaerobic biocell at very low concentrations, with a mean concentration of $5.0 \ \mu g \ L^{-1}$. This was below the WWTP effluent's monthly average NPDES limit for lead.

Total suspended solids were non-detect in all effluent samples. Sulfide concentrations in effluent from the anaerobic biocell ranged from 0.5–1.1 mg L⁻¹ following the maturation period. This range was considered ideal because it confirmed that sulfate reduction and alkalinity generation were occurring, but removal of excess sulfide was not problematic. Sulfide was non-detect in WWTP effluent, effluent from the anaerobic biocell's aerating cascade and the effluent from the aerobic limestone tank.

Full laboratory alkalinity and acidity results are presented in Table 1, Table 2 and Table 3. Mean net alkalinity results are presented in Fig. 3. Mean net alkalinity for WWTP effluent, effluent from the aerobic limestone tank and effluent from the anaerobic biocell was -8.9 mg L^{-1} , -8.2 mg L^{-1} and 22.5 mg L⁻¹, respectively. The anaerobic biocell increased mean WWTP effluent net alkalinity by 353 %.

In the Ceriodaphnia dubia (water flea) portion of the chronic WET tests only the effluent from the anaerobic biocell was considered as passing. The WWTP effluent and effluent from the aerobic limestone tank tests would have failed. The No Observable Effect Concentration (NOEC) for survival and reproduction, Lethal Concentration 50 (LC50) and Toxic Units are summarized in Table 4.

Sample Date	Alkalinity mg L ⁻¹	Acidity mg L ⁻¹	Net Alkalinity mg L ⁻¹
Dec. 3, 2012	7.1	25.0	-17.9
Dec. 5, 2012	8.8	0.0	8.8
Dec. 7, 2012	7.5	25.0	-17.5

Table 1 WWTP Effluent Alkalinity and Acidity Results

Sample Date	Alkalinity mg L ⁻¹	Acidity mg L ⁻¹	Net Alkalinity mg L ⁻¹	
Dec. 3, 2012	7.0	0.0	7.0	
Dec. 5, 2012	10.4	25.0	-14.6	
Dec. 7, 2012	8.1	25.0	-16.9	

 Table 2 Aerobic Limestone Tank Effluent Alkalinity and Acidity Results

Sample Date	Alkalinity mg L ⁻¹	Acidity mg L ⁻¹	Net Alkalinity mg L ⁻¹
Dec. 3, 2012	20.2	0.0	20.2
Dec. 5, 2012	25.0	0.0	25.0
Dec. 7, 2012	22.2	0.0	22.2

Table 3 Anaerobic Biocell Effluent Alkalinity and
Acidity Result

Sample Source	NOEC Survival Re	NOEC production	LC50	Toxic Units
WWTP Effluent	100%	6.25%	>100%	2.94
Aerobic Limestone Tank Effluent	100%	6.25%	>100%	3.24
Anaerobic Biocell Effluent	100%	100%	>100%	<1

Table 4. Ceriodaphnia dubia Chronic WET TestResults



Fig. 3 Mean Net alkalinity Results

In the Pimephales promelas (fathead minnow) portion of the chronic WET tests the WWTP effluent, effluent from the aerobic limestone tank and effluent from the anaerobic biocell were all considered as passing. For all three tests the NOEC for survival and growth was 100 %, the LC50 was >100 % and the Toxic Units were <1.

Conclusions

Pilot test data demonstrates that anaerobic biotreatment generated sufficient alkalinity to move WWTP effluent from net-acid to net-alkaline and increased the likelihood that WWTP effluent will consistently pass chronic WET tests. Pilot test data does not indicate that aerobic limestone dissolution can generate sufficient alkalinity to move WWTP effluent from net-acid to net-alkaline and increase the likelihood that WWTP effluent will consistently pass chronic WET tests. Additional chronic WET testing has been recommended to confirm these initial positive results.

References

- Gusek JJ, Figueroa LA (2009) Mitigation of Metal Mining Influenced Water – Vol 2. Society for Mining Metallurgy and Exploration, Littleton, Colorado, 164 pp
- Oates JAH (1998) Lime and Limestone: Chemistry and Technology, Production and Uses. WILEY-VCH Verlag GmbH, Weinheim, Germany, 455 pp
- USEPA (2002) Short-term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms: Fourth Edition (EPA-821-R-02-013). U.S. Environmental Protection Agency, Office of Water, Washington, District of Columbia, 350 pp

Study on Capping Options For Overburden Encapsulation to Prevent Acid Mine Drainage in Lati Coal Mine, Kalimantan, Indonesia

Rudy Sayoga Gautama¹, Ginting Jalu Kusuma¹, M. Sonny Abfertiawan¹, Arief Wiedhartono², Firman Gunawan², Iin Lestari³, Reynaldi Simbolon¹, Melinda Rose Diana¹

¹ Department of Mining Engineering, Faculty of Mining & Petroleum Engineering, Institut Teknologi Bandung, Indonesia ² PT Berau Coal, Indonesia ³ PT Lorax Indonesia, Indonesia

Abstract Lati coal mine in Kalimantan, Indonesia suffers from Acid Mine Drainage (AMD) because its overburden and interburden are dominated by potentially acid forming (PAF) material. One of the methods employed to prevent the formation of Acid Mine Drainage in the overburden dump area is encapsulation or capping of the PAF material. It is conducted by creating a barrier system which encapsulates the acidic overburden in order to minimize oxygen diffusion and surface water infiltration. This paper discusses the studies conducted to develop the most appropriate method of AMD management, particularly for the implementation of encapsulation method. The studies to be reviewed are compaction characteristics, NAF layer and the potential to use coal combustion ash.

Keywords acid mine drainage, dry cover, compaction, NAF layering, coal combustion ash utilization

Introduction

Lati coal mine is one of the four currently-running mine sites owned and operated by PT Berau Coal. The mine is located in East Kalimantan Province of Indonesia (Fig. 1) and has been operating since 1995. The Lati mine is the biggest mine site at PT. Berau Coal with a production capacity of 15 Mt of coal per year and more than 120×10^6 m³ of overburden movement annually. The coal deposits are mined using the conventional open pit mining method, using shovels and trucks as the main mining equipment for both overburden removal as well as coal mining.

Lati coal mine is suffering from Acid Mine Drainage (AMD) since most of the overburden as well as inter-burden materials are classified as potentially acid forming (PAF). According to the recent geochemical rock model, the amount of PAF material is up to 80 %. AMD was not considered as an important environmental issue at this mine until 2007 when it was discovered that AMD had impacted the water quality of the river Ukud, located in the southern part of the mining area. The pH values monitored in the river were between 3 to 4 (Abfertiawan and Gautama 2011). Since then, along with the increasing awareness on the en-



Fig. 1 Lati Coal Mine

vironmental protection, several studies have been conducted to identify the most appropriate and effective methods to minimize the AMD by considering the conditions of the site as well as available resources.

For surface coal mines, there are generally two sources of AMD generation. The first source is the mine pit, because of exposure of PAF material in the pit wall which could not be avoided. The second source is the overburden dump, mainly the out-pit overburden dump. Overburden often contains pyrite which can oxidise and generate long-term AMD in large quantities. At the overburden dump, AMD is potentially generated at the surface and subsurface depending on the water percolation and oxygen ingress. Based on the factor of AMD generation, the idea of AMD prevention is how to minimize water as well as oxygen. This way, the oxidation of sulfide mineral could be minimized.

A dry cover system is commonly used to minimize AMD generation in the overburden dump. The main objectives of a dry cover system are to minimise the influx of water and provide an oxygen barrier. The types of dry cover vary from single cover to multi-layer cover. Generally, it can be classified into three categories: resistive cover, store and release cover and mixed/novel type cover. A resistive cover is a method that reduces the permeability of the disposal overburden. It is commonly made from clay as well as compacted clay to minimize the percolation of water as well as oxygen diffusion. Store and release covers rely on the storage capacity of a certain layer of cover in which the precipitation in the wet season is stored and subsequently released as evaporated moisture in the dry season, therefore preventing further water percolation into the acidic waste. The last type of cover is a combination of either resistive and store and release cover as well as the application of an oxygen consuming layer (such as the organic waste or low reactive material); thus, preventing the oxygen ingress into the protected waste underneath in addition to the limited water deep infiltration (Shimada *et al.* 2011).

The effectiveness of the encapsulation and layering is governed by the availability of capping materials, the general balance between acid producing and acid neutralizing materials, the type and reactivity of acid-consuming material, the nature and flow of water through the dump, and chemical armoring of alkaline materials.

In the case of Lati mine, the limited amount of non-acid forming material is the main issue in the AMD management. Encapsulation of PAF material should be optimized to achieve the pre-defined criteria. The result of several studies covering compaction characteristics, multi-layer NAF material and the use of coal combustion ash will be discussed in the following section.

Studies for Capping Options Compaction Test

The study on compaction was intended to understand the effect of compaction on the permeability of certain materials. Two types of rock samples, namely SS-NAF and CS-PAF were taken from Lati Mine Pit West. Those two rock samples represented the typical rock composition at Lati mine in which NAF material is typically sandstone whereas PAF material is in general claystone.

In the laboratory, the air dried samples were crushed and screened until it could pass a no 4 sieve (<4.75 mm). Five mixes with different moisture content were made by adding water as much as 150 mL, 300 mL, 450 mL, 600 mL, and 750 mL to each samples. The mixed samples were then loaded to the compaction mold with three compaction layer stages. The compaction in each layer was conducted by 25 blows using a standard hammer for the proctor test. Part of the compacted specimen was sampled for dry density determination and the rest of the specimen was formed and loaded into a permeability test unit to measure the hydraulic conductivity of the specimen using a constant head method.

Compaction test results indicated that the dry density of NAF material which was predominantly sandstone was generally lower than the density of claystone PAF material (Fig. 2 left). This similar trend was also shown in the hydraulic conductivity measurements (Fig. 2 right). The maximum dry density of NAF material was 1.71 g/cm³ obtained on 11.3 % moisture content and the hydraulic conductivity value was as low as 1.28×10^{-7} m/s, while the maximum dry density of 1.85 g/cm³ of PAF material obtained on 15.9 % moisture content and the lowest hydraulic conductivity value of 4.67×10^{-8} m/s.

This compaction study led to the conclusion that compaction should be implemented to the sandstone NAF material for use as a capping material. Optimum capping performance to prevent oxygen diffusion and water infiltration seems difficult to achieve mainly because of the limited thickness of the capping layer due to the limited amount of this material type.

NAF Layer Simulation

Simulation of different layers of NAF and PAF materials has been conducted in the laboratory to understand the performance of NAF material in preventing AMD generation. Using a modified free draining column leach test with a height of 300 mm and a diameter of 150 mm (Fig. 3) different scenarios of layering NAF and PAF materials were simulated. There

were columns used for a control. The results of the four columns represented NAF mudstone and NAF sandstone. The characteristics of the samples obtained from static test are shown in Table 1.

As shown in Table 1 neither the NAF mudstone nor the NAF sandstone have a neutralizing capacity. This characteristic was verified in the control columns containing both materials. The pH values of leachates from simulated columns with different amount of NAF materials are shown in Fig. 4.

For the first 6 weeks the pH of leachates from all four columns were still neutral, meaning that oxidation of PAF material beneath the NAF layer had not started. Afterwards pH values in columns containing sandstone (both 25 % and 50 %) dropped to less than 3. It seems that oxidation of PAF materials in both columns already took place without any neutralization process. But it did not happen in the columns containing a mudstone layer. It can be explained that the oxidation process of PAF material did not occur until week 23 even in the column containing 25 % PAF mudstone.

The oxidation of PAF materials in the sandstone columns could occur because the sandstone layer has a higher permeability to let oxygen diffuse through the sandstone layer. On the other hand, NAF mudstone has lower permeability and became a physical barrier for oxygen diffusion into the PAF material beneath.



Fig. 2 Compaction characteristics of rock samples from Lati Mine



Coal Combustion Ash (fly and bottom ash) utilization

Since the NAF material in Lati mine is much lower in quantity than the PAF material with a PAF/NAF ratio of 80 %/20 % it is necessary to study the options to utilize materials found in the surrounding area. One of the options was to utilize coal combustion ash (fly and bottom ash) from a nearby coal fired power plant.

The weathering process of overburden materials and blending of overburden and coal ash were simulated in the laboratory using-amodified free draining column leach test with a height of 250 mm and a 100 mm diameter Buchner funnel. There were seven different scenarios being simulated, consisting of four blending scenarios and three layering scenarios. Detailed explanation and discussion on this study has been presented in 2010 (Gautama *et al.* 2010).

A summary of the study is as follows; the evaluation results showed that generally, permeability in all columns is decreasing. Since the permeability in the control columns consisted of 100 % fly ash and the bottom ash did not show any significant change, it could be concluded that the decrease in the permeability in the blending and layering columns might be resulted from the weathering of rock materials.

A higher decreasing infiltration rate occurred in the fly ash blending columns compared to that in the bottom ash blending columns. Lower permeability was identified in blending of smaller portion of FA (20 % compare to 30 %). Significantly different conditions were identified when the fly ash blending column was compared to the fly ash layering column. The filling of ash particles in the pores of rock samples resulted in a lower permeability

D 1 ///	Tot. Sulfur ^{*)}	MPA**)	ANC**)	NAPP**)	Paste	oH NAG pH	NAG**)		
Коск Туре					pH		pH 4.5	pH 7	ANC/MPA
CS-1(PAF)	0.88	26.93	0.00	26.93	6.80	3.55	3.85	2.25	0
CS-2(NAF)	0.17	5.20	5.74	-0.54	9.20	8.72	0	0	1.10
SS(NAF)	0.20	6.12	1.51	4.61	7.55	6.63	0	0.12	0.25

MPA: Maximum Potential Acidity; ANC: Acid Neutralizing Capacity; NAPP: Net Acid Producing Potential; NAG: Net Acid Generating; MS: Claystone; SS: Sandstone. *) in %; **) in kg H_2SO_4/t

Table 1 Geochemical characteristics of samples



Fig. 4 pH Value of leachates

in the blending column compared to that in the layering column.

The decreasing permeability due to the weathering process could be important in improving the performance of capping in the encapsulation of PAF material. Covering the PAF material with layers of coal combustion ashes and with a blended rock and coal combustion ashes could be an appropriate option in preventing the AMD generation in the waste dump.

The pH values in the fly ash blending column was higher than that in the bottom ash blending but still lower than that in the layering column (Fig. 5). A similar trend was also found in eC and TDs. This indicated that the alkalinity of fly ash was more reactive and stable than bottom ash due to a smaller grain size and more effectiveness in neutralizing acid. Compared to the blending column, the layering mix of fly ash showed higher pH values meaning higher neutralizing performance.

Discussion

Encapsulation of PAF material has been defined as the most appropriate method in preventing AMD generation in overburden dumps. Particularly in Lati mine where the overburden as well as interburden is dominated by PAF material (approximately 80 %) the implementation of encapsulation has not been without its issues. It is therefore necessary to study different options of capping material or strategies to optimize AMD prevention.



Fig. 5 Result of coal combustion ash study: leachate parameters vs. time

The compaction study on NAF material indicated that sandstone could only be compacted to a hydraulic conductivity as low as 10^{-7} m/s which might be insufficient to avoid oxygen diffusion and water infiltration into the capping layer. Increasing the thickness could not be implemented since the amount of sandstone is limited. An appropriate compaction technique should be developed accordingly.

In fact, NAF material in Lati mine has a low neutralization capacity. Studies on different layering schemes of NAF and PAF material has shown that the neutralization process of generated AMD did not occur. A layer of NAF should function as a capping material rather than a neutralizing one.

Due to its characteristics, fly and bottom ash from the nearby power plant could be used as a neutralizing agent as well as an impermeable layer to prevent oxygen diffusion and water infiltration, particularly fly ash. Fly ash blending seems to be the best option because the alkalinity of fly ash is more reactive and stable than bottom ash. The particle grain size of fly ash which is smaller than bottom ash also became an important factor in the reactivity of the neutralizing process. The coal combustion ash, particularly fly ash, could be used as an alternative material to prevent AMD generation.

Closing Remarks

Lati mine suffers from an AMD problem since most of the overburden and interburden material is classified as potentially acid forming (PAF). Lack of AMD management in the past has led to the AMD impacting the water quality of Ukud river. Even seepage from already rehabilitated overburden dump has a low pH.

Besides starting to geochemically characterize the overburden and interburden material and development of rock distribution model,Lati mine should study the most appropriate and reliable method in preventing AMD. Encapsulation has been considered to be the best method. To support this method different capping options have been studied.

Since most NAF material consists of sandstone it is important to develop a compaction strategy of sandstone as barrier layer to reduce its permeability. Most NAF material have a very low neutralizing capacity. Coal combustion ash from a nearby power plant is another potential source for alkaline material. Unfortunately the power plant's capacity is small, meaning that the amount of ash produced is small.

Acknowledgements

The authors thank PT Berau Coal for their support in this research

References

- Abfertiawan S, Gautama RS (2011) Development of Catchment Area Approach in Management of Acid Mine Drainage. In: Rüde TR, Freund A, Wolkersdorfer C. Mine Water – Managing the Challenges – 11th International Mine Water Association Congress. Aachen: RWTH Aachen: 241–246
- Gautama RS, Kusuma GJ, Lestari I, Anggana RP (2010) Weathering Behaviour of Overburden-Coal Ash Blending in Relation to Overburden Management for Acid Mine Drainage Prevention in Coal Surface Mine. In: Wolkersdorfer Ch, Freund A. Mine Water & Innovative Thinking: Sydney, Nova Scotia (CBU Press): 417–421
- Lambe TW (1951) Soil testing for engineers. John Wiley and sons Inc, New York, 162 p
- Shackelford CD, Javed F (1991) Large-Scale Laboratory Permeability Testing of a Compacted Clay Soil, Geotechnical Testing Journal 14(2), 171–179
- Shimada H, Kusuma GJ, Hiroto K, Sasaoka T, Matsui K, Gautama RS, Sulistianto B (2012) Development of a New Covering Strategy in Indonesian Coal Mines to Control Acid Mine Drainage Generation: A Laboratory-scale Result, International Journal of Mining, Reclamation and Environment 26(1), 74–89
- The International Network for Acid Prevention (INAP), (2009) Global Acid Rock Drainage Guide (GARD Guide). www.gardguide.com

Control of Tailing Seepage through Reactive Chemical Amendments

Jeff GILLOW¹, Adam GRIFFIN², Lee CHRISTOFFERSEN¹, Craig DIVINE¹, Michael HAY³, Phil DEDYCKER¹

 ¹ARCADIS U.S., Inc., 630 Plaza Drive, Highlands Ranch, Colorado, 80129, USA, Jeff.Gillow@arcadis-us.com, Lee.Christoffersen@gmail.com, Craig.Divine@arcadis-us.com, Phil.DeDycker@arcadis-us.com
 ²ARCADIS U.S., Inc., 1100 Olive Way, Suite 800, Seattle, Washington, USA, Adam.Griffin@arcadis-us.com
 ³ARCADIS U.S., Inc., 4999 Pearl East Circle, Suite 200, Boulder, Colorado, 80301, USA, Michael.Hay@arcadis-us.com

Abstract Seepage from legacy tailings impoundments presents significant potential for leachate transport into adjacent groundwater and surface waters. Seepage typically retains the chemical composition of the milling chemistry and may exhibit undesirable chemical attributes, such as alkaline pH, lixiviant, sulfate, or elevated concentrations of trace elements or radionuclides. Seepage management is a major environmental effort in modern mining operations and legacy properties. Reactive phosphate amendment was evaluated at a legacy uranium mill tailings impoundment. The results of this work indicate that reactive chemical amendments may be an alternative or supplemental option to traditional physical methods of seepage control for some applications.

Keywords tailings, uranium, source control, seepage, amendments

Introduction

Tailings are typically transported in a slurry form to a tailings impoundment. In subaerial disposal, tailings are then discharged into the impoundment through a single point (which must be relocated occasionally) or through spigots, both of which create a succession of overlapping deltas (Vick 1990). Similar to natural depositional settings, coarser tailings (sands) settle from suspension close to the point of discharge, creating beaches. Finer tailings (slimes) are carried into the interior of the impoundment and tend to settle in the standing water of the decant pond. Both particle size and pulp density affect this segregation (Vick 1990). In some operations, tailings are cycloned prior to deposition to mechanically separate the sands and slimes, increasing the relative proportion of slimes tailings deposited in the impoundment. The separated sand tailings are often used to construct the embankment of the impoundment (EPA 1994).

The deposition of tailings slurry creates significant vertical and horizontal heterogeneity in geotechnical and hydraulic properties throughout the impoundment. Sands and slimes tailings exhibit considerable variability in permeability, density, plasticity, compressibility, consolidation, shear strength, and stress parameters, which impact the design, stability, and drainage of the impoundment (Vick 1990). Vertical and horizontal variability in hydraulic permeability is the primary consideration for the evaluation and management of seepage; layers of relatively high permeability sands are interbedded with relatively low permeability slimes, creating a complex hydrogeological regime (EPA 1994).

Review of Tailing Seepage Control

Understanding both the hydraulics and geochemistry of tailings seepage is important for effective mitigation as well as management. The direction and quantity of seepage flow is controlled by the vertical and horizontal heterogeneity of hydraulic permeability created by interbedded sands and slimes tailings. The movement of seepage is dominant in the relatively high permeability sands, which create preferential flow paths that may or may not be laterally as well as vertically continuous. Seepage flow can also be affected by hydraulic properties of the impoundment foundation and underlying aquifer, which determine the level of saturation and hydraulic connection between the impoundment and the aquifer (Vick 1990).

The chemical composition of tailings seepage can have a significant effect on adjacent water quality. The chemistry of tailings leachate typically retains the chemical composition of the milling process, which may exhibit undesirable characteristics, such as extreme pH, salinity, lixiviant (bicarbonate, cyanide, or acid), sulfate, or elevated concentrations of trace elements or radionuclides. Additionally, the oxidation of sulfides in legacy (partially unsaturated) tailings impoundments may create acid rock drainage and metal leaching (ARD/ML) concerns. Because of these possible characteristics, seepage may represent a risk to environmental or human health (Vick 1990).

Seepage mitigation and management methods can take either physical (hydraulic) or chemical approaches. Traditional seepage control methods are physical, and include seepage barriers, seepage return systems, liners, and hydraulic containment. While these methods reduce seepage transport through water management, in many cases, physical controls create an additional waste stream that requires management as well as treatment. Alternatively, chemical seepage control methods reduce leachate transport through geochemical alterations and ultimately reduce the mobility of chemical constituents in the leachate. Chemical seepage controls, which can be implemented in situ in impoundments, may be a preferable alternative or supplemental option to traditional physical methods for some applications.

Phosphate Mineral Precipitation Applied to Control Seepage Water Quality

An effective chemical mitigation approach for the treatment of dissolved metals includes removal from the aqueous phase via precipitation. This approach can be a challenge for the oxidized form of uranium (U[VI]), which tends to be highly soluble under typical tailing seepage geochemical conditions. A strategy currently under investigation involves the in situ precipitation of U(VI) within uranyl phosphate phases. The strategy involves injecting a soluble form of phosphate, which can react with uranium and other groundwater constituents (including calcium) to form a host of low-solubility uranium-containing phosphate phases. These include uranium phosphate pure phases such as chernikovite (H[UO₂PO₄]×4H₂O), autu- $(Ca[UO_2PO_4]_2 \times xH_2O)$, and nite saleeite (Mg[UO₂PO₄]₂×10H₂O) as well as uranium-substituted calcium phosphate phases such as apatite (Ca₅[PO₄]₃[F,Cl,OH]) (Fuller et al. 2002; Fuller et al. 2003; Fanizza et al. 2013). Generation of these phosphate phases also provides a long-term barrier for uranium treatment via sorption (Fuller et al. 2002; Fuller et al. 2003).

A challenge with the implementation of this injection-based approach is the distribution of phosphate in the subsurface before precipitation occurs. For example, phytic acid and tribasic sodium phosphate have the potential to precipitate rapidly in the vicinity of the injection well, limiting distribution and reducing aquifer permeability (Wellman et al. 2007; references therein). An approach currently under evaluation involves the injection of phosphate as tripolyphosphate. This phosphate polymer is relatively soluble compared to orthophosphate, allowing for enhanced distribution, while providing a long-term source of orthophosphate in the aquifer as the polymer hydrolyzes (Wellman et al. 2007; Vermuel et al. 2009).

Methods

Laboratory tests were performed on tailings samples and porewater collected from a tailings impoundment at a former uranium mill site in order to optimize the implementation strategy in the field. The tailings impoundment at the site has been actively flushed with water to accelerate movement of seepage to the underlying aquifer, where it is collected and treated ex situ to remove uranium. The laboratory tests were performed to understand the concentrations and chemical forms of uranium in tailing sands and slimes zones before implementing pilot testing activities described below. The relative abundance of different chemical forms of uranium present in the tailing sands and slimes was determined using a selective extraction approach. Sandsand slimes-dominated zones exhibited similar fractional abundance of uranium entrapped in mineral phases (65 to 80 % of total uranium), suggesting that a small fraction (20 to 35 %) of the uranium present in the tailings impoundment is potentially mobile. The majority of the sorbed uranium was weakly sorbed (i.e. desorbable by NaCl solution), while a slightly more than half of the mineral-bound uranium was in a form extractable by nitric acid (i.e. present in amorphous and crystalline metal oxide phases).

Field Tests of In Situ Uranium Phosphate Precipitation

A pilot-scale field testing program (Pilot Test) was implemented in the tailings impoundment, targeting the dissolved uranium phases in the tailings porewater. The primary objective of the Pilot Test was to evaluate the effectiveness of tripolyphosphate at immobilizing uranium *in situ*. In addition to demonstrating immobilization, specific objectives of the Pilot Test included 1) characterizing the *in situ* kinetics of the tripolyphosphate hydrolysis and precipitation reactions, 2) determining the injectability of the tripolyphosphate solution and subsequent distribution and transport in the tailings, and 3) evaluating any secondary geochemical as well as hydrogeological effects of tripolyphosphate (*e.g.* mobilization of other contaminants and reductions in hydraulic conductivity). To this end, the Pilot Test was conducted in three phases: hydraulic characterization, tripolyphosphate injection, and performance monitoring.

Hydraulic Characterization

Tracer testing was conducted to characterize the injection and hydraulic parameters of the impoundment in the Pilot Test area. Conservative (*i.e.* non-reactive, non-sorbing) tracers were injected into the proposed injection well. Two tracers were used concurrently: bromide (as potassium bromide) and a dye tracer fluorescein (as sodium fluorescein). The pilot test network is shown in Fig. 1. Wells were screened from 12 to 27 m below the surface of the tailings (total depth of the tailing was 30 m). Samples were taken from mid-point within the screened interval (approximately 20 m below the surface of the tailings). Tailing material was comprised of slimes (fine grained material) and sands.

Pilot Test Injections

Uranium immobilization through phosphate precipitation is inhibited in the alkaline envi-



Fig. 1 Pilot Test well network ("INJ" is the injection well; wells labeled "W" are monitoring wells).

ronment of the tailings impoundment (due to the presence of highly soluble uranium carbonate complexes), so tripolyphosphate injections required a pH adjustment to lower pH and an addition of calcium. Prior to injecting tripolyphosphate, the tailings within the Pilot Test well network were "conditioned" with sulfuric acid metered into the injection supply water until a pH response was observed at the dose response monitoring wells (closest to the injection well). The Pilot Test proceeded when the field team determined that the pH adjustment caused no adverse effects (e.g. significant off-gassing or heat generation) that required additional engineering controls. In total, 12,900 L of pH-adjusted supply water were injected prior to injecting the tripolyphosphate solution.

The amendment solution used for the Pilot Test injections comprised tripolyphosphate, calcium chloride, and sulfuric acid mixed with the supply water. The target pH for the amendment solution was 5. The amendment solution also included conservative tracers: Rhodamine WT and deuterium. In total, 63,000 L of pH-adjusted amendment solution were injected over 8 days, delivering more than 105 kg of tripolyphosphate. The injection rate averaged approximately 23 L/min over the course of the injections. Seven monitoring events were conducted before or during active injections, and 12 post-injection monitoring events were conducted over 125 days to evaluate the performance of the tripolyphosphate amendment.

Pilot Test Results

Based on the results of post-injection performance monitoring, phosphate breakthrough curves were developed for the monitoring wells in the Pilot Test well network (Fig. 2). Peak phosphate concentrations were observed at the dose response wells during the injection because these wells were within the injection radius of influence (ROI); however, phosphate concentrations quickly declined in the upgradient and side-gradient wells after injections ended. Phosphate concentrations remained elevated in the downgradient dose response well (W-1) and peaked at downgradient monitoring well (W-2) after injections. In these two wells, phosphate concentrations were sustained long enough for uranium to be effectively immobilized and thus were the focus of continued monitoring.

The concentration of dissolved uranium and the pH (as measured in the laboratory) at these two downgradient wells are compared in Fig. 3. The pH-adjusted amendment solution decreased the ambient pH, which exceeded 8,



to a minimum of 6.7 and 7.7 for W-1 and W-2, respectively. This pH decrease was maintained more than 30 days post-injection at these two downgradient wells, whereas the pH quickly rebounded to ambient levels at the other monitoring wells.

Because of the sustained phosphate concentrations and pH decrease at W-1 and W-2, concentrations of dissolved uranium decreased significantly. Uranium concentrations were reduced to minimums of 0.464 and 0.300 mg/L at W-1 and W-2, respectively (Fig. 3) Using the baseline uranium concentrations measured before the Pilot Test injections, these concentrations represent 62 % uranium removal in W-1 and 67 % removal in W-2. It is important to note that, when pH increased post-injection. uranium concentrations in W-1 and W-2 did not return to baseline concentrations, indicating the stability and insolubility of the uranium-calcium-phosphate precipitate that was formed.

However, when evaluating performance, uranium concentrations of the injected amendment solution must be considered. The pore water from the nearby well used to supply water for the Pilot Test injections had higher concentrations of uranium (ranging from 2.6 to 3.5 mg/L) than the baseline concentrations in the monitoring wells in the Pilot Test well network. To correct for the additional uranium in the amendment solution, the deuterium analytical results were used; the normalized deuterium concentrations represent the fraction of the sampled water that is injected water from the amendment solution. Using this approach to correct the uranium immobilization calculations, 80 - 90 % of the uranium was immobilized within the treatment area. In addition, it was noted that tripolyphosphate was significantly retarded in the injection zone of the Pilot Test. This retardation is most likely due to adsorption of the polyphosphate onto tailings solids.

Conclusions

Conventional physical (hydraulic-based) approaches to seepage management at tailings impoundments often cannot prevent impacts to adjacent water quality. Reactive chemical approaches hold promise for fundamentally changing the tailings pore water chemistry, resulting in source control via reduced mobility of major and trace elements. Challenges related to amendment delivery and distribution within an impoundment, and overcoming extremely alkaline conditions that were unfavorable for uranium precipitation, were evaluated in the Pilot Test discussed here.



Fig. 3 Uranium concentration and pH at downgradient monitoring wells.

The Pilot Test successfully demonstrated that tripolyphosphate can be used to immobilize uranium *in situ* in tailings impoundments, even in the extreme hydrogeological and geochemical conditions of a legacy uranium tailings impoundment. Up to 81 % of uranium was immobilized where pH adjustments and phosphate concentrations were sustained long enough for precipitation to occur. More importantly, the phosphate minerals that were formed were stable and did not re-dissolve when the pore water geochemistry returned to pre-injection conditions.

Secondary geochemical and hydraulic effects of this approach can be successfully managed. During the Pilot Test, there was no indication of precipitate fouling of the injection system as well as the tailings matrix. Further, off-gassing and heat generation from the pH adjustment were minimal and successfully mitigated. These factors were effectively controlled throughout the Pilot Test and did not affect performance. The results demonstrate that, through a detailed understanding of tailings chemistry and hydraulics, reactive chemical amendments can be employed to control and improve seepage water quality.

References

Fanizza, M.F., H. Yoon, C. Zhang, M. Oostrom, T.W. Wietsma, N.J. Hess, M.E. Bowden, T.J. Strathmann, K.T. Finneran, and C.J. Werth. 2013. Pore-Scale Evaluation of Uranyl Phosphate Precipitation in a Model Groundwater System. Water Resources Research 49(2), 874–890.

- Fuller, C.C., J.R. Bargar, J.A. Davis, and M.J. Piana. 2002. Mechanisms of uranium interactions with hydroxyapatite: Implications for groundwater remediation. Environmental Science & Technology 36, pp. 158–165.
- Fuller, C.C., J.R. Bargar, and J.A. Davis. 2003. Molecularscale characterization of uranium sorption by bone apatite materials for a permeable reactive barrier demonstration. Environmental Science & Technology 37, pp. 4642–4649.
- U.S. Environmental Protection Agency (EPA). 1994. Design and Evaluation of Tailings Dams. Technical Report. EPA530-R-94-038/NTISPB94-201845. April.
- Vick, S.G. 1990. Planning, Design and Analysis of Tailings Dams. BiTech Publishers Ltd.
- Vermeul, V.R., B.N. Bjornstad, B.G. Fritz, J.S. Fruchter, R.D. Mackley, D.P. Mendoza, D.R. Newcomer, M.L. Rockhold, D.M. Wellman, and M.D. Williams. 2009. 300 Area Uranium Stabilization through Polyphosphate Injection: Final Report. Pacific Northwest National Laboratory. PNNL-18529. June.
- Wellman, D.M., E.M. Pierce, E.L. Richards, B.C. Butler, K.E. Parker, J.N. Glovack, S.D. Burton, S.R. Baum, E.T. Clayton, and E.A. Rodriguez. 2007. Interim Report: Uranium Stabilization Through Polyphosphate Injection. Pacific Northwest National Laboratory. PNNL-16683. July.

Incorporating Wall Rock Runoff into Pit Lake Water Quality Modeling in the Arid Western United States

Briana GREER, Andrew NICHOLSON, Steve HELGEN, Sean KOSINSKI

Integral Consulting Inc., 285 Century Place, Louisville, Colorado, USA, bgreer@integral-corp.com

Abstract Constituent mass loading from pit wall runoff is increasingly incorporated into pit lake water quality models. In arid climates, pit wall runoff is a small portion of the pit lake water balance, but can be an important contributor to the chemical mass balance. Review of publicly available documents for recent pit lake models in the western United States demonstrates the importance of quantifying the effects of runoff coefficients, water quality, and pit geomorphology on wall runoff mass contributions to pit lakes.

Keywords pit wall runoff, pit lake chemistry

Introduction

Factors affecting the quantity and quality of pit wall runoff include climatic conditions and the geochemical and morphologic nature of the pit wall (Schafer and Eary 2009). Weathering results in accumulation of finer-grained materials on pit benches that may store more water than unweathered benches of competent crystalline rock, resulting in reduced runoff. Increased weathering of pit walls may also increase reactive surface area associated with finer materials, potentially decreasing pit wall runoff quality. Furthermore, the overall effect of pit wall runoff must be considered in the context of runoff interaction with groundwater quantity and quality. The influent runoff may have an ameliorating or degrading effect on pit lake water quality depending on the pit stratigraphy and groundwater quality.

Recently permitted open pit mines in the arid western United States have modeled pit wall runoff quantity and quality in several different ways. In some cases runoff has been considered negligible. Where pit wall runoff has been included in the pit lake model, the percentage of precipitation that is considered runoff varies from 20 to 100 %. Runoff water quality has been assigned based on wall washing, meteoric water mobility procedures (MWMP), synthetic precipitation leachate procedures (SPLP), humidity cell tests (HCT), as well as a combination of these analyses. While it was determined in one pit that 95 % of the pit lake mass came from groundwater, in another case pit wall runoff was determined to be the primary influence on pit lake water quality.

In this paper, fictional simplified pit lake models using total dissolved solids (TDS) to represent mass loading are used to explore the effects pit wall runoff in pit lake models. Consideration of assigned runoff quality, runoff coefficients, and pit morphology in a typical arid climate illustrate the potential effects of each parameter. The simulations demonstrate the importance of evaporative draw on groundwater, offsetting effect on the importance of pit wall runoff in arid climates. These simplified conceptual models can be used to assess the importance of runoff in predicting pit lake water quality before implementing an entire pit lake model.

Recent considerations of pit wall runoff in pit lake models

Recently, pit wall runoff has been incorporated in pit lake predictions at several mines in the arid western United States. However, each site has a different pit infilling period, runoff coefficient, and runoff was represented by a different analytical procedure at each pit. Pit infilling and runoff coefficients are directly, and complexly, related to the site geology, hydrology, pit shape, and material weathering (Schafer and Eary 2009, INAP 2012). These same four parameters, with the addition of available geochemical data, were often considered in selecting an analytical basis for assigning pit wall runoff quality. Considering the number of factors affecting pit wall runoff quantity and quality a wide variety of pit runoff modeling methods is expected; no single approach will be applicable to all pits.

Pit A is a backfilled pit in Nevada which would preclude the \approx 16 ha pit lake predicted to form in the no action alternative. Approximately 30 % of the wall rock was predicted to be non-acid generating, with a substantial percentage having uncertain acid generation potential. Pit wall runoff was considered negligible to the overall pit lake water balance in this case based on hydrologic modeling (Table 1). While pit wall runoff was small, mass associated with the runoff was acknowledged to increase the pit lake mass load consistent with the overall conclusion that several constituents would exceed regulatory guidance.

Pit B, located in Arizona, is a ≈ 263 ha, ≈ 610 m deep, open pit mine. Non-ore materials were characterized as limited in sulfide and abundant in carbonates. 220 years after mining the pit was projected be a 90 % full, with a ≈ 335 m deep lake of generally good quality. Pit wall runoff volumes were simulated using a stochastic element varying between 20 % and 40 % of the total precipitation on the pit wall (Table 1) and accounted for approximately a quarter of the steady state water balance. Pit wall runoff quality was represented by SPLP data for non-acid generating rocks and a combination of HCT and SPLP data for acid generating rocks. Runoff was allocated to the exposed rock types based on surface area percentage. While the model predicted 95 % of the pit lake mass loading was derived from groundwater, key constituents As, Pb, Hg, Se, and Tl were derived largely from pit wall runoff in the simulations (Table 1).

Located in Nevada, Pit C was incrementally expanded by \approx 85 ha to reach \approx 526 ha and 488 m deep. Pit geology was dominated by volcanics and alluvium. Pit wall runoff was based on the final four weeks of HCT, or MWMP when HCT was not available (Table 1). The HCT and MWMP results were scaled to adjust for field conditions. Pit C lake water quality was predicted to be circum-neutral to alkaline with As, F, and TDS in excess of regulatory reference values after 200 years of infilling, corresponding to a 335 m deep lake with a surface area of \approx 158 ha. The pit wall runoff was \approx 2 % of the overall pit lake influent through 200 years.

Pit D, located in Nevada, is a ≈295 ha, ≈ 762 m deep, open pit mine. Pit D lithologies include non-acid generating quartz apatite porphyry as well as quartz porphyry, rhyolite, and Ordovician sedimentary rock types which are subdivided based on acid generation potential. ≈15 % of the exposed pit surface was classified acid generating material. The pit was projected to be a little over half full after 200 years, with a \approx 259 m deep lake. Pit D lake water quality was projected to be circum-neutral with few exceedances of Nevada standards. Pit D lake modeling water balance was taken directly from a hydrologic model which included pit wall runoff. Based on time step volumes, pit area, and precipitation rates, runoff was approximately 50 % of pit wall rainfall. Pit wall runoff loading was based on average HCT efflu-

Pit	Precipitation cm/a	Evaporation cm/a	Infilling Duration	Runoff Coefficient	Analytical Basis	
A	29.2	115.6	Backfilled/220	negligible	None	
В	43.4	181.6	215	0.2-0.4	HCT/SPLP	۱
С	17.0	118.1	200	≈0.2	HCT(4wks)/MWMP	1
D	23.1	95.3	>600	≈0.5	HCT (ave)	l

Table 1 Pit Lake water quality models mentioning pitwall runoff; meteorology, infilling period, and analyticalbasis of runoff water quality.

Wolkersdorfer, Brown & Figueroa (Editors)

ent concentrations scaled by half an order of magnitude to account for differences in grain size (Table 1). All HCTs ran in excess of 50 weeks. Mass loading was weighted to the exposure of each lithology. While no comparison of mass loading sources was presented, pit wall runoff accounted for 62 % of inflow in early time and 48 % at year 200.

Simplified Pit Wall Runoff Models Method

Simplified models based on TDS were used to evaluate the influence of pit wall runoff on pit lake water quality, and did not include equilibrium chemistry and mass loading from inundated pit walls. Terminal pit lakes forming in two different shaped pits were considered, each pit was 457 m deep, with planar areas of \approx 202 ha, and \approx 405 ha at the ground surface (fig.1). Each pit has a specific volume ("*V*" in m³) and lake area ("*LA*" in m²) as a function of stage ("*S*" in m) based on the pit geometry.

Time-stage relationships (fig. 2), which would normally be provided by a groundwater model, were calculated as an exponential function of the pit geometry provided stage. Time functions were altered to allow for different infilling periods and equilibrium stages. At equilibrium stage, the stage, volume, and lake area were held constant as time proceeded.

Based on the changes in stage (ΔS), pit lake volume (ΔV), lake area (ΔLA), as well as the assigned precipitation and evaporation rates, water volumes attributed to evaporation (E), direct precipitation (P_d), indirect precipitation (P_i), and groundwater inflow (GW_{in}) were calculated for each new time step as described below.

$$E = \Delta LA \times E_{\text{rate}} \times \Delta T \tag{1}$$

$$P_{\rm d} = \Delta LA \times P_{\rm rate} \times \Delta T \tag{2}$$

$$P_{i} = LA_{max} - (\Delta LA) \times (P_{rate} \times \Delta T) - P_{d}$$
 (3)

Where:

 E_{rate} = Evaporation rate

 $P_{rate} = Precipitation rate$

 LA_{max} = maximum planar pit surface area ΔT = elapsed time (years)

The change in pit lake volume (ΔV) can be described by the following volumetric water balance:



$$\Delta V = GW_{\rm in} - E + P_{\rm i} + P_{\rm d} \tag{4}$$

Based on the relation above, time step groundwater inflow volume can be calculated as follows:

$$GW_{\rm in} = \Delta V + E - P_{\rm i} - P_{\rm d} \tag{5}$$

In the simplified pit lake models direct precipitation was assumed to have no dissolved mass. Pit wall runoff was calculated from the indirect precipitation rates as described above and assigned a runoff coefficient, thus limiting the amount of indirect precipitation entering the pit to 20 %, 50 %, or 80 %, of the total indirect precipitation. In all cases the evaporation was set to 1.2 m per year and precipitation rates were set to 0.3 m per year to reflect the precipitation and evaporation rates in the arid western United States (Table 1).

Groundwater quality was consistently assigned a concentration of 100 mg/L TDS. Runoff water quality was assigned TDS concentrations of 100, 300, and 500 mg/L, depending on the simulation. At each time step the respective water quality was applied to the runoff volume and the groundwater inflow volume to determine the mass added to the pit lake during the time step. Additional mass from each water source was incrementally summed and cumulated and the cumulative total divided by pit lake water volume to represent pit lake water quality.

Simplified Pit Wall Runoff Models Results

Simplified pit lake model results reveal that infilling time has minimal importance on groundwater quality; however, only cases where groundwater is equivalent to, or better than, runoff quality were considered. The effects of runoff coefficient, runoff water quality, and pit geometry produced significant changes in water balance which drive pit lake quality. The results presented here reflect the overall mass load delivered to the pit lake in TDS, no mass has been removed from the simulated pit lake solution via the precipitation of solids that would decreased the dissolved mass in a real pit lake. Therefore, the concentration increases shown here are generally over represented.

Increasing runoff percentage, not surprisingly, increased the pit lake TDS. In the case of a 202 ha, 457 m deep pit, filling to an equilibrium stage of 305 m deep over \approx 150 years, with a runoff quality of 500 mg/L and groundwater quality of 100 mg/L the effects of runoff coefficient were visible (fig. 3). However, over the 1000 year simulation, groundwater accounted for 69-76 % of the influent volume and runoff only accounted for 2-10 %. In this case, where runoff water quality was substantially worse than groundwater quality, runoff accounted for 14-41 % of the pit lake mass load at 1000 years. There would be no runoff coefficient effect on pit lake water quality if runoff water quality was equal to groundwater quality. Where runoff water quality is better than groundwater quality increasing the runoff coefficient would have an ameliorating effect on pit lake water quality, decreasing pit lake concentrations with increasing runoff coefficient.

Pit lake water quality was also affected by runoff quality. For the same pit as discussed above, with runoff held to 50 % of pit wall precipitation, the effect of runoff qualities ranging from 100 mg/L to 500 mg/L were noticeable over a 1000 year simulation (fig. 4). In all three simulations presented in Fig. 3, groundwater accounted for 72 % of the influent volume, while runoff accounted for 6 %. Mass associated with groundwater accounted for 71–92 % of the pit lake mass and runoff accounted for 8–29 % of the mass in the pit lake over the 1000 year period depending on runoff quality.

Simulations performed for two different pit shapes, both (472 m) deep and both filling to 305 m deep produced disparate results. One pit had a surface expression of 202 ha, while the other had a larger catchment area of 404 ha (fig. 1). In both cases (fig. 5) runoff quality was 500 mg/L; however, the larger pit resulted in increased runoff, thus increasing the



Fig. 3 Pit lake TDS concentration (mg/L) as a function of time for a 202 ha pit with a runoff quality of 500 mg/L at 20 % (- - -), 50 % (- \cdot -), and 80 % (--) runoff, reaching equilibrium stage at 150 yrs.

Fig. 4 Pit lake TDS concentration (mg/L) as a function of time, reaching equilibrium stage at 150 yrs, for 202 ha pit at 50 % runoff with a runoff quality of 100 (- - -), 300 (--), and 500 (- --) mg/L.

Fig. 5 Pit lake total dissolved solid concentration (mg/L) as a function of time for a 457 m deep, filling to 305 m deep over \approx 150 years, groundwater quality of 100 mg/L at 50 % runoff with a runoff quality of 500 mg/L and pit acreages of 202 ha (- - -) and 404 ha (--) respectively.

runoff mass load to the pit. Runoff accounted for 11 % of the influent volume, and 44 % of the mass in the larger pit. Groundwater accounted for 67 % of the influent volume and 56 % of the mass. In the smaller pit, runoff accounted for 6 % of the volume and 30 % of the mass, while groundwater was 72 % of the influent volume. Unlike the previously discussed examples, these two examples have different infilling functions and there is a substantial difference in volume in between these two simulations.

Conclusions

Several expected results related to water balance and water quality are demonstrated through simplified pit lake water quality models that include runoff. The simplified models show the effects of pit morphology and runoff coefficient on runoff quantity and water balance. Runoff water quantity is typically small in arid climates, offset in water balance by the ever-present evaporative draw on groundwater. Evaporative consumption of pit lake water keeps groundwater inputs high, even at equilibrium stage, unless the pit lake is small in comparison to the pit. Despite the potentially small water quantities associated with runoff, it can load significant mass to the pit lake when runoff quality is poor in comparison to groundwater quality.

In some recent pit lake models runoff coefficients were assigned a value based on professional judgment with no references, despite demonstrating a potentially substantial effect on pit lake water quality. Runoff coefficients are dependent on precipitation rate and duration (on an individual storm basis), whether it falls as rain or snow, pit bench width, hydrologic characteristics of the rock, pit aspect, and evaporation/sublimation (Prohaska and Dragišić 1991). One component of the water balance that was not considered in recent pit lake models, or this effort, is the interflow derived from pit wall precipitation. Empirical runoff coefficient data from existing pits, or as a pit develops, could be useful in further defining the complex parameter of runoff coefficients and interflow.

Runoff water quality is typically assigned a constant value for each lithology based on an

analytical procedure, as seen in recent pit lake models. In general MWMP, SPLP, and wall washing stations on loose walls are likely to have higher TDS than average or late term HCT results. Of the recent cases, results from the HCT are more likely to capture the acidity and metals generated through the oxidation of sulfide bearing rocks. The use of net acid generation test results on acid generating materials to capture the behavior of acid generating lithologies could also be useful in assigning pit wall runoff quality. However, pit wall runoff concentrations may not be constant. As pit walls weather, reactive surface area is likely to increase, thus increasing mass loading to runoff. Acid generating rocks are more likely to disaggregate, resulting in increased surface area subject to oxidation over time. In this regard, a model that considers runoff quality on a kinetic and mass-balanced basis (instead of a constant concentration basis) might be an improvement to the state of the art. In many cases, the pit wall could be considered miniature waste dumps spread across the benches of the pit.

References

- INAP (2012) Global Acid Rock Drainage Guide. www.gardguide.com
- Schafer WM, Eary LE (2009) Approaches for Developing Models of Pit Lake Geochemistry. In: Castendyk DN, Eary LE (Eds), Mine Pit Lakes Characteristics, Predictive Modeling, and Sustainability, Society of for Mining, Metallurgy and Exploration, 115—126
- Prohaska S, Dragišić V (1991) Methodology of Computation of Flood Wave Hydrograph in Deep Open Pits. Proceedings, 4th International Mine Water Association Congress, September 1991, Ljubljana, 109 – 117.

The Adoption of the Soil Chemical Equilibrium Approach to Solving Hydrogeochemical Problems

Andrew HARLEY

Tetra Tech Inc., 350 Indiana St, Golden, Colorado, 80401 USA, andrew.harley@tetratech.com

Abstract While hydrogeochemical reactions are well documented, focus is on thermodynamics of the aqueous phase, especially as it pertains to precipitation-dissolution reactions. Except in highly permeable systems, groundwater has sufficient time to react with minerals within solid phases that take in consideration other reactions including ionic excannge. Generally these reactions occur at far from equilibrium and in relatively dilute aqueous solutions similar to unsaturated soil conditions. The Proactive Monitoring approach of Mulvey (1998) was modified to include soil chemical equilibria reactions, including using both pe and pH to specify the redox status of aqueous systems. Understanding the hydrogeochemical environment in a proactive manner allows for more appropriate decision making with respect to management, treatment and regulatory issues.

Keywords hydrogeochemistry, proactive monitoring, redox

Introduction

Numerous graphical and numerical interpretation are basic tools in hydrochemical studies (Zaporozec 1972) to describe groundwater chemical behavior as determined by initial water sources, the medium through which it travels and subsequent reactions. Mulvey (1998) proposed that these can be described in terms of soil chemical reactions, especially ionic exchange. Ion exchange reactions reduce the concentrations of some ions, introduce new ions and leave others to migrate unimpeded, producing a leachate front that can potentially provide a more accurate monitoring methodology of leachates at mine sites that are generated within tailings facilities and waste rock dumps. Key to this approach is the use of ratios rather than absolute ionic concentrations, especially where mine leachate (ML) differs from native exchangeable or groundwater cations (N), expressed as:

ML/N

where $ML = 100 \times 3$ most dominate, lease reactive cations within the mine leachate

N = 3 most dominate groundwater or soil/rock exchangeable cations.

When this approach was applied to an open-pit mine site that had been subsequently backfilled with organic material prior to the cessation of dewatering, it was found that a modification was required to take into account redox reactions. Following the guidelines of Mulvey (1998) soil chemistry fundamentals were employed to describe groundwater hydrogeochemistry.

Site Description

The site (Fig. 1) covers an approximate area of 3.2 ha located in the Perth suburb of Maddington, Western Australia. The site is located on the eastern edge of the Swan Coastal Plain, within the Guildford Formation geological unit (Gozzard 1983). The Guildford Formation comprises of sediments deposited during the Quaternary Pleistocene period (10–20 Ma) and is described as sandy clay, white grey/brown, with fine to coarse grained sub angular to rounded sand, with component clays of moderate plasticity. The water table is approximately 1.0-4.0 m below the surface and re-

(1)



Fig. 1 Site layout showing location of monitoring wells. Red outline delineates area of investigation. Blue outline delineates extent of open pit mining.

gional groundwater quality (Davidson 1995) is characterised as having:

- TDS concentrations greater than 2,000 mg/L;
- nitrate (NO₃⁻) concentrations greater than 1 mg/L;
- sulfate (SO₄²⁻) concentrations less than 100 mg/L with Cl/SO₄ ratios of between 20 and 30.

Groundwater quality is a reflection of previous agricultural activities (including dairy farming) and the presence of sulfides within the Guildford Formation.

Groundwater bores surrounding the site have water levels ranging between 2.5 and 3.5 m below the surface. Available information regarding water quality indicates that total dissolved solid (TDS) values range from 170 – 4,000 mg/L.

Clay was extracted from the site between 1946 and 1985. At the completion of brick making operations, the pits were reportedly backfilled with inert construction waste by the landowners at that time. However uncontrolled deposition of drums, timber, vegetable matter and garden waste material also occured creating a complex source of contaminants to enter the groundwater system.

Field Investigation and Observations

Seventeen borings, including 3 nested wells, were installed. Boreholes located within the natural sediments of the Guildford Formation had the following stratigraphy:

- generally unconsolidated clayey fill material across the site to depths of approximately 0.5 and 2.5 mbg (metres below grade), overlying alluvial sediments of predominately stiff grey to white sandy clay, with varying amounts of sand and gravel and varying degrees of stiffness;
- laterite gravel layers varying in colour from red to yellow up to 200 mm thick at depths between 4.0-6.0 mbg;
- a white medium grained saturated silty sand at approximately 7.0-8.0 mbg; and
- grey to white sandy clay to clayey sand below 8.0 m.

Boreholes located within the clay pits had the following stratigraphy:
- generally unconsolidated clayey fill material across the site to depths of approximately 2.5 mbg;
- waste fill material within the clay pits comprising organic matter and rubbish (bricks, concrete, wood, plastic, metal);
- natural materials below the base of the pits were stiff, grey with yellow mottled sandy clay, encountered at various depths.

Groundwater levels were approximately 16 m AHD. Overall groundwater flow is approximately west southwest to southwest at a gradient of 0.001. Groundwater samples collected within the clay pit indicated the presence of pesticides above site criteria, while samples collected outside the clay pits had no detectable pesticide concentrations.

Conceptual Site Model

Concentrations of several analytes allowed for the principles proposed by Mulvey (1998) to be used to develop a monitoring program. However, use of the proposed ML/N formula of Mulvey (1998; Equation 1) did not provide sufficient interpretation of the groundwater monitoring data. Further examination of the data and use of ratios has been used to develop a conceptual model of groundwater beneath the site, including the quality and movement of the leachate, as discussed below.

To highlight the breakthrough of displaced native cations, Equation 1 was modified to include only two ML cations:

$$ML/N = \frac{K + NH_4^{+}}{Mg + Ca + Na} \times 100$$
 (2)

Given the complexity of the of the site chemistry, the use of Equation 2 was still insufficient to adequately describe all the variability in groundwater chemistry observed at the site. Lindsay (1979) describes the use of pe + pH as a convenient single-term expression for defining the redox status of aqueous systems. The use of pe (-log of electron activity) allows for electrons to be treated as reactants and products so that both chemical and electrochemical equilibria can be expressed by a single equilibrium constant. When ML/N is plotted against pe and pH (Fig. 2), a series of classes of groundwater in the vicinity of the site can be described, including three leachate classes and four background classes.

Leachate Classes

- **Class 1** The groundwater from BH1 in the western edge of the western clay pit has the lowest ML/N ratio of the leachate due to the lower NH₄⁺ concentration.
- **Class 2** Boreholes located in the middle of the western clay pit (BH3A, BH3, BH6) have the lowest redox values and higher ML/N ratios (6.19-9.98) due to higher NH4⁺. BH3 and BH6, in the lower portion of the clay pit, have K and NH4 concentrations lower than borehole BH3A screened in the upper portion of the aquifer, indicating either earlier disposal or more putrescible matter.
- **Class 3** he eastern clay pit has a different leachate signature than the western clay pit, with higher ML/N ratios due to higher K and NH4. The higher ML/N ratios indicate that the western pit was either filled after the eastern pit or contains more putrescible matter.

Background Groundwater Classes:

- **Class 4** BH2 is located between the eastern and western landfill, showing characteristics of leachate, with a negative redox and nitrate levels < 0.1 mg/L. NH₄⁺ and HCO₃⁻ concentrations were lower than the than leachate concentrations. TDS is at the lower range of leachate. Dewatering during mining may have generated sulfate and bicarbonate. Alternatively, groundwater may be impacted by the precursor of fermentative leachate
- **Class 5** Surface groundwater within the Guildford Formation indicates the influence of leachate within the pit, although redox values are positive. Groundwater collected from BH7 and BH11, down gradi-



Fig. 2 Groundwater Classes.

ent of the clay pits have higher NH_4^+ and HCO_3^- and lower nitrate levels than BH13, upgradient of the clay pits. The Cl/SO_4^{2-} ratios indicate that pyrite has been oxidised during the dewatering process associated with mining. TDS concentrations are elevated due to high bicarbonate and sulfate, or the precursor to landfill leachate (the fermentative phase) is passing these bores.

- Class 6 Shallow background bores BH13 is up gradient of the clay pits intersecting the water table and BH11 is cross gradient, screened between 6.0 and 8.0 mbg. Both wells have TDS values less than 1,000 mg/L nominal NH4⁺ and NO3⁻ greater than 1 mg/L. Native cation ratios (Cl/HCO3⁻ and Cl/SO4²⁻) indicate that mine dewatering has influenced the chemistry of these wells.
- **Class 7** The deeper well has the characteristics most typical of groundwater in the Guildford Formation (Davidson 1995)

A conceptual site model is presented in Fig. 3 and is summarised as follows:

- Potential sources of contamination: Three clay pits contain waste fill below the water table provide a source of leachate to groundwater.
- Chemicals of concern: Concentrations of metals, hydrocarbons and pesticides have

been detected in soil and groundwater samples collected within the clay pit.

• Potential transport mechanisms and exposure pathways: The site is currently vacant and all infrastructure has been removed. The waste material is covered with a minimum of 1.5 m of fill. The pits have been excavated into clayey material with a clayey sand lens has been observed at approximately 9.0-10.0 mAHD.

Natural attenuation involves the net reduction of contaminants in soils and groundwater through dispersion, dilution, (bio)degradation, volatisation, irreversible sorption as well as radioactive decay. Although leachate has been detected in the clay pits and appears to be leaving the site, attenuation is occurring over short distances. Using an average NH₄⁺concentration as an analogue for the movement of the leachate out of the clay pit, the rate of attenuation can be calculated to the nearest down gradient monitoring well. The eastern clay pit has an average concentration of NH4⁺ of 17 mg/L, reducing to 5 mg/L in borehole BH7, 10 m outside the pit, indicating that approximately 1.2 mg NH4⁺ is attenuated per metre. Based on this rate, the remaining leachate plume will attenuated within an additional 4.2 m.

Based on the available data, there is chemicals of concern above freshwater guidelines



Fig. 3 Conceptual site model.

were not been detected in boreholes outside of the clay pit. Further, ongoing impact to the regional aquifer is likely to minimal due to the following factors:

- the leachate has a chemical signature indicative of the long term landfill decay which is in agreement to the time since completion of the landfill (approximately 20 years; Knight and Beck 1987);
- landfill decay will continue, reducing the concentration of leachate components;
- conservative estimate of groundwater flow of 0.001 m/d (0.2 m/a) has been calculated;
- vertical attenuation can also be demonstrated by chemical data collected from boreholes BH11, BH11A and BH11B
- there is no evidence that BH11A has been impacted by leachate, but clearly shows impacts from dewatering and nearby horticultural activities;
- dewatering during mining produced SO₄²⁻ with adequate electron acceptors (concentrations in groundwater > 20 mg/L) for biodegradation (King and Beck 1997);
- nitrate levels in background bores (> 1 mg/L) are also suitable for nitrate reduction (Knight and Beck 1987)

Based on the data collected at this site, the intended land use at the site and current land use in proximity to the site, the environmental impact of leachate identified at the site is not considered to present a risk to the environment. A monitoring program was proposed based on the establishment of groundwater classes. As such basic groundwater chemistry parameters only were measured, greatly reducing analytical costs

Conclusions

A graphical representation of groundwater monitoring data is proposed using basic groundwater parameters expressed as a function of single-term expression for defining the redox status of aqueous systems. Understanding the hydrogeochemical environment in a proactive manner allows for more appropriate decision making with respect to management, treatment and regulatory issues.

Acknowledgements

The author thanks Phil Mulvey, Environmental Earth Sciences, for introducing the concept of Proactive Monitoring and for ongoing discussions around the importance of soil science in hydrogeology.

References

- Davidson WA (1995) Hydrogeology and groundwater resources of the Perth Region, Western Australia. Western Australia Geological Survey, Bulletin 142
- Gozzard JR (1983) Armadale Part Sheets 2033 I & 2133 IV, Perth Metropolitan Region, 1:50,000 Environmental Geology Series, Geological Survey of Western Australia
- Knight M, Beck G (1987) Modelling the long term dynamic behaviour of selected groundwater quality parameters in a domestic waste landfill at Lucas Heights, Sydney. International Conference of

Groundwater Systems Under Stress. Brisbane, QLD, May 1986, Australian Water Resource Council Conference Series No 13, 475–490

- Lindsay WL (1979) Chemical Equilibria in Soils. John Wiley & Sons, New York.
- Mulvey PM (1998) Groundwater Modeling. Mining Environmental Management. July 1998.
- Zaporozec A (1972) Graphical interpretation of water quality data. Ground Water, 10, 32–43

Addition of a Rate Limit to a Shrinking Core Oxidation Model for Predictive Modeling of Mine Water Quality

Steven Helgen, Andrew NICHOLSON, Briana Greer

Integral Consulting Inc., 285 Century Place, Louisville, Colorado, USA, shelgen@integral-corp.com

Abstract One of the more difficult problems in predictive modeling of mine water quality is accurate representation of sulfide mineral oxidation and the associated leaching of acid, metals, and other constituents. Shrinking core models (SCM) of sulfide oxidation are often used to represent oxidation kinetics; however, the SCM cannot represent increasing oxidation rates observed in laboratory tests. Addition of a rate limiting term to the SCM overcomes this limitation and allows modeling the full range of rate behavior. The resulting model provides more accurate representation of rate behavior of different lithologic materials, resulting in more accurate water quality predictions.

Keywords Sulfide oxidation modeling, rate limit, mine water quality

Introduction

Shrinking core models of pyrite oxidation (Davis and Ritchie 1986a-c) are widely used to represent the kinetics of sulfide mineral oxidation for predictive modeling of water quality in mine dumps, tailings impoundments, and mine pits. Recently there has been increased scrutiny of mine water quality predictions and the current state of predictive modeling of mine water quality. A key limitation of the classic SCM is the assumption that the sulfide oxidation rate can only decrease over time as oxidation progresses. This assumption is based on the theory that oxygen diffusion to reaction sites will be the primary limiting factor at the mine scale, where an abundance of sulfide minerals typically creates an oxygen demand in excess of the oxygen diffusion rate. However, in cases when oxygen availability is not the limiting factor (e.g. laboratory tests, nearsurface environments, and where advection or convection occurs) oxidation rates are sometimes observed to increase with time, typically accompanied by a decrease in pH and a dramatic increase in acid and metals release. In these cases, the classic SCM will under-predict the degree of oxidation and associated release of acid and metals.

In the classic SCM (Davis and Ritchie 1986a-c; Homma et al. 2004) reaction rates are limited only by two-stage diffusion of oxygen to a reaction site. In the first stage, oxygen diffusion through air-filled pores or fractures in mine materials is constrained by a diffusion coefficient representative of the porous media (D1). In the second stage, diffusion to a reaction site within a mineral grain is constrained by a second diffusion coefficient representing an oxidized rind (D2). The SCM will generate an infinite rate on a fresh surface: as a result. an initial oxidized thickness must be set. As oxidation progresses an increasingly thick rind forms as the unreacted core shrinks, resulting in a decreasing oxidation rate. However, in laboratory tests oxidation rates are observed to increase over time in some materials as pH decreases, a behavior that cannot be represented by the SCM.

During laboratory humidity cell tests (HCT), one commonly observed behavior is consistent with the assumptions of the classic shrinking core model. In these instances, the release of iron, sulfur and acidity decreases over time, creating cumulative release plots that approach an asymptote as oxidation progresses toward 100 % (Fig. 1a; HCT 9). It is hy-



Fig. 1 Cumulative sulfate release (a, left) and pH (b, right) in decreasing (HCT 9) and increasing (HCT 24) rate humidity cell tests

pothesized that in these cases the decrease in rate corresponds to an increasing limitation of diffusion to deliver oxygen across an increasingly thick oxidized rind consistent with SCM assumptions.

Occasionally, increasing oxidation rates are observed in kinetic tests (Fig. 1a; HCT 24). In this example, as pH decreases to 3 and below (Fig. 1b; HCT 24) a corresponding exponential increase in the release of sulfate and iron is observed. There are a number of possible explanations for increased rates observed at lower pH, including dissolution of secondary oxide mineral phases, increased bacterial populations and activity, and increased oxidation by ferric iron. Here it is hypothesized that pH decreased to a point capable of dissolving secondary oxide minerals, thereby eliminating the oxidized rind around the unreacted core. Under these conditions, the oxidized rind ceases to be the rate-limiting factor assumed in the shrinking core model, and abundant dissolved ferric iron is suddenly available to facilitate oxidation.

None of these potential behaviors are captured in the SCM, where the rate can only decrease over time as the unreacted core shrinks and oxygen must traverse a thicker and thicker rind of oxidized material to reach a reaction site.

Williamson and Rimstidt (1994) presented pyrite oxidation rate laws derived from labo-

ratory experiments as functions of H⁺, dissolved oxygen, and dissolved ferric and ferrous iron concentrations. More recently, Rimstidt and Vaughan (2003) and Lapakko and Antonson (2006) presented comparisons of rate law predictions to observed oxidation rates in laboratory experiments, with the latter describing how rates observed in humidity cell tests tended to be closer to rate law predictions above pH 6 and 2 to 8 times faster than predicted at pH 3.3 to 5.0. These results indicate that the aqueous rate laws also do not fully capture the range of behavior observed in HCTs.

Methods

An empirically fit rate limiting term was added to the SCM to account for the initial oxidation rate of a fresh surface and allow for an increasing rate as oxidation progresses. Results of adding a rate limiting term to the shrinking core model include the ability to model the full range of behavior observed in materials during humidity cell testing, including both decreasing rates resulting from diffusion across an increasing distance to the unreacted core, and increasing rates resulting from decreasing pH and associated dissolution of secondary oxide minerals.

An implementation of the Davis-Ritchie shrinking core model (Davis and Ritchie 1986a-c; Molson *et al.* 2005) was coded in Mi-



Fig. 2 Model verification (symbols) over base plot from Davies Ritchie 1986a Fig. 3

crosoft Visual Basic for Applications in Microsoft Excel using a novel numerical implementation that allows the addition of a simple rate limit term to the formulation. The model code was verified against the original Davis-Ritchie code and reproduced the original results satisfactorily (Fig. 2).

The classic shrinking core model requires that a pre-existing oxidized rind exists on the grains being modeled in order to avoid an infinite oxidation rate at the model start, generally applied as an unoxidized radius of 0.95 (5% oxidized initial condition). This approach does not allow for modeling of fresh sulfide surfaces commonly found in material ground for humidity cell tests and in recent mine materials. Alternate rate limiting was added to the model code by including a rate limit term that is invoked if the rate limit is less than the rate calculated from the D₂ diffusion coefficient. local oxygen content, and thickness of the oxidized rind. The rate limit is incorporated as an initial rate representing 0 % oxidation, and an ending rate representing the rate at 100 % oxidation. The instantaneous rate is linearly interpolated as oxidation proceeds from o to 100 %.

There are two instances where the alternate rate limit may be invoked; first, when the shrinking core code generates an unrealistically high oxidation rate if the oxidized rind is thin or non-existent. In this case, a standard oxidation rate from literature or calibration to a HCT is used to set the initial rate. Second. if the calibration data set demonstrates an increasing rate over time the alternative rate limit is invoked to represent the rate of sulfide oxidation at the grain scale (e.g. replacing the D2-derived rate). Under the alternative rate limit, the local availability of oxygen still limits the overall maximum rate of oxidation (i.e. diffusion at the dump scale limited by D1 is an overriding control on oxidation rate).

Model parameters are presented in Table 1 for the two HCTs (9 and 24) examined here. Model results demonstrate that with the alternate rate limit added, the model is capable of fitting both increasing (Figs. 3–4) and decreasing rates observed during kinetic tests (Figs. 5– 6).

Fig. 3 illustrates an increasing rate over time accompanied by a decrease in pH from 4 to 2 (Fig. 1b) which appears to have resulted in dissolution of secondary oxide minerals re-

LICT	Pyrite	D2	Initial Rate Limit	End Rate Limit
HCI	wt. %	(m²/d)	(mg py/kg-day)	(mg py/kg-day)
HCT 9	4	7.4E-8	200	-
HCT 24	2.3	-	8	112

Wolkersdorfer, Brown & Figueroa (Editors)

sulting in an exponential rate increase. Other factors that may contribute to the increasing rate include greater activity of oxidizing bacteria at lower pH and increased oxidation by ferric iron.

Fig. 4 illustrates the close agreement between the rate limit model results and the actual cumulative sulfur release data from HCT24. It should be noted that the shrinking core model is not capable of creating an upward inflecting curve. There has been discussion in mining and regulatory circles regarding how long HCT tests should run. In a minimum 20 week test (140 days) it would be possible to approximate a shrinking core model fit to the early time data that would predict a decreasing rate beyond 140 days. As can be seen in Figs. 3 and 4, a shrinking core model with a decreasing rate would greatly underestimate the ultimate production of acid and metals from this material.

Figs. 5 and 6 illustrate a fit of the classic shrinking core model to an HCT with a higher sulfide content (4 %) but higher effluent pH



Model vs. HCT Oxidation Rate



0

0

100

200

300

Day

400

500

600

(generally 5–6; Fig. 1b) that appears to have allowed formation of secondary oxide mineral rinds. These conditions do not violate the assumptions of the SCM and a reasonable fit can be achieved. In this example, the oxidation rate started out very high (Fig. 5), decreasing over time. This behavior is also apparent in the shape of the cumulative sulfur release curve, which rises steeply before inflecting convexly toward the limit imposed by the total sulfur content of the material.

Conclusions

Oxidation rate behavior is dependent on pH, with strongly acidic conditions (pH 2–3) associated with increasing rates over time and mildly acidic conditions (pH 5–6) generally associated with decreasing rates over time. In between, a variety of rate behaviors can occur including relatively constant rates and transitioning from one behavior to another. Increasing oxidation rates violate the simplifying assumptions of the SCM, which is unable to model anything but a decreasing rate as ox-



Fig. 5 Shrinking core model fit to decreasing rate HCT9



Model vs. HCT Cumulative S Released

Fig. 6 Shrinking core model fit to cumulative sulfur release in HCT9

Wolkersdorfer, Brown & Figueroa (Editors)

idation progresses. As a result, the classic SCM may under-predict acid and metal release from the most reactive materials, particularly in the later stages of oxidation. It is hypothesized that the different rate behaviors are primarily related to pH and the solubility of secondary oxide minerals. In the case where secondary oxide minerals accumulate in a rind around unreacted sulfide grains, the assumptions of the classic SCM are met and reasonable fits to data can be obtained. However, in cases where pH decreases sufficiently to partially or completely dissolve secondary oxide minerals, or prevent their precipitation entirely, oxidation rates are observed to increase. In order to model this behavior, it is necessary to add a rate limit function to the shrinking core model. This addition allows fitting of both increasing and decreasing rates, as well as transitional behaviors between these end points.

Reproducing kinetic test results (HCTs) is a simple test of an oxidation model that indicates whether the numerical model is capable of reproducing the full range of oxidation behavior observed in different mine materials. Given the considerable uncertainties already inherent in scaling from laboratory to field scale, it is important to verify that a model can accurately represent more controlled laboratory tests. Accuracy and utility of mine water quality predictive modeling depend on how well the model implementation reflects the actual conditions being modeled. In the case of oxidation modeling of sulfide-bearing mine materials, introducing a rate limit term to the SCM can simulate the varied oxidation kinetics of different lithologies and alteration types observed in HCTs, increasing the accuracy of water quality predictions.

Acknowledgements

The authors thank General Moly for allowing use of the humidity cell data presented here.

References

- Davis, G.B. and Ritchie, A.I.M. 1986a. A model of oxidation in pyritic mine wastes: part 1 equations and approximate solution. Appl. Math Modelling, Vol. 10, October, 314–322.
- Davis, G.B. and Doherty, G. 1986b. A model of oxidation in pyritic mine wastes: part 2: comparison of numerical and approximate solutions. Appl. Math Modelling, Vol. 10, October, 323–329.
- Davis, G.B. and Ritchie, A.I.M. 1986c. A model of oxidation in pyritic mine wastes: part 3: import of particle size distribution. Appl. Math Modelling, Vol. 11, December, 417–422.
- Homma, S., Ogata, S. Koga, J, and Matsumoto, S. 2005. Gas-solid reaction model for a shrinking spherical particle with unreacted shrinking core. Chem. Eng. Sci. Vol. 60, 4971–4980.
- Lapakko, K.A. and Antonson, D.A. 2006. Pyrite oxidation rates from humidity cell testing of greenstone rock. Conference proceedings of 7th ICARD March 26–30, St. Louis, MO.
- Molson, J.W., Fala, O., Aubertin, M., Bussiere, B. 2005. Numerical simulations of pyrite oxidation and acid mine drainage in unsaturated waste rock piles. J. of Contaminant Hydrology Vol. 78, 343–371.
- Rimstidt, J.D. and Vaughan, D.J. 2003. Pyrite oxidation: A state-of-the-art assessment of the reaction mechanism. Geochim. Cosmochim. Acta, Vol. 67, No. 5, 873–880.
- Williamson, M.A. and Rimstidt, J.D. 1994. The kinetics and electrochemical rate-determining step of aqueous pyrite oxidation. Geochim.Cosmochim. Acta, Vol. 58, No. 24, 5443–5454.

Numerical Simulation of Total Suspended Solid Concentration in Oil Sands Tailings Ponds

Jianhua JIANG¹, Adam AUCKLAND¹, Dejiang LONG¹, Ian MACKENZIE², Michael BENDER¹

¹Golder Associates Ltd., 2535 – 3rd Ave. SE, Calgary, AB, T2A 7W5, Canada; Jianhua_Jiang@golder.com, Dejiang_Long@golder.com, Michael_Bender@golder.com, Adam_Auckland@golder.com ²Teck Resources Ltd., 205 – 9th Ave SE, Calgary, AB, T2G 0R3 Canada; Jan.Mackenzie@teck.com

Abstract The three-dimensional hydrodynamic and sediment transport model COSED-UF was used to help assess total suspended solid concentration in oil sands tailings ponds in support of planning level engineering design of a tailings pond. Before implementation, the applicability of the model was assessed using the published suspended solid concentration data for Syncrude's Mildred Lake Settling Basin. This assessment shows that the model results of the suspended solid concentrations were generally in good agreement with the published data. This paper describes the main methodology and results of the modeling study.

Keywords Oil sands, tailings pond, lutocline, resuspension, TSS, COSED-UF.

Introduction

Large tailing ponds have been constructed or are planned for oil sands mining projects near Fort McMurray, Alberta, Canada. The tailings ponds are used for managing the tailings from the bitumen extract process. Oil sands tailings typically contain a mixture of solvent, solids (clay, silt, and sand), water, residual bitumen, salts, metals, and organic compounds (Gosselin et al. 2010). The coarse solids in the tailings settle out quickly in the tailings ponds, leaving the fine solids (clay and silt) to form fluid fine tailings, which are stored and left to gradually settle. A layer of water known as a 'free water cap' is maintained in the tailings ponds to facilitate solid settling and to reduce resuspension of the fine solids due to windwave action. The water in the free water cap usually has a relatively low Total Suspended Solid (TSS) concentration and is recycled for use in the bitumen extraction process to reduce water withdrawal from the Athabasca River. The TSS concentration in the free water cap (Fig. 1) is of particular concern for the operation and management of the tailings ponds, because high TSS levels affect the recycle use of the tailings pond water and may reduce the efficiency and life-span of process cooling systems.

The TSS level in the tailings ponds is influenced by the processes of deposition, vertical mixing and resuspension of the fine solids, which tend to aggregate into large flocs in the tailings ponds due to cohesiveness. Typically, three distinct vertical layers (Lawrence et al. 1991, Ward et al. 1994) are developed in the tailings ponds. The development of this vertical distribution of the solids has been observed in the Syncrude's Mildred Lake Settling Basin (MLSB), as shown in Fig. 1. The upper layer, known as the mixed layer or the free water cap, has relatively low TSS concentrations, with uniform vertical distribution of concentration usually less than 0.1% by weight. The intermediate layer or transition zone, known as the immature Thin Fine Tailings (TFT)or lutocline, contains neutrally buoyant fine particles and is characterized by sharp TSS concentration gradient (0.1 % to 15 % by weight within less than a meter)and water density gradients (Ward et al. 1994). The fine particles in the lutocline layer can be entrained into the free water cap under wind-driven current effects and wave actions. The lower layer, known as



Fig. 1 Measured solids concentration profiles in Mildred Lake settling basin (Ward et al. 1994).

the dense layer or the Matured Fine Tailings (MFT), is characterized by high solids concentrations, 15 % to 60 % by weight. The solids in the MFT layer are usually stationary and are only subject to resuspension under extremely strong wind events and wave action.

Ward et al. (1994) described an energy balance approach for simulating wind driven resuspension in the tailings ponds by assuming that wind energy and TSS potential energy are in an equilibrium state. The simulation model by Ward et al. (1994) was developed specifically based on the data for the Syncrude's MLSB. This approach does not account for processes such as wind-driven current effects and wave action on vertical mixing and bottom sediment resuspension, lutocline development, density gradient effects resulting from thermocline and lutocline, flocculation settling, and TSS spatial variation. Moreover, the energy balance relationship involves a single calibration parameter, which is highly dependent on tailings material properties and tailings pond geometry. Therefore, the calibrated model for the MLSB cannot be easily transferred to the other tailings ponds.

Currently, some oil sands mining projects are using a number of measures to reduce the TSS level in the tailings ponds, such as injecting CO_2 to increase settling velocity, increasing the free water cap depth to minimize wave effect on resuspension, and reducing pond size to minimize fetch and wave height. In tailings pond design, engineers need input information such as the relationship between TSS (levels and exceedance probabilities) and pond geometry (free water cap depth and pond size). To date, there has been no published study on modeling the effects of the free water cap depth and pond size on TSS levels. Lawrence et al. (1991) derived a relationship between minimum pond depth and fetch based on maximum near-bottom orbital wave velocity and critical velocity for bottom sediment resuspension. This simple approach did not directly or explicitly account for the effects and processes mentioned above, in particular the wind-driven current and lutocline entrainment. As a result, this relationship can only be used as a conceptual and qualitative tool for tailings pond engineering planning and design.

This paper presents the application of the integrated, three-dimensional (3D) hydrodynamic and sediment transport mode ICOSED-UF. The COSED-UF model is capable of simulating the effects of tailings pond size and depth on TSS levels and providing information for tailings pond planning, design, and operation. The application involved substantial efforts to adapt and evaluate the 3D model using the published TSS and water temperature data from the MLSB. This paper describes the methodology and results of the modeling study.

Approach

The COSED-UF model used in this study is a highly integrated, fully 3Dhydrodynamic, multiple size class cohesive and non-cohesive sediment transport, morphodynamic, wind wave, particle tracking and water quality model. The model, originally developed at the University of Florida, is a public domain program and has been applied in Environmental Impact Assessments (EIA) and in support of engineering design for a large number of coastal, river, lake, and mine resource development projects over the past decade. It was accepted as a reliable EIA tool by Canadian government agencies, first nation groups, and Environment Canada. To validate it as a reliable tool for simulating tailings pond solid resuspension and TSS concentrations under wind-driven current effects and wave action, the model was evaluated using the published TSS and temperature data from the Syncrude's MLSB, which layout plan is shown in Fig. 2.

The Syncrude's MLSB was built in late 1970's. It has a size of approximately 6×3 km,

a surface area of more than 12 km², and a free water cap of 5 m during the period when the published TSS measurements were obtained. The TSS concentrations and water temperatures were measured at 1 m depth and 700 m offshore from the pond's SW corner during an open water season from September 4 to November 7, 1991 (Ward *et al.* 1994).

The COSED-UF model was set up for the MLSB with a rectilinear grid (horizontal resolution of 500 m by 500 m and a vertical resolution of 0.25 m). The model simplified the MLSB geometry as a rectangular domain with a constant water cap depth of 5 m, and the inflow and outflow were not accounted for in the study. The following physical processes were simulated in the model: air-water momentum and heat exchanges, wind-driven current, wind-generated wave, water density gradient effects due to thermocline and lutocline, flocculation settling, lutocline development, vertical mixing and bottom sediment resuspension under current, and wave effects. The model inputs include hourly wind speed and direction, air temperature, dewpoint temperature. and cloud cover data from the Fort Mc-Murray Airport climate station. A lutocline



Fig. 2 A map showing MLSB geometry and survey site (dot; Ward et al. 1994).

Wolkersdorfer, Brown & Figueroa (Editors)

layer was initialized using the measured MLSB solids content profiles (Fig. 1) with a thickness of 1 m and maximum TSS concentration of 25,000 mg/L. The initial TSS concentration in the free water cap was set equal to 600 mg/L. The flocculation settling velocity was calculated as a function of TSS concentration (Jiang and Mehta 2000).

Applicability Evaluation

In testing the model application, a number of model parameters were adjusted to achieve the best agreement with the published data, mainly flocculation settling velocity, critical velocity for solid resuspension, Secchi depth (a measure of water clarity), light extinction coefficient for water, and bottom sediment temperature. In the thermal simulation, the typical parameters found in northern lakes for the Secchi depth (1.0 m), light extinction coefficient (0.45 m^{-1}) and bottom sediment temperature (4 °C) were found to be applicable for the MLSB, and the modeled time series of the near-surface water temperatures are in very good agreement (Fig. 3) with the observations. Measurements of the MLSB temperature after October 29, 1991 were taken under ice-cover conditions which were not modeled by COSED-UF. Therefore, the simulation results should not be compared to the observations during this period.

Most of the model testing efforts involved adjusting the flocculation settling velocity and critical velocity for solid resuspension (Jiang et al. 2013). The flocculation settling velocity introduced in Jiang and Fissel (2012) was used in the model, and appropriate parameters included in the settling velocity formula were chosen such that the suspended fine solids settled at a speed consistent with the observed TSS data from the MLSB. The critical velocity for solid resuspension was set equal to 0.05 m/s, which was reported in Lawrence et al. (1991) and based on laboratory flume experiments. The modeled time series of the nearsurface TSS concentrations at the survey site are generally in very good agreement with the observations (Fig. 4), and the modeled TSS time series patterns are consistent with the wind events (not shown). The modeled TSS profiles (Fig. 5) exhibit very uniform TSS concentrations in the free water cap and very sharp TSS gradient in the near-bottom lutocline layer, which are consistent with the observations (Fig. 1).

Noteworthy discrepancies are observed in mid-September and late October (Fig. 4),



Wolkersdorfer, Brown & Figueroa (Editors)



Fig. 4 Time series of the modeled TSS concentrations at the survey site, with comparison to the observations.

and might be caused by either inflow effects, which were not considered in this study, or onsite wind event effects. The wind data recorded at the Fort McMurray Airport climate station, about 50 km south of the MLSB, were used in the model because the wind data collected by Ward et al. (1991) at MLSB were not available in a digital format for use in this study. A visual comparison shows that on average, the wind speeds recorded at MLSB are higher than those at Fort McMurray by about 20 - 50 %. A factor of 1.1 was thus applied to the Fort McMurray wind data so that the peak wind speeds during the modeling period were comparable to those recorded at MLSB. The inflow conditions, such as discharge and TSS concentration, are believed to play important part for the TSS levels in the pond (Ward et al. 1991). However, the inflow effects were not considered in this modeling study because of unavailable inflow information.

Conclusions

Modeling TSS concentrations in oil sands tailings ponds is a very challenging task because of the unique processes characterized by the flocculation settling, development of the thin lutocline layer with sharp TSS gradient, vertical mixing across the lutocline and resuspension of the bottom sediment in the MFT layer under wind-driven current effects and wave action. The applicability assessment of the fully 3D, integrated circulation-wave-sediment-geomorphology numerical model, COSED-UF, for simulating the TSS concentrations in oil sands tailings ponds was conducted based on the published TSS data for the MLSB. The modeling results show that the model is a robust and reliable tool in simulating TSS concentrations in the tailings pond, and providing valuable information for supporting the engineering planning, design, and operation of the tailings ponds. The application and development of this model are ongoing. Future applications may include simulation of TSS concentrations in oil sands mine pit lakes that contain fine tailings. Future development of the model may include inclusion of an ice module, a MFT layer consolidating module, and an MFT layer thermal processes module.

Acknowledgements

Teck Resources Ltd., Canada is acknowledged for providing the funding for this modeling study. Acknowledgement is also extended to Jerry Vandenberg and Ian Halket of Golder Associates for their valuable support and discussion.

References

- Gosselin P, Hrudey SE, Naeth MA, Plourde A, Therrien R, KraakGVD, Xu Z (2010) Environmental and Health Impacts of Canada's Oil Sands Industry. The Royal Society of Canada Expert Panel, The Royal Society of Canada, 414 pp.
- Jiang J, Auckland A, Long D (2013) Modelling of Total Suspended Solids (TSS) Concentration in the External Tailings Pond. Unpublished Technical Report by Golder Associates Ltd., Calgary, AB, Canada, 12 pp.
- Jiang J, Fissel DB (2012) Modeling sediment disposals in offshore waterways, British Columbia, Canada. In: Proceedings of the Twelfth Estuarine and Coastal Modelling, ed. M.L. Spaulding, American Society of Civil Engineers, p 392–414.
- Jiang J, Mehta AJ (2000). Lutocline behavior in highconcentration estuary. Journal of Waterway, Port, Coastal and Ocean Engineering, 126(6), p 324–328.
- Lawrence GA, Ward PRB, MacKinnon, MD (1991) Windwave-induced suspension of mine tailings in disposal ponds – a case study. Canadian Journal of Civil Engineering.18(6).1047–1053.
- Ward PRB, Lawrence GA, MacKinnon MD (1994) Wind Driven Resuspension of Sediment in a Large Tailings Pond. Proceeding from the International Symposium on Ecology and Engineering, Oct 29 – Nov. 3, 1994.p VI-37 to VI-57.

Reactive transport modeling at uranium *in situ* recovery sites: uncertainties in uranium sorption on iron hydroxides

Raymond H. JOHNSON¹, Hlanganani TUTU²

¹Crustal Geophysics and Geochemistry Science Center, U.S. Geological Survey, Denver, Colorado, USA, rhjohnso@usgs.gov ²Molecular Sciences Institute, School of Chemistry, University of Witwatersrand, Johannesburg, South Africa, Hlanqanani.Tutu@wits.ac.za

Abstract Geochemical changes that can occur down gradient from uranium *in situ* recovery (ISR) sites are important for various stakeholders to understand when evaluating potential effects on surrounding groundwater quality. If down gradient solid-phase material consists of sandstone with iron hydroxide coatings (no pyrite or organic carbon), sorption of uranium on iron hydroxides can control uranium mobility. Using one-dimensional reactive transport models with PHREEQC, two different geochemical databases, and various geochemical parameters, the uncertainties in uranium sorption on iron hydroxides are evaluated, because these oxidized zones create a greater risk for future uranium transport than fully reduced zones where uranium generally precipitates.

Keywords uranium, reactive transport, modeling, sorption

Introduction

Groundwater users proximal to uranium *in situ* recovery (ISR) sites are concerned about influences on local groundwater quality. Within a uranium deposit, the local groundwater can be elevated in uranium, radium, and radon concentrations, but surrounding groundwaters are often much lower in radionuclide concentrations and can meet drinking water standards.

Uranium ISR in the United States is generally achieved by leaching reduced uranium ore zones with water containing increased concentrations of oxygen and carbon dioxide, which makes the uranium more soluble (fig. 1). Geochemical changes that may or may not occur outside of the recovery zone are important for local groundwater users, regulatory agencies, and other stakeholders to understand when evaluating the potential effects on surrounding groundwater quality. Fig. 1 illustrates a generic uranium *in situ* recovery facility where the blue stars represent monitoring wells that are continually tested for any changes in groundwater quality. In areas with reducing conditions downgradient (where pyrite as well as organic carbon are present) uranium should be precipitated as well as strongly sorbed to the organic carbon, because this is how the original uranium ore was emplaced. However, if downgradient solid-phase materials consist of sandstone with iron hydroxide coatings (no pyrite or organic carbon), sorption of uranium on iron hydroxides is most likely the controlling factor for any future mining-related uranium in groundwater. In Fig. 1, the groundwater flow during the formation of uranium ore would have been from left to right (or oxidized to reduced). A reversal in the current groundwater flow pattern would make post-recovery groundwater contact the oxidized solid phase. Such changes in groundwater flow patterns through geologic time are common at uranium ISR sites (based on the author's experience). Using different parameters, the uncertainties in uranium sorption on iron hydroxides are evaluated, because these oxidized zones could create a greater potential



Fig. 1 Generic uranium in situ recovery facility (not to scale). Blue box indicates main recovery zone and blue stars indicate groundwater monitoring wells.

for future uranium transport than fully reduced zones.

Methods

One-dimensional reactive transport simulations using PHREEQC (Parkhurst and Appelo 1999) were created to represent long-term groundwater flow away from a restored uranium ISR site (fig. 2). Each cell is 5 m with 8 cells characterizing the ISR zone (40 m) and 32 cells for the downgradient transport zone (160 m). Groundwater monitoring wells are often installed at a certain distance away from the ISR zone (fig. 2). No dispersion was included. No geochemical reactions were considered in the ISR zone; whereas, downgradient reactions included calcite equilibrium and sorption of uranium on iron hydroxides. The initial conditions used local background groundwater quality for the downgradient zone and groundwater quality in the ISR zone was the same as background except for higher concentrations of oxygen, sodium, chloride, carbon dioxide, and uranium (discussed below). All incoming groundwater during a simulation was of background groundwater quality. In these simulations, the dimensions and all the groundwater and solid-phase geochemistry are based on the proposed Dewey-Burdock uranium ISR site near Edgemont, South Dakota, USA (Powertech 2009). However, the procedures and results can be generically applied to any uranium ISR site.

Geochemical model testing included variations in (1) the geochemical database, (2) postrecovery ISR zone groundwater quality, (3) amount of iron in the downgradient solid phase, (4) downgradient calcium concentrations, and (5) post-recovery ISR zone carbon dioxide concentrations. Two different geochemical databases were used with the geochemical modeling: (1) the WATEQ4F database (Ball and Nordstrom 1991) that is provided upon downloading the PHREEQC program, and (2) a modified version of the PHREEQC database (herein referred to as the "updated database") with more recent thermodynamic data on uranium carbonate complexes (Guillaumont et al. 2003) and calcium-uranyl-carbonate/magnesium-uranyl-carbonate complexes (Dong and Brooks 2006). These updated and new complexes influence the amount of



Wolkersdorfer, Brown & Figueroa (Editors)

uranyl ion in solution that is available for sorption on iron hydroxides. The same thermodynamic data for uranium sorption on iron hydroxides is used for both databases and is based on Dzombak and Morel (1990). Differences in predicting uranium sorption on iron hydroxides were simulated using post-recovery restored groundwater (uranium = $200 \,\mu\text{g/L}$, oxygen = 8 mg/L, all other constituents = incoming groundwater) and postrecovery groundwater that was not restored (uranium = 50 mg/L, oxygen = 500 mg/L,sodium = 0.5 mol/L, and chloride = 0.5 mol/L, all other constituents = incoming groundwater). These post-recovery groundwater constituents are approximate values for simulation only and were not measured values (the Dewey-Burdock site is only proposed at this point).

The resulting patterns of uranium concentrations were very similar in the restored and unrestored scenarios with the only difference being total uranium concentrations. As a result, only the restored scenarios are presented. Solid-phase iron concentrations of 500 ppm and 2,500 ppm were evaluated based on preliminary iron extraction results from the Dewey-Burdock site. For the simulations, these Fe amounts are converted to an equivalent hydrous ferric oxide (HFO, FeOOH). Because uranium concentrations were very sensitive to the presence of calcium with the updated database, a simulation with lower calcium concentrations in the downgradient groundwater was added. Initial simulations used a calcite saturation index of 0.0 (fully saturated) and simulations with lower calcium concentrations used a calcite saturation index of -0.5 (slightly undersaturated). Background calcium concentration is 365 mg/L. The resulting calcium concentration in the downgradient zone with a saturation index of 0.0 is 387 mg/L and a saturation index of -0.5 produces a calcium concentration of 316 mg/L. In addition, a high carbon dioxide concentration with a log pCO_2 of 0.5 was compared to the natural groundwater conditions of -1.5.

Results

The resulting simulations are shown at 25 years post-restoration (figs. 3–10). The key parameter changes that are evaluated are differences in the 1) database, 2) solid-phase iron hydroxide amount, 3) calcium concentrations, and 4) carbon dioxide concentrations. Differences in the databases are critical in influencing the amount of sorption of uranium on iron hydroxides. The key addition in the updated database was the inclusion of $Ca_2UO_2(CO_3)_3^{O}$ and $CaUO_2(CO_3)_3^{2-}$ complexes based on Dong and Brooks (2006). For example, the inclusion of these calcium-uranyl-carbonate complexes makes uranium much more soluble and decreases the uranium sorption potential (figs. 3-6). A MgUO₂(CO₃)²⁻ complex from Dong and Brooks (2006) was also added, but the influence of this complex in separate simulations (not presented), given the Mg concentration that was evaluated. created a minimal influence on uranium concentrations (which may not be the case at sites with higher Mg concentrations). Simulations that used only the updated uranium carbonate complexes based on Guillaumont et al. (2003) compared to the WATEQ4F database (Ball and Nordstrom 1991) without the added calcium-uranyl-carbonate complexes, showed no difference in uranium concentrations (not presented).

For iron, a five-fold increase in iron concentrations and the updated database show a retardation in the uranium movement (figs. 3, 5), as expected. Note that the "apparent dispersion" in uranium concentrations (fig. 3) is not dispersion included in the simulations, rather it is created by the sorption/desorption of uranium to iron hydroxides through time. For either iron concentration, the WATEQ4F database shows strong sorption of uranium (figs. 3–6).

Because the updated database relies heavily on calcium-uranyl-carbonate complexes, a lower calcium concentration was tested as described in the methods section. The results (figs. 7, 8) show how sensitive the simulations are to slight changes in calcium concentra-



Fig. 3 Uranium concentrations in groundwater at 25 years with 2,500 mg/L Fe. Green line is with no sorption, blue line is with updated database and red line is with WATEQ4F database.



Fig. 5 Sorbed uranium concentrations at 25 years with 2,500 ppm Fe. Blue line is sorption with updated database and red line is with WATEQ4F database .



Fig. 7 Uranium concentrations in groundwater at 25 years with 2,500 ppm Fe. Green line is with no sorption, blue line is with updated database and calcite saturation index (SI) set to 0.0. Brown line is with updated database and calcite saturation index set to -0.5.



Fig. 4 Uranium concentrations in groundwater at 25 years with 500 ppm Fe. Green line is with no sorption, blue line is with updated database and red line is with WATEQ4F database.



Fig. 6 Sorbed uranium concentrations at 25 years with 500 ppm Fe. Blue line is sorption with updated database and red line is with WATEQ4F database.



Fig. 8 Uranium concentrations in groundwater at 25 years with 500 ppm Fe. Green line is with no sorption, blue line is with updated database and calcite saturation index (SI) set to 0.0. Brown line is with updated database and calcite saturation index set to -0.5.



Fig. 9 Uranium concentrations in groundwater at 25 years with 500 ppm Fe and CO2 in recovery zone of log pCO2 equal to 0.5 and downgradient calcite equal to 0.15 weight percent. Green line is with no sorption, blue line is with updated data-

base and red line is with WATEQ4F database.



Fig. 11 Uranium concentrations in groundwater at cell 9, the first cell downgradient from the uranium recovery zone. Simulation uses the updated database and the parameters are 500 ppm Fe, a log pCO2 in the recovery zone of 0.5, and downgradient calcite equal to 0.15 weight percent.

tions. The lower Ca concentrations produce more sorption of uranium and thus slower movement and lower of uranium concentrations in the downgradient groundwater (figs. 7, 8).

Higher carbon dioxide concentrations in the recovery zone are quite likely as CO_2 is often used in the uranium ISR process. For Fe=500 ppm and the updated database, the increased CO_2 (log $pCO_2 = 0.5$) dissolves downgradient calcite (saturation index, SI=0), keeps Ca and alkalinity in solution, and makes uranium mobile in the groundwater (fig. 9). The



Fig. 10 Uranium concentrations in groundwater at 25 years with 500 ppm Fe and CO2 in recovery zone of log pCO2 equal to 0.5 and infinite calcite. Green line is with no sorption, blue line is with updated database and red line is with WATEQ4F database.



Fig. 12 Sorbed uranium concentrations at cell 9, the first cell downgradient from the uranium recovery zone. Same simulation database and parameters as Fig. 11.

large decrease in uranium concentrations at approximately 120 to 140 m was unexpected (fig. 9). Because the calcite concentration at the Dewey-Burdock site is low (0.15 weight percent), the lowered pH created by the higher CO_2 concentration consumed all of the calcite in the first downgradient cell (cell 9). Adding an infinite amount of calcite created conservative transport conditions for uranium using the higher CO_2 scenario (fig. 10). Output from the higher CO_2 and lower calcite scenario was examined further by examining the uranium in solution and the sorbed uranium in cell 9 through time (figs. 11, 12). The abrupt decrease of uranium concentrations in cell 9 at 5 years corresponds to the time when all the calcite in that cell has been dissolved, due to the acidity produced by the additional CO₂. The resulting drop in pH increases the sorption of uranium to the iron hydroxides (fig. 12). Through time, as the background groundwater begins to enter cell 9 and the ISR zone groundwater moves downgradient, the subsequent increase in pH decreases the uranium sorption and releases uranium back into the groundwater (figs. 11, 12). It is noteworthy that as desorption occurs, uranium can reach concentrations in groundwater that are actually higher than the original post-restoration uranium concentration of 200 μ g/L (fig. 11).

Conclusions

These simulations provide insight for predicting likely downgradient uranium concentrations based on ultimate restoration goals at uranium ISR sites. However, this procedure relies on assumed amounts of iron hydroxides (based on preliminary site data) and their assumed sorption strengths (based on literature values and new information on calciumuranyl-carbonate complexes). At actual uranium ISR sites, site predictions could be improved using 1) actual groundwater quality from the post-restoration ISR zone, 2) actual downgradient mineralogy (i.e. amount of Fe and calcite), and 3) batch or column studies of true sorption potential in the downgradient zone. Without these data, the resulting uncertainty in uranium sorption is quite high, which could produce very different predictions in future mine-related uranium concentrations (figs. 3-10). In any case, the results from onedimensional reactive transport modeling provide a powerful tool for determining controlling parameters and assisting scientists in evaluating current and future site conditions. The unexpected "split plume" shown in Fig. 9 is a case where the amount of solid-phase calcite along with the updated database created unusual results. However, these results can be explained based upon further evaluation of the geochemical processes (figs. 11, 12).

Acknowledgements

The authors thank Gary Curtis, U.S. Geological Survey, Menlo Park, California, for providing the updated PHREEQC database with the latest thermodynamic data. Funding for this research was provided by the USGS Mineral Resources Program.

References

- Ball JW, Nordstrom DK (1991) WATEQ4F—User's manual with revised thermodynamic data base and test cases for calculating speciation of major, trace and redox elements in natural waters. U.S. Geological Survey Open-File Report 90–129, 185 p
- Dong W, Brooks SC (2006) Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺) using anion exchange method. Environ. Sci. Technol. 40:4689—4695
- Dzombak DA and Morel FMM (1990) Surface complexation modeling—Hydrous ferric oxide. New York, John Wiley, 393 p
- Guillaumont R, Fanghanel T, Fuger J, Grenthe I, Neck V, Palmer D, Rand MH (2003) Update on the Chemical Thermodynamics of Uranium, Neptonium, Plutonium, Americium and Technetium. Elsevier, Amsterdam
- Parkhurst DL and Appelo CAJ (1999) User's guide to PHREEQC (Version2)—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water-Resources Investigations Report 99–4259, 310 p
- Powertech (2009) Dewey-Burdock project, application for NRC uranium recovery license Fall River and Custer counties, South Dakota—Environmental report, Docket No. 040–09075, ML092870160 (http://pbadupws.nrc.gov/docs/ML0928/ML09287 0160.html)

Controls on zinc uptake from circum-neutral mine drainage in freshwater biofilms

Ashley JONES¹, Michael ROGERSON², Gillian GREENWAY³, William M. MAYES¹

¹ Centre for Environmental and Marine Sciences, University of Hull, Scarborough YO11 3AZ, UK, a.jones.hull@gmail.com
² Geography, Environment and Earth Sciences, University of Hull,Hull HU6 7RX, UK
³ Department of Chemistry, University of Hull, Hull HU6 7RX, UK

Abstract This paper presents results from in vitro flask and flume experiments using freshwater biofilms sourced and cultivated from a mine-impacted stream in North Yorkshire, UK. Flask experiments showed the rapid uptake of Zn from the water column into biofilms. This uptake was not light dependant and suggests chelation of Zn by negatively charged functional groups in extracellular polymeric substances (EPS) secreted within the biofilm are the key sink for Zn. Long term monitoring of flume systems also showed area adjusted removal rates up to 1.2 g Zn m⁻²d⁻¹ which is consistent with many other biologically-mediated treatment systems.

Keywords Mine water, Biofilm, Remediation, Zinc, Mesocosm

Introduction

Although the terms acid mine drainage (AMD) and acid rock drainage (ARD) prevail in the literature, many metal mine discharges are of circum-neutral pH owing to the buffering of acidity generated by sulphide weathering by carbonate-rich country rock. Over 6 % of rivers in England and Wales have recently been identified as having metal pollution at levels exceeding aquatic life standards due to discharges from metal mines (Mayes et al. 2009). Assessments of the pH distribution of such discharges suggest 85 % have a pH between 6 and 8, while around 5 % have pH <4 (Mayes et al. 2010; Jones et al. 2013). The most common metal pollutants in these circum-neutral discharges are Zn > Pb > Cd > Cu (Jarvis and Mayes 2012). Many researchers are currently investigating low-cost technologies to strip such mobile metals from waters, notably Zn, given its ubiquity and toxicity to aquatic life at modest concentrations (Alabaster and Lloyd 1980). These passive technologies encompass bioreactors, sorbent media as well as low-cost reactants based on recycled industrial by-products (Gandy and Jarvis 2012, Mayes et al. 2011, Warrender *et al.* 2011). While all have shown promise in various settings, the perennial ambitions to develop treatment technologies that can ally effective metal removal with low residence time, small land footprint and treatment longevity still remain elusive for many circumneutral metal mine waters.

In recent years, studies on biofilms have found they are capable of storing large inventories of trace metals (Rogerson et al. 2008). Biofilms are communities of cyanobacteria, sulphate reducing bacteria and photosynthetic diatoms, held together in a matrix of extracellular polymeric substances (EPS). The biofilm EPS is formed as a product of bacterial metabolic reactions, and although the EPS components can be highly variable dependent on what bacterial strains are present, they typically comprise of polysaccharides and proteins, nucleic acids, lipids and humic substances (Sutherland 2001). EPS molecules contain the ionisable function groups, carboxyl, phosphoric, amine and hydroxyl, all of which give the EPS a net negative charge (Hullebusche et al. 2003). This negative charge allows the EPS to sequester cationic

metals (Me²⁺) from the water column. The EPS effectively protects an ecosystem, inhabited by cyanobacteria and photosynthetic microbes, governed by processes that are independent of those occurring in the bulk water column (Bisset et al. 2008). During daylight hours photosynthetic microbes utilise carbon dioxide which increases pH, while during night time hours when respiration predominates carbon dioxide is released and thus the pH lowers. Bisset et al. (2008) observed that despite water column fluctuations in pH of between 7.8 and 8.9, the pH at the biofilm surface was 9.4 in the light and 7.8 in the dark. The implications of this internal pH change are two-fold. Internal changes in pH can result in chelated metals being released from the EPS (Hullebusch et al. 2003). However, in alkaline streams the increased pH and chelation of Ca²⁺ by the biofilm can promote carbonate precipitation within the film, a potential sink for other divalent metals (Me²⁺), and a process that would not occur otherwise by thermodynamic means alone (Rogerson et al. 2008). Recent field assessment of biofilm Zn concentrations in circum-neutral streams draining areas of former Pb and Zn mining in North Yorkshire, UK, showed median Zn concentrations of 1800 mg/L (range: 800-4100 mg/L), a bioconcentration factor of over 3500 from the water column under baseflow conditions (Jones et al. 2013). There is therefore considerable opportunity to use biofilm as a tool to remediate areas that are affected by mine drainage. However, further research is needed to elucidate the pathways for metal uptake (e.g. biomineralization versus sorption) and permanence of metal removal in biofilms. This paper aims to assess these processes through in-vitro experiments of biofilms cultured from mine-impacted streams. This serves both to improve our understanding of biolfims as a control on contaminant transport in mine-affected streams, but also to underpin approaches to harness biofilms for polishing treatment applications metal mine discharges.

Methods Batch experiments

Static batch experiments are a useful tool for answering a specific question, and were suit-

answering a specific question, and were suitable to compare the effects that separate treatments to the biofilm had on metal concentrations in solution. For each experiment using an agitated flask method, 150 mL of mine water was placed into a cleaned 250 mL conical flask with 5 g of biofilm. Biofilm was collected on the day of the experiment and transported in such a way that would avoid any denaturing of the biofilm quality. Biofilm and water was collected from Dukes Level mine discharge (Lat 54°04'43N, Long 1°57'41W), a major mine drainage level with ambient Zn concentrations of 950 μ g L⁻¹ and major ion chemistry characterised by Ca²⁺–HCO₃⁻–SO₄²⁻-dominated waters. Each experiment was left for 21 days in a controlled environment laboratory which was set up to simulate summer conditions in the UK (ambient air temperature set at 18 °C ±1 °C, with 8 hours UV light/d). Treatments were applied to the flasks to observe the different effects of photosynthesis on metal uptake. Each flask was wrapped in a material to alter the amount of UV light that passed through to the biofilm. This was done on a four treatments that ranged through full light (FL: 6.82 kLux), high light (HL: 4.83 kLux), low light (LL: 2.64 kLux) and no light (NL: 0 kLux) exposures. After the incubation period, biofilm flasks where sampled for aqueous metal concentration. A filtered (0.45µm) 14 mL sample of water was taken and acidified immediately in preparation for trace metal analysis by a Perkin Elmer OES optima 5300DV Inductively Coupled Plasma Optical Emission Spectrometer. A blank and standard suite where analysed every 15 samples to check instrument calibration, and wavelengths were selected in accordance with standard methods (USEPA Method 200.7).

Flume Experiments

Continuous flow flume experiments were adapted from previous work by Pedley *et al.* (2009), with the objective of observing long-

term cycling of biogeochemical parameters, and assessing the influences on trace metal mobility in a controlled environment. The novelty of this system is built around the culture and long term maintenance of biofilm communities collected from environmentally relevant field sites: in this case metal mine impacted streams in North Yorkshire, UK. The flume experiments had a recirculating design permitting the experiment to proceed under controlled environmental conditions with no external influence. The flume consists of a 50cm long, 7 cm wide polycarbonate gutter, lined with carbonic fabric and small rocks to aid colonisation and, given the flow rates applied, increase water turbulence throughout the vertical water column (Fig. 1). Gutter was housed in a purpose built Perspex flume box. Flow was driven by a Waston Marlow 300 series tube pump, with four 313D pump head attachments (Watson Marlow, Falmouth, UK), running at 55 rpm, through peristaltic tubing (1.6 mm wall, 4.8 mm bore). The mesocosm was subjected to a 8:16 day:night light cycle (light: Thorn Lopak 250 W HPS-T sodium lamp), in a windowless, air conditioned laboratory (ambient air temperature 18 °C \pm 1 °C).

Two flumes where colonised with biofilm (sourced as per flask experiment), and one was

sterilised before the experiment with an 10 % acid rinse (HNO₃), ethanol rinse and finally ultrapure (18 Ω) water rinse, and left uncolonised to act as control flume. Electrodes where placed in the flumes to constantly monitor pH (Pinpoint pH monitor, American Marine Inc.) and conductivity (Pinpoint Conductivity Monitor – Freshwater Hardness, American Marine Inc.). 14 mL water samples were taken every three days to establish initial trends of total metal removal in the system. Water analysis proceeded as per flask experiments. Non-parametric statistical tests were applied to discontinuous percentage data in Minitab v. 15. Geochemical analysis is undertaken using PHREEQC Interactive 2.18.3 and the WATEQ4F database

Results and discussion Batch experiments

Static batch experiments show biofilm is capable of high levels of metal uptake, with an average metal uptake of 80 %, and a maximum of 99 % removal. Control data (empty flask and water) show Zn is still being removed, most likely due to sorption onto glassware or precipitation from the water column (Fig. 2). However, the removal of Zn is significantly lower (Kruskal Wallis: H: 20.4, $d_{\rm f}$: 4, p<0.001) in con-



Fig. 1 Schematic diagram of continuous flow experimental apparatus



Fig. 2 % Zn removal in batch experiments

trol treatments (median of 36 % Zn removal) than in the biofilm occupied flasks (median 74 % Zn removal) suggesting that biofilm is responsible for the bulk of Zn removal from the water column (Fig. 2). There is no significant difference in median Zn removal rates between the light treatments and those with no light present (Kruskal Wallis: H: 6.69, d_{f} : 3, p =0.08). However, while the data suggests that metal uptake is not affected by changes in light intensity (*i.e.* metal removal continues with no light present), it is important to note the small volumes of water used and the amount of zinc in the sample vessel was finite.

Other studies have shown how divalent metal uptake into biofilms is chemoselective via chelation of divalent metals by extracellular polymeric substances (EPS); a process which usually favours ions those with a low charge density (z_i²/r_i ratios; Rogerson et al. 2008). The replenishment of EPS would require a light source in order to keep the phototrophic component of the biofilm alive and its structural integrity maintained over long periods of time. By the end of the experiment, the NL biofilm is completely degraded and is in a fine "powdery" form, whereas the biofilms FL, HL, and LL are still functioning as normal with its structural integrity maintained. The removal of Zn from the NL flask suggests it is possible that metal removal occurred before



Fig. 3 Zn removal over time in mesocosms

biofilm degradation in the NL flask. This uptake in the absence of growth is consistent with chelation of ions within the EPS matrix as opposed to direct uptake within photosynthesising organisms.

Flume experiments

The flume experiments proceeded for 66 days and Fig. 3 shows the systematic decline in dissolved Zn in the water column, with 78 % of initial Zn removed by the biofilm. The control flume (with sterilised biofilm - shown as dashed lines in Fig. 3) show initial Zn removal, which levels off after around 3 weeks. Both the active (non-sterilised) flumes (number 1 and 2) show Zn removal which continues until the end of the trial, albeit at slightly lower rates with time. These patterns are again consistent with the abiotic removal of metals from the water column by EPS in the sterilised treatments and the production of new EPS in active flumes maintaining removal over the longer term: a total of $\approx 9.5 \text{ m}^3$ of water was circulated through each flume. The abrupt spike in flume 2 after day 22 is likely to be due to entrainment of a small amount of organic debris in the sample. Observations of water pH highlight the micro-environment created by the biofilm which would be conducive to greater sorption of Me²⁺ and also potentially shift saturation of key mineral phases (notably ZnCO₃, CaCO₃ and

рН	CaCO ₃	ZnCO ₃	ZnO (a)	Table 1 Saturation indices for selected phases under different pH conditions: am- hient mine water nH hiofilm	
Mine water (7.16)	-1.03	-1.13	-2.10		
Flume (daytime: 9.18)	1.71	-1.98	0.29		
Flume (nighttime: 7.87)	0.00	-0.98	-0.16	daytime pH and biofilm	
				nighttime pH.	

amorphous Zn oxides) towards solid phase precipitation. Water pH of the original mine water ranges from 6.38 to 7.71 (mean of 7.16; n = 15), while the mean daytime pH obtained from sensors within the biofilm is 9.18 (range 7.81-9.70, n = 245). This is consistent with the observed geochemical micro-environment in other calcifying biofilm mesocosms (e.g. Bissett et al. 2008) where daytime pH values far higher than those common in the bulk water column are apparent due to photosynthetic carbon utilisation. Table 1 highlights the differences in saturation state for some relevant phases based on differences in water column and biofilm pH alone, without taking into account potential concentration of divalent metals by EPS chelation. It is apparent that the biofilm pH leads to waters supersaturated in amorphous zinc oxide and calcite, which could play a key role in direct Zn uptake, or through sorption or co-precipitation onto calcite (e.g. Zachara 1991). The differences in daytime and nighttime pH are also stark, highlighting a key potential control on diel cycling of Zn in the water column (Nimick et al. 2011).

Management implications

Previous attempts to remove Zn from mine discharges have had mixed results. The adaptation of anoxic limestone drains to encourage smithsonite (ZnCO₃) precipitation has been investigated at field scale and although showing initial promise, removal rates of 10 - 30 % were a product of the difficulty of maintaining narrow geochemical operating conditions under field conditions (Nuttall and Younger 2000). Much research effort has also gone in to developing bioreactors or sorbent-based systems for mine water removal. Although sulphate-re-

ducing bioreactors have typically been focussed on highly acidic mine waters (where alkaline media and action of sulphate reducing bacteria help buffer the pH), there have been successful applications of bioreactors for circum neutral waters. For example Gandy and Jarvis (2012) report average area-adjusted Zn removal rates of 0.4 g m⁻²day⁻¹ in pilot field systems in northern England. However, maintaining efficient flow distribution through dense reactors and concerns over the waste status of spent organic and metal-rich substrate remain issues to be overcome. Sorbents. or reactive media are another option that have been explored by many workers. Generally sorbents are capable of high metal removal rates, up to 99 % removal of zinc) which initially sounds promising, however, this level of uptake can only be maintained for small volumes of water (≈ 200 L), as functional sites for metals to sink to are saturated, the removal efficiency drops (Warrender et al. 2011). Furthermore, while modest volumetric removal rates have been maintained for reasonable timescales in field sorbent-based systems, these effects have been ascribed to the colonisation of biofilm communities on the surface of the sorbent media (e.g. Mayes et al. 2009b). The advantage of the biofilm is that it is a community of living organisms, so the EPS which they create, is constantly being replenished. This effectively means that sites for metal uptake are constantly being produced, resulting in higher efficiencies being maintained. Comparisons of preliminary data here with other mine water treatment schemes reveal similar metal removal rates in terms of area adjusted removal rates. The area adjusted removal rates rely on a calculation between residence time

(the time taken for water to flow through the flume system) and flow (L/s), which takes into account the metal load removed per unit surface area of biofilm per day (g m⁻²d⁻¹). The mean removal rates for the flumes was $0.16 \text{ gm}^{-2}\text{d}^{-1}$ (min = 0.13, max = $0.20 \text{ gm}^{-2}\text{d}^{-1}$) which was achieved with a 9.6 minute mean residence time. Pilot and field studies utilising algal mats have been seen to achieve a similar order of magnitude of Zn removal with removal rates of 0.47 g m⁻²d⁻¹ and 0.25 g m⁻²d⁻¹ respectively observed (Kalin 1998). The removal rates documented here are also well above the range of those quoted for wetland systems (*e.g.* Gillespie *et al.* 1999, Song *et al.* 2001).

Conclusions and further work

Biofilm holds the potential to be a low cost, passive remediation tool. Biofilms are ubiquitous in circum-neutral pH, metal-rich waters and play a crucial role in the diel and seasonal cycling of trace elements (e.g. Nimick et al. 2011). The laboratory studies here highlight how natural biofilm communities can be readily cultured and maintained under controlled conditions in the laboratory. Under these conditions, zinc removal was consistent and longlived; the production of EPS appears to replenish sites for metal uptake within the biofilm. Zn removal rates are consistent with many other systems, but it is the low residence time and longevity of treatment without maintenance that are most promising for developing biofilms into a treatment option. Harnessing these low-energy biological processes in remote locations, where modest Zn concentrations impact headwater streams of otherwise high amenity value, could provide a new approach in mine water treatment. Future work is concentrating on elucidating these uptake mechanisms in greater detail through a range of solid phase assessments, assessing the permanence of Zn removal, and evaluating the scope for engineering systems at full scale. The latter will also include laboratory evaluation of synthetic EPS for Zn removal. Given the evidence here suggests that the Zn uptake is only indirectly controlled by photosynthetic processes and it is the EPS production that maintains effective removal through chelation of Me²⁺, there may be considerable scope for enhancing metal removal with synthetic EPS. Determining these specific metal uptake pathways and optimal operating conditions are going to be crucial to underpin field development of effective biofilm-based treatment systems in the future.

References

- Bissett A, Reimer A, De Beer D, Shirasishi F, Arp G (2008) Metabolic microenvironmental control by
- photosynthetic biofilms under changing macroenvironmental temperature and pH conditions.Applied Environmental Micropalaeontology 74:6306 – 6312
- European Commission (2000) Directive 2000/60/EC Establishing a framework for community action in the field of water policy. ["The Water Framework Directive"]
- Gandy CJ, Jarvis AP (2012) The influence of engineering scale and environmental conditions on the performance of compost bioreactors for the remediation of zinc in mine water discharges. Mine Water and the Environment 31: 82–91.
- Gillespie WB, Hawkins WB, Rodgers JH, Cano ML, Dorn PB (1999) Transfers and transformations of zinc in flow-through wetland microcosms. Ecotoxicology and Environmental Safety 43:126–132
- van Hullebusch ED, Zandvoort MH, Lens PNL (2003) Metal immobilisation by biofilms: Mechanisms and analytical tools. Reviews in Environmental Science and Biotechnology, 2:9–33
- Jarvis AP, Mayes WM (2012) Prioritisation of abandoned non coal mine impacts on the environment SC030136/R2: the national picture. Environment Agency Report SC030136/R14
- Jones A, Rogerson M, Greenway G, Mayes, WM (2013) Mine water geochemistry and metal flux in a major historic Pb-Zn-F orefield, the Yorkshire Pennines, UK. Environmental Science and Pollution Research, accepted, in press
- Kalin M (1998) Biological polishing of zinc in a mine waste management area, in: Geller W, Klepper H, Salomons W, (Eds.), Acidic Mining Lakes: Acid Mine drainage, Limnology and Reclamation. Springer,

Heidelberg, p 321–334.

- Nimick D, Gammons CH, Parker SR (2011) Diel biogeochemical processes and their effect on the aqueous chemistry of streams: A review. Chemical Geology 283:3–17
- Nuttall CA, Younger PL (2000) Zinc removal from hard, circum-neutral mine waters using a novel closed bed limestone reactor. Water Research 34:1262–1268
- Mayes WM, Gozzard E, Potter HAB, Jarvis AP (2008) Quantifying the importance of diffuse mine water pollution in a historically heavily coal mined catchment. Environmental Pollution 151:165–175
- Mayes WM, Johnston D, Potter HAB, Jarvis AP (2009) A national strategy for identification, prioritisation and management of pollution from abandoned non-coal mine sites in England and Wales. I. Methodology development and initial results. Science of the Total Environment 407: 5435–5447
- Mayes WM, Potter HAB, Jarvis AP (2009b) Novel approach to zinc removal from circum-neutral mine waters using pelletised recovered hydrous ferric oxide. Journal of Hazardous Materials 161: 512–520
- Mayes WM, Davis J, Silva V, Jarvis AP (2011) Treatment of zinc-rich acid mine water in low residence time bioreactors incorporating waste shells and methanol dosing. Journal of Hazardous Materials 193: 279–287

Pedley M, Rogerson M, Middleton R (2009) Freshwater

calcite precipitates from in vitro mesocosm flume experiments : a case for biomediation of tufas. Sedimentology 56:511–527

- Rogerson M, Pedley M, Wadhawan JD, Middleton R (2008) New insights into biological influence on the geochemistry of freshwater carbonate deposits. Geochima et Cosmochimica Acta 72:4976–4987
- Song Y, Fitch M, Burken J, Nass L, Chilukiri S, Gale N, Ross C (2001) Lead and Zinc removal by laboratoryscale constructed wetlands. Water Environment Research 73:37 – 44
- Sutherland I (2001) Biofilm exopolysaccharides: a strong and sticky framework. Microbiology 147(Pt 1) : 3–9.
- Warrender R, Pearce NJG, Perkins WT, Florence KM, Brown AR, Sapsford DJ, Bowell RJ, Dey M (2011) Field Trials of Low-cost Reactive Media for the Passive Treatment of Circum-neutral Metal Mine Drainage in Mid-Wales, UK. Mine Water and the Environment 30:82–89
- Zachara JM, Cowan CE, Resch CT (1991) Sorption of divalent metals on calcite. Geochimica et Cosmochimica Acta 55:1549–1562.

Release of metals from unprocessed and processed black shale due to natural weathering

Lovisa Karlsson, Stefan Karlsson, Bert Allard, Viktor Sjöberg, Mattias Bäckström

Man-Technology-Environment Research Centre, Örebro University, 70182 Örebro, Sweden, bert.allard@oru.se

Abstract Black shale was mined and processed for recovery of hydrocarbons in Kvarntorp, some 200 km SW of Stockholm, Sweden, during 1942–66. Remains from the mining period is a deposit with 40 Mm³ of crushed shale residues: Unprocessed fine-grained shale as well as processed shale. The deposit is still hot; oxidation of sulphides as well as burning of hydrocarbons are still in progress some 50 years after closure. Weathering of the shale leads to releases of metal-rich leachates which will increase with time. The release of metals from pristine shale as well as weathered shale (exposed to the atmosphere for 50 years) and two different processed shale residues have been studied using water of different pH as leaching solution, to simulate extreme pH-variations in environmental waters: 3.0 (determined by oxidation of iron sulphides), 5.5 (buffered by carbon dioxide), 8.5 (buffered by calcite) and 12.5 (buffered by calcium hydroxide). Extraction of cationic elements was substantial (several percent of the total content) for Ca and Mg, as well as Ni, Co and U at pH 3, and very high (up to 50–60 %) for anionic elements (V, Mo, As) at pH 12.5. Especially the high-temperature processed shale would be a potential source for As and Mo at high pH. The pH-dependence of the weathering processes should be considered when future remediation (or metal recovery) processes and strategies are designed.

Keywords Black shale, alum shale, weathering, leaching

Introduction

Black shale (alum shale) of Late Cambrium age is abundant in southern Sweden. The shale consists of K-feldspars (3-8 %), illite (24-41 %), chlorite (1-5 %), calcite (1-4 %), quartz (18-34 %), pyrite (5–17 %), organic carbon (5–20 %), and other mineral constituents (up to 8 %) (Andersson et al. 1985). Black shale was mined and processed for recovery of hydrocarbons in Kvarntorp, 200 km SW of Stockholm (N 59°08', E 15°17') during 1942–66. Remains from this period is a deposit (height 100 m, diameter 700 m) containing some 40 Mm³ of shale residues of three categories: Unprocessed finegrained shale, black processed shale (remains after recovery of hydrocarbons by dry distillation), and red processed shale (remains after pyrolysis or incineration, largely free from organic carbon as well as sulphides). The deposit is still hot; oxidation of sulphides and burning

of hydrocarbons are still in progress 50 years after closure of all mining operations. Weathering of the shale leads to releases of metalrich leachates, however still limited since large parts of the deposit are dry. Major releases of metals can be anticipated when the deposit has cooled and is water saturated, which will happen eventually. The weathering rate will be dependent on the chemical conditions created by the water that will percolate through the deposit. Most important would be pH, determined by the weathering process itself, or buffered by some other process or by agents present, notably carbonates associated with the shale. Also the presence of complexing agents, in particular organic acids (e.q. humic/fulvic substances, microbial exudates) would be of importance for the mobilisation of metals. The purpose of the present project is to assess the extent of natural weathering of shales and shale process residues when exposed to water at various pH, representing the maximum pH-range that may be anticipated under environmental conditions (but without the presence of potentially complexing ligands).

Previous studies of the black shale and this mining area are given by Bäckström (2010), Allard *et al.* (2011) and Karlsson *et al.* 2012, as well as in the MSc-thesis by Karlsson (2013).

Materials and methods *Shale samples*

Four categories of shale residues were collected from the mining area:

- 1. Shale (S); pristine black shale, sampled from a block in the shale formation $(0.5 \times 0.1 \text{ m})$
- Weathered shale fines (WF); crushed already during the mining but deposited without processing, size <1 cm
- **3.** Red processed shale (RPS); pyrolysed (incinerated) shale
- **4.** Black processed shale (BPS); partially processed shale, remains after dry-distillation

The shale samples were dried (35 °C, 48 h), crushed and sieved, and two size fractions were selected for characterisation and for the leaching tests: 2.0-0.5 mm and <0.5 mm

Leaching tests

Batch-wise leaching tests (all four shale categories) were performed at constant L/S-ratio (10; 230 g/2.3 L) and at room temperature (ca. 20 °C) with water of different pH:

- **1.** 3.0, representing sulphide (pyrite) oxidation
- **2.** 5.5, representing carbon dioxide/water equilibrium
- **3.** 8.5, representing calcite/water equilibrium
- **4.** 12.5, representing calcium hydroxide/ water equilibrium

5. pH set by the shale itself; no pH-adjustments and no buffer added

All of the selected pH-levels are observed at the mine site: pH 2.8–3.5 in leachates from pristine shale, pH 7.5–8.5 in carbonate dominated areas, pH 12–12.5 in an area where cement residues were deposited, and pH of 5–6 in most of the other areas at the site (surface waters with dissolved atmospheric CO₂). The shallow groundwater in the area is Ca-SO₄-CO₃dominated with a pH around 8.

Adjustment of pH (with NaOH or HNO₃) was made at regular intervals, except for series (e). Samples of the aqueous phase were taken after 1 hr, representing starting conditions, 5 d, and 26 d: 40 mL of the aqueous phase was removed, centrifuged (10 000 rpm, 15 min) and analysed. Continued sampling and analysis will be made after 4 months and 20 months.

The selected L/S-ratio of 10 is high enough that no formation of sparingly soluble precipitates would be expected, except possibly after long exposure times.

Chemical analysis of leachates

Analysis of elements (ICP-MS, Agilent 7500), organic carbon (DOC, Schimadzu TOC-U; also spectrophotometry, HP 8453), sulphate (ion chromatography, Metrohm), as well as pH, were performed following standard procedures.

Characterisation of solid samples

The crushed and sieved shale samples were characterised:

- XRF (Spectro Xepos); chemical composition, major elements
- ICP-MS (after digestion); element composition
- XRD (PRO Powder, PANalytical); mineral phases

No analyses of the surface/mass ratios were made. However, the shale samples originate from the same shale horizon and are crushed and sieved to the same particle size, and no major differences in surface/mass ratios between the four materials are expected.

Results and discussion

Diffractograms (XRD) of the original samples, prior to the leaching, illustrate the presence of major minerals (fig. 1). Differences in phase composition between the materials are minor, except for S and RPS. The peaks corresponding to pyrrhotite and possibly ettringite (as well as pyrite, at 2Θ around 33° and 37°) that are present in S have disappeared in RPS, and the peaks corresponding to calcite have been reduced. XRD before and after leaching (26 d) did not differ significantly. The elemental composition of the shale, defined by the dominating minerals (*e.g.* feldspars, clays, quartz, as well as calcite, sulphides) is illustrated in fig. 2, based on elemental analysis of the solid materials (by XRF, two size fractions, and by ICP-MS, after digestion).

The four materials originate from the same shale formation, although not from identical locations. Concentrations of major elements are similar in S, WF and BPS, while the concentrations of Mg and Ca (as well as of S and P) are lower in RPS than in the others.

A summary of the concentration levels is given in table 1.



Fig. 1 Diffractograms for shale S (top) and red processed shale RPS (bottom) (2 Θ from 5 to 30°)



Wolkersdorfer, Brown & Figueroa (Editors)

"Reliable Mine Water Technology"

Conc.	Element	_
>10 %	Si, O, C	-
10 – 1 %	Al, Fe, S, K	Table 1 Concentration
1-0.1 %	Ca, Mg, Ti, P, Na	ranges (from XRF) for major
1000 – 100 mg/kg	V, Cl, Mo, Ba, Y, U, Ta, Cu, Rb	and trace elements in the
100 – 10 mg/kg	Ni, Mn, As, Ce, Pb, Sr, Ag, Co, Zn, Ga, La, Th, W	shale.

Leaching tests

The releases of some major and minor elements from the pH-controlled systems, series (a)-(d), are summarised in table 2. In series (e), the resulting pH after 26 d was 3.0, 2.8, 6.1 and 5.4 for S, WF, RPS and BPS, respectively. The element releases from S and WF in (e) and at pH 3.0 in (a) were almost identical, as well as the releases from RPS and BPS in (e) and at pH 5.5 in (b). No formation of precipitates were observed after 26 days.

Evidently there were still non-oxidized Fesulphides in WF (as well as in S) giving pH around 3, but not in RPS or BPS, as confirmed by XRD. The presence of reactive sulphides in WF that had been exposed to the atmosphere and precipitation during some 50 years was unexpected. The minor amounts of carbonates in the processed shales RPS and BPS were not sufficient for buffering pH to levels around 8.

The high releases of Ca (as well as Mg and Sr) at pH 3.0 indicate a progressive dissolution

of carbonates, when present, as well as weathering of feldspars and mica.

The release of cationic metals, originally present in the sulphide phase, was minor, except for Ni at low pH (S, BPS) and Co (S). Also the release of U was substantial at low pH. The releases of the elements V, Mo and As were high for all systems at pH 12.5, when the elements would exist predominantly as anions. This is particularly the case for the RPS-samples, where 28 %, 61 % and 55 %, respectively, of the total content were released after only 26 d.

Sulphate is the dominating anion that was released by leaching, besides carbonate. The fractions of the total sulphur content extracted after 26 d were 0.48 %, 1.2 %, 0.10 % and 2.0 % for S, WF, RPS and BPS, respectively. Besides the reduced sulphur (pyrrhotite) in both S and WF there was also sulphate (anhydrite) in all four shale categories.

Organic carbon was detected in all samples, including the pyrolysed (incinerated) RPS,

W/F RPS BPS ς pН 3.0 5.5 8.5 12.5 3.0 5.5 8.5 12.5 3.0 5.5 8.5 12.5 3.0 5.5 8.5 12.5 0.08 0.01 0.01 0.14 AI 0.65 0.14 0.01 0.64 0.42 0.02 0.01 0.02 37 0 08 0 08 2 0 1.1 0.04 0.01 0.02 0.23 0.01 0.01 0.03 0.02 0.03 0.04 0.21 0.02 < < 0.01 Fe **23 17 10** 0.11 21 20 19 16 **10** 3.9 1.0 0.37 **32 12 5.4** 0.16 Ca Mg 4.1 3.4 1.8 0.04 0.77 0.70 0.55 0.03 2.3 1.2 0.41 0.18 7.8 3. 1.7 0.09 9 0.17 0.01 < 0.69 0.02 < < 0.26 0.12 0.10 0.15 28 0.02 0.03 0.08 7.0 v 0.35 0.13 0.85 **24** 0.06 0.01 1.8 24 0.04 0.19 1.3 61 < 0.12 1. 4.1 Mo 0 0.80 0.91 0.75 1.0 1.0 1.3 0.92 1.4 0.79 0.90 0.91 1.1 12 12 13 14 Ba 0.13 0.01 0.07 0.19 4.5 0.91 0.02 0.22 1.6 0.03 0.01 0.01 2.6 0.14 0.27 0.94 ш $Cu \quad 0.32 \ 0.06 \ 0.01 \ 0.03 \quad 0.12 \ 0.01 \ 0.04 \ 0.06 \quad 0.08 \ 0.01 \ 0.02 \ 0.15 \quad 0.06 \ < \ 0.02 \ 0.32$ **14 9.6** 1.3 0.12 0.50 0.37 0.03 0.06 0.13 0.03 0.06 0.04 2.8 0. 0.05 0.08 Ni 45 0.95 0.62 0.01 0.02 5.1 0.65 0.13 0.22 15 3.8 0.70 0.13 3.2 2.7 0.92 0.04 Mn 0.21 0.08 0.01 **7.9** 0.09 0.01 0.01 1.2 0.16 0.19 0.38 55 0.03 < 0.05 4.2 As Pb 0.26 0.07 0.02 0.02 0.01 < 0.03 0.02 0.02 0.05 0.07 0.27 < < 0.02 **5.6** 4.0 2.1 0.54 **7.8** 6.9 0.88 7.6 3.0 0.47 0.39 0.50 **5.0** 1.5 0.92 0.39 Sr Co 18 13 0.72 0.44 4.4 0.38 Zn 1.0 0.64 0.07 0.05 0.31 0.06 0.04 0.07 0.34 0.05 0.05 0.07 0.31 0.04 0.02 0.03

Table 2 Percentage leached of total element content after 26 d.



Fig. 3 Absorbance spectra for WF (left) and RPS (right), (26 d, pH 12.5)

as illustrated by the absorbance spectra of the leachates at pH 12.5 after 26 d, fig. 3. This organic material corresponded to a concentration (from DOC in solution) of some 30 mg C/kg for S and 100–150 mg/kg for WE, RPS and BPS. This is largely secondary carbon from coatings of biological origin that has been accumulated during more than 50 years of exposure to precipitation and the atmosphere. The highest level was obtained for RPS which evidently creates a local regime of pH around 6, to compare with pH<3 for WF.

Conclusions

Extraction of cationic elements was substantial (several percent of the total content) for Ca and Mg, as well as for Ni, Co and U at low pH, and very high (up to 50–60 %) for anionic elements (V, Mo, As) at pH 12.5. Especially the high-temperature processed shale would be a potential As and Mo source at high pH. The pH-dependence of the weathering processes must be considered when future remediation (or metal recovery) strategies are designed.

The continued release of metals, as well as the formation of secondary minerals (and alterations of the original phase composition) will be studied in the continuation of the project (sampling and analysis after 4 months and 20 months).

Acknowledgements

The authors thank Kumla municipality for access to the Kvarntorp area for sampling.

Thanks also to B Bergström and B-N Isaksson for assistance with XRD-analyses (at Dept of Occupational Medicine, Örebro Univ. Hospital). The preparation and leaching of samples were performed at the laboratory at SAKAB AB. The project has financial support from the SAKAB Kumla Foundation for Environmental Research.

References

- Allard B, Bäckström M, Häller S, Karlsson S, Panova E, Grawunder A (2011) Water chemistry and trace metal concentrations in an acidic alum shale pit lake – effects of liming In Rüde T R, Freund A, Wolkersdorfer C (Eds). Proc. Internat. Mine Water Association Congr. IMWA 2011, Aachen, p 503–508
- Andersson A, Dahlman B, Gee DG, Snäll S (1985) The Scandinavian alum shales. Sveriges Geologiska Undersökning, SER. Ca Nr 56, Uppsala, 50 pp
- Bäckström M (2010) Environmental impact from an alum shale deposit, Kvarntorp, Sweden – present and future scenarios. In Wolkersdorfer C, Freund A (Eds). Proc. Internat. Mine Water Association Symp 2010, Sydney, p 551–554
- Karlsson L (2013) Release of metals from unprocessed and processed shale from Kvarntorp. MSc-thesis, Örebro University, 62 pp
- Karlsson L, Bäckström M, Allard B (2012) Leaching of sulfidic alum shale waste at different temperatures. In Price WA, Hogan C, Tremblay G (Eds). Proc. 9th Internat. Conf. on Acid Rock Drainage ICARD 2012, Ottawa (CD-ROM, 11 p)
A simple modeling approach for an acid generating, backfilled mine pit

Natalie A Kruse Daniels¹, Larry Breckenridge², Colin P Kruse²

¹Environmental Studies, Voinovich School of Leadership and Public Affairs, Ohio University, Athens, Ohio United States of America;

²Global Resources Engineering, Ltd., Centennial, Colorado, United States of America

Abstract Modeling post-closure mine water quality is a key step in mine planning. The Corani project is a silver-lead-zinc mining development project that currently has natural acid rock drainage (ARD) and acid mine drainage (AMD) from abandoned mines. Existing AMD has a pH as low as 2 and acidity as high as 2000 mg/L as $CaCO_3$. The mine will produce approximately 200 million tons of waste rock, some of which will be placed in the mine pit to avoid the formation of an acidic pit lake. The mine pit will be backfilled with acid-generating waste rock over five years. Following closure, the pit backfill will be rapidly flooded to mitigate ARD formation. The acid generating salts (AGS) that accumulate during operations and backfilling will be mobilized when the pit is rapidly flooded (first-flush). After saturation, a modest quantity of water (\approx 2.5 L/s) will discharge from the backfilled pit and will require treatment.

AGS will create poor water quality in the first-flush, and water flow-through will produce improving water quality over time. To simulate the behavior of the water quality over time, a PHREEQC model was created. On-site kinetic weathering tests have provided over one year of weathering data using a barrel test method. Simulated weathering rates for acid producing waste rocks were calibrated to on-site weathering tests. The backfill is modeled with a Control Volume approach, tracking the quantity of total acidity. Initial AGS is augmented by sulfide weathering under saturated conditions, and transported by groundwater flow-through. Acidity beyond saturation remains in the pit to be dissolved and transported over time. Due to the saturation and encapsulation of the waste, acidity will be transported at a higher rate than continued acid generation in the backfill.

The pit chemistry model accounts for the highly acidic first-flush and the moderately acidic long-term discharge. Since the site has uncommon climatological factors, the on-site kinetic data was key in determining appropriate rates of acid generation. The model results suggest that while the pit discharge may require long-term treatment, if the pit is filled rapidly, the period of first-flush acidity production can be minimized and water with more moderate chemistry can be treated in the long-term.

As mines search for alternative methods of waste disposal, in-pit waste dumps are becoming more common. This approach to water quality prediction applies site kinetic data with widely-accepted modeling software to estimate the discharge from a backfilled pit over time.

Keywords zinc, lead, silver, acid base accounting, PHREEQC

Holistic View of Water Affection in the Mercury Mining District of Asturias (Spain)

Jorge Loredo, Almudena Ordóñez, Rodrigo Álvarez

Oviedo School of Mines, 13 Independencia Street, 33004, Oviedo, Asturias, Spain, jloredo@uniovi.es

Abstract In this paper, a summary of hydrogeochemical data for surface and groundwater of the Asturian mercury mining district (NW Spain) is presented and discussed. Low mobility and solubility of mercury, together with the presence of arsenopyrite and arsenical pyrite in the paragenesis of the deposits has led most of the samples to exceed US EPA limits for arsenic content.

Keywords mercury mining, arsenic, sediments, surface water

Introduction

Asturias (NW Spain) is a region with a prominent mining tradition: it is considered to be the most important mercury mining district of Spain behind Almadén, which was the most significant one worldwide (Loredo *et al.* 2010). An intense mining activity was carried out during the XIX and XX centuries; during the 1970s, related with the global mercury crisis, all the mines were closed with no restoration programs. Being that so, abandoned mine facilities and spoil heaps with mine wastes as well as tailings configure the current heritage of the past mercury mining activity.

The Asturian mercury mining district is constituted by small-size hydrothermal-type cinnabar mineralizations with a common mineralogical feature: the presence of arsenopyrite and arsenical pyrite in the paragenesis (Loredo et al. 2003a; Larios et al. 2012). At the disposal sites, mineral weathering is an inevitable phenomenon that led to the release and mobilization of mercury, arsenic and related metals to the surrounding environment (e.g. surface and groundwater, soils, sediments, air). In this paper, a review of the eight main mining sites that belong to the Asturian mercury mining district is undertaken, summarizing all the available hydrogeochemical data.

Area of study

From all the mercury mineralized areas existing in the region (about 18 evidences, according to Luque and Gutiérrez-Claverol 2006), only eight sites are considered here; those which are more significant from an environmental viewpoint (all of them were included in the "Inventory and Characterization of Contaminated Soils of Asturias", Gobierno del Principado de Asturias 2002). In the most important mining sites, metallurgical activity was also conducted (see Luque and Gutiérrez-Claverol (2006) for additional information).

Six mining sites (La Peña-El Terronal, Los Rueldos, La Campa del Trave, La Soterraña, Brañalamosa and Maramuñiz, see Fig. 1) are located, from a geological viewpoint, in the Cantabrian Zone (following the traditional Iberian Massif division of Lotze 1945), specifically in the domain kwon as "Central Coal Basin" (Julivert 1971). Mercury mineralization is supposed to be related to Permian-age hydrothermalism, being sandstones the host rocks and, in a lesser extent, thin limestone levels of Carboniferous age. A more detailed description of the geological features of the mercury occurrences is presented in Ordóñez *et al.* (2013).

The two remaining mining sites (Caunedo and Olicio, see Fig. 1), also related to Permian



Fig. 1 Location of the studied mine sites within the Cantabrian Zone (1: La Peña-El Terronal; 2: Los Rueldos; 3: La Campa del Trave; 4: La Soterraña; 5: Brañalamosa; 6: Maramuñiz; 7: Caunedo; 8:Olicio).Modified from Bastida (2004).

hydrothermalism, are located in the Somiedo Unit (west part of the Cantabrian Zone) and Ponga Unit (East of the Cantabrian Zone) respectively. In the first case, the enclosing rocks are limestones and dolostones of Cambrian age, while the Olicio deposit is mainly embedded in thick Carboniferous organic-rich dark limestones.

Methods

Water

Downstream of each mine site, surface water (SW) samples from the nearest watercourse were collected. Groundwater flows across underground mining voids in a similar way to that occurring in karst aquifers: there are multiple flow paths with a wide range of hydraulic conductivity and unpredictability. For this study, groundwater was sampled at mine portals (mine drainage, MD), natural springs and man-made drills (here denominated as groundwater, GW).

Water samples were collected in plastic bottles and refrigerated until analysis. In order to preserve their physic-chemical characteristics (such as keeping metals in solution)each sample was acidified by adding two HNO₃ drops. Once filtered, both surface and groundwater samples were analyzed for Mo, Cu, Pb, Zn, Ag, Ni, Co, Mn, Fe, As, U, Au, Th, Sr, Cd, Sb, Bi, V, Ca, P, La, Cr, Mg, Ba, Ti, B, Al, Na, K, W and Tl by ICP-MSat ACME Analytical Laboratories in Vancouver (Canada). Minimum detection limit for Hg was established at 10^{-4} mg L⁻¹.The number of water samples analyzed at each mine site is presented in table 1.Surface water flow was determined when possible by means of a Hanna current meter.

Sediments

Sediment samples (here called stream sediments) were collected from the upper 20 cm in the streambed of the nearest watercourse to each mining site, within a distance of 1 km downstream from the considered mining site. About 1 kg of sediment was recovered per sample (by using a ceramic shovel). Samples were dried, sieved and analyzed by X-ray fluorescence (XRF) by means of a portable Niton XRF analyzer. The number of samples analyzed at mine each site is presented in table 2.

Results *Water*

valer nalytic

Analytical and physic-chemical results for mine drainage, surface and groundwater for each mine site are presented in table 1:

US EPA indicates that a concentration exceeding 10^{-8} mg L⁻¹ Hg in stream waters may result in chronic effects to aquatic life (USGS 2005). In respect to As, the US EPA standard is set at 0.01 mg L⁻¹ As (US EPA 2012).

	n	pl	н	EC (µS cr	n ⁻¹)	Flow (L s ⁻¹)	As (mg L	⁻¹)	Hg (µ	g L ⁻¹)
		Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
					La Pe	eña-El Terro	nal				
MD	1		3.0		4	<1	<1		1.6	<0.1	<0.1
sw	38	6.9-9.2	7.8	531-1,223	886	89-310	122	0.2-7.9	3.3		<0.1
GW	5					-	-	0.0-3.2	0.6	0.3-9.3	2.7
		La Soterraña									
sw	27	6.9-9.1	7.7	289-2,027	1,366	0.01-0.8	0.2	0.3-171	39	<0.1	<0.1
GW	4					-	-	16-475	179	1.0-14	6.1
					В	rañalamosa	I				
MD	2	7.3-8.0	7.7	239-600	420	<1	<1	0.03-1.8	0.9	<0.1	<0.1
sw	6	7.1-8.6	8.0	186-380	277	77 <10 <10 <0.001-1.9		0.5	<0.1	<0.1	
GW	6	7.3-8.0	7.6	183-617	357	-	-	<0.001-1.8	0.8	<0.1	<0.1
					I	Maramuñiz					
MD	1		8.0		352	<1	<1		0.01		0.6
SW	3	8.5-8.7	8.6	130-200	173	<10	<10	<0.001-1.9	1.0	<0.1	<0.1
					L	os Rueldos					
MD	26	1.8-7.6	3.9	4,522-6,830	5248	<1	<1	2.4-18	7.3	<0.1	<0.1
SW	38	6.9-9.7	7.9	880-1310	1152	0.1-4.1	2.9	0.06-6.0	0.4	<0.1	<0.1
GW	4					-	-	<0.001-0.02	0.01	0.6-1	0.8
						Olicio					
SW	3	8.0-8.6	8.2	300-540	443	<10	<10	< 0.001-0.03	0.02	<0.1-3	1.3
GW	2					-	-	< 0.001-0.04	0.01	0.7-0.9	0.8
						Caunedo					
MD	1		8.3		210	<1	<1		0.02		0.3
sw	4	7.9-8.4	8.0	100-340	255	<10	<10	<0.001-0.002	0.001	0.4-1.0	0.7
GW	2	8.4-8.5	8.5	250-350	300	-	-	<0.001	<0.001	0.5-0.7	0.6
					La Ca	mpa del Tr	ave				
MD	8	2.2-3.3	2.8	290-940	645	0.1-0.2	0.1			0.3-10	2.1
SW	21	2.6-8.7	6.7	160-820	380	0.1-5.0	2.2			0.2-23	2.4

Table 1 In situ measured parameters and mercury and arsenic contents in water samples (Gobierno del Principado de Asturias 2002; Loredo et al. 2003a; 2003b; 2005; 2006); MD=Mine drainage;

 SW=Surface water; GW=Groundwater.

As it can be noted from data on table 1, the highest arsenic concentration (up to 475 mg L⁻¹) of the analyzed water samples was found at La Soterraña mine site. It should be pointed out that mine drainage at La Peña-El Terronal and Los Rueldos mine sites also contain high dissolved arsenic levels, and most of the sampled waters exceed the above-cited US EPA limit. With regards to mercury, and due to its low solubility, the 2.4×10^{-3} mg L⁻¹ Hg maximum concentration recommended by the USEPA is not generally exceeded (excepting occasionally at La Soterraña, La Peña-El Terronal, La Campa del Trave and Olicio).

Taking into account the average flow of the sampled watercourses as well as their mean arsenic concentration, the average annual arsenic mass load carried to the Caudal River exceeds 12 t. Due to the high flow of this river, there is a great dilution, being arsenic undetectable in its water (Loredo *et al.* 2010). However, presumably, part of the arsenic load is retained in the river sediments, becoming a potential risk for the aquatic ecosystems.

Arsenic and mercury contents in groundwater are generally higher than those found for surface waters, probably due to infiltration of polluted leachates from wastes, both stored on surface (spoil heaps) and sub-superficially buried. On the other hand, Loredo *et al.* (2006) reported that the concentration of mercury organometallic species in mine drainage and spoil heap leachates is below 2 mg L⁻¹.

Sediments

It would be reasonable (as it was pointed out by previous studies: Gray *et al.* 2004; Gosar 2008; Gosar and Tersic 2012) to expect high

	As	Ва	Cd	Со	Cr	Cu	Fe	Hg	Ni	Pb	Sb	Zn	
	•		•	La	Peña-E	l Terro	nal (n=	43)	•		-		
Min	9		8			31	2.0	1		9	36	18	
Max	1,680		53			73	5.5	30		283	146	306	
Mean	483		18			39	2.9	16		33	75	46	
St. Dev.	320		7			9	0.7	6		41	21	46	
					La Sot	erraña	(n=41)						
Min	645	102	0.2	3	8	15	0.4	12	6	5	1.9	39	
Max	62,184	573	0.3	19	22	125	17	3,267	38	2,060	8.9	3,620	
Mean	11,310	338	0.3	11	15	49	4.1	627	22	106	5.4	475	
St. Dev.	11,577	333	0.1	11	9	23	2.7	841	22	326	4.9	713	
					Braña	lamosa	(n=4)						
Min	22	51	0.1	11	13	16	2.6	2.7	21	16	0.7	70	
Max	35	88	0.2	14	14	21	3.1	107	27	20	1.6	82	
Mean	26	75	0.2	13	13	18	2.8	51	25	19	1.0	78	
St. Dev.	6	16	0.1	1.2	0.8	2.0	0.2	44	2.7	1.6	0.4	5.7	
					Mara	muñiz	(n=3)						
Min	48	65	0.1	15	15	19	3.0	0.5	29	21	0.7	88	
Max	796	79	0.2	16	16	25	3.8	62	32	23	2.1	110	
Mean	456	74	0.1	15	15	21	3.4	23	31	22	1.3	97	
St. Dev.	379	8	0.1	0.7	0.8	3.3	0.4	34	1.7	1.2	0.7	12	
					Los Rı	leldos	(n=31)						
Min	32	29	<0.2	<1	1	13	1.4	9	1	24	780	32	Table 2 Elemental concen-
Max	46,931	42	<0.2	<1	12	195	38	1,260	9	4,032	1,254	383	trations in sediment sam-
Mean	18,229	38	<0.2	<1	8	41	13	132	5	1,101	1,076	80	nles from six mine sites (Go-
St. Dev.	14,097	5			3	36	8.9	226	2	1,153	205	68	hierne del Dringing de de
					0	icio (n=	=3)						bierno del Principado de
Min	30	23	<0.2	6.0	6.0	19	0.8	92	12	9.0	4.7	10	Asturias 2002; Loredo et al.
Max	98	39	0.2	17	9.0	47	1.4	250	35	61	11	22	2003a; 2003b; 2005; 2006).
iviean	/4	33	0.1	13	1.1	36	1.2	1/2	25	27	8.2	16	Contents in mg kg ⁻¹ , except-
St. Dev.	38	8.7	0.1	6.1	1.5	15	0.4	79	12	29	3.1	6.0	ing Fe (%).

mercury concentrations in stream sediments downstream of mine sites, usually in the form of cinnabar (USGS 2005). Results of the analyzed sediments (six mine sites: La Peña-El Terronal. Los Rueldos. La Soterraña. Brañalamosa, Maramuñiz and Olicio) are shown in table 2.

Very high arsenic concentrations have been detected at La Soterraña (up to $62,184 \text{ mg kg}^{-1}$) and Los Rueldos (up to 46,931 mg kg⁻¹), followed by La Peña-El Terronal (up to 1,680 mg kg⁻¹). Average arsenic contents are 5 (Brañalamosa) to 3,600 (Los Rueldos) times higher than normal arsenic concentrations in stream sediments for unpolluted areas (about 5 mg kg⁻¹, WHO 2001).Mercury contents are not so extreme, but very high at La Soterraña (up to $3,267 \text{ mg kg}^{-1}$), Los Rueldos (up to 1,260 mg kg⁻¹) and Olicio (up to 250 mg kg⁻¹). Average mercury contents are 16 (La Peña-El Terronal) to 600 (La Soterraña) times higher than the mean Hg content in world sediments (1 mg kg⁻¹, WHO 2001).

Conclusions

In the Asturian mercury mining district, as a consequence of past mining and metallurgical operations, there is a significant environmental impact, reflected in elevated concentrations of mercury and arsenic in mine drainage, surface and groundwater, as well as stream sediments. Although all the mines were closed about 40 years ago, this mining district has kept on releasing considerable quantities of these elements into the environment.

High metal and metalloid concentrations (especially arsenic) are found in mine drainage; spoil heap leachates in a humid environment severely affect surface and groundwater, as well as stream sediments and also aquatic ecosystems. Thus, fish consumption and water uses should be controlled, in spite of the decrease of arsenic concentrations when it is diluted in a major watercourse.

Acknowledgements

The authors thank Asturian Government and the Spanish Ministry of Economy and Competitiveness for the financial support during the last years.

References

- Bastida F (2004) Zona Cantábrica. In: Vera JA (Ed), Geología de España, SGE-IGME, p 25–49
- Gobierno del Principado de Asturias (2002) Inventario y caracterización de suelos contaminados. Technical unpublished report
- Gosar M(2008) Mercury in river sediments, floodplains and plants growing thereon in drainage area of Idrija mine, Slovenia. Polish J Environ Stud 17(2):227-236
- Gosar M, Tersic T(2012) Environmental geochemistry studies in the area of Idrija mercury mine, Slovenia. Environ Geochem Health 34:27–41
- Gray JE, Hines ME, Higueras PL, Cadatto IA, La Sorsa BK (2004) Mercury speciation and microbial transformations in mine wastes, stream sediments, and surface waters at the Almadén mining district, Spain. Environ Sci Technol 38:4285–4292
- Julivert M (1971) Decollement tectonics in the hercynian Cordillera of North West Spain. Amer Jour Sci 270(1):1-29
- Larios R, Fernández-Martínez R, Álvarez R, Rucandio I (2012) Arsenic pollution and fractionation in sediments and mine waste samples from different mine sites. Sci Total Environ 431:426–435

- Loredo J, Álvarez R, Ordóñez A (2005) Release of toxic metals and metalloids from Los Rueldos mercury mine (Asturias, Spain). Sci Tot Environ 340:247–260
- Loredo J, Ordóñez A, Álvarez R (2006) Environmental impact of toxic metals and metalloids from the Muñón Cimero mercury-mining area (Asturias, Spain). J Hazard Mater 136(3):455-467
- Loredo J, Ordóñez A, Baldo C, García-Iglesias J (2003a) Arsenic mobilization from waste piles of the El Terronal mine, (Asturias, Spain). Geochem Explor Env A 3(3):229-237
- Loredo J, Pereira A, Ordóñez A (2003b) Untreated abandoned mercury mining works in a scenic area of Asturias (Spain). Environ Int 29:481–491
- Loredo J, Petit-Dominguez MD, Ordóñez A, Galán MP, Fdez-Martínez, R, Álvarez R, Rucandio MI (2010) Surface water monitoring in the mercury mining district of Asturias (Spain). J Hazard Mater 176:323–332
- Lotze F (1945) Zur Gliederung der Varisziden der lberischen Meseta. Geotektonische Forschungen 6:78–92
- Luque C, Gutiérrez-Claverol M (2006) La minería del mercurio en Asturias; Rasgos históricos. Eujoa Artes Gráficas, Oviedo, Spain, 548 pp
- Ordóñez A, Álvarez R, Loredo J (2013) Asturian mercury mining district (Spain) and the environment: a review. Environ Sci Pollut Res (in press)
- US EPA (2012) Basic Information about the Arsenic Rule. http://water.epa.gov/lawsregs/rulesregs/ sdwa/arsenic/Basic-Information.cfm (accessed April 2013)
- USGS (2005) Environmental geochemistry of mercury mines in Alaska. Fact Sheet 94–072. http://pubs. usgs.gov/fs/fs-0072-94 (accessed April 2013)
- WHO (2001) Arsenic and arsenic compounds. Environmental Health Criteria 224. www.inchem.org/documents/ehc/ehc/ehc224.htm (accessed April 2013)

Hydrological Impact Assessment within a Natura 2000 Protection Area in Northern Scandinavia

Sarah Lyle¹, Andrew Barnes², Michael Stewart³

¹ SRK Consulting (UK) Limited, Churchill House, 17 Churchill Way, Cardiff, CF10 2HH, UK, slyle@srk.co.uk ² SRK Consulting (UK) Limited, Churchill House, 17 Churchill Way, Cardiff, CF10 2HH,, UK, abarnes@srk.co.uk³ Kaya Consulting, Conference House, 152 Morrison Street, Edinburgh, EH3 8EB, UK, michael.stewart@kayaconsulting.co.uk

Abstract Numerical groundwater models, surface water catchment models and geochemical mixing models have been developed to simulate the pre-operational, operational and post-closure groundwater system, hydrological conditions and surface water quality at a mine site in northern Scandinavia. Baseline water quality is good with the exception of one watercourse that is negatively affected by uncontrolled releases of surface water from a historical tailings pond. Generally modelling predicts limited impacts on surface water flows and water quality for most key parameters.

Keywords Hydrological impact assessment, tailings, pit lake, Natura 2000 protection area

Introduction

A hydrological impact assessment (HIA) has been undertaken for the Hannukainen iron ore-copper- gold project in northern Scandinavia (Fig. 1). There is a long history of mining in the area with the most recent activity between 1969 and 1996. Disused facilities include waste rock dumps (WRDs), open pits and a tailings pile located 11km south of the mine site that contains approximately 6.6 Mt of tailings waste from iron, copper and gold ore processing.

It is proposed that the disused open pits will be dewatered and further exploited. Waste will be streamed; potentially acid forming waste (PAF), non acid forming rock (NAF) and overburden (OB). The tailings pile will be expanded to hold about 6 Mm³ of high-sulphide (High-S) tailings, contained within a fully lined (base and sides) tailings management facility (TMF), and 43 Mm³ of low intensity magnetic separation (LIMS) tailings, deposited directly above the existing tailings. During mine operations contact water will be treated where necessary and discharged to the Muonionjoki, a large regional river, via a 15 km pipeline. The Muonionjoki forms the border between Finland and Sweden making it of interest to both national and international regulatory bodies.

Rivers in the vicinity of the site comprise a known habitat for the endangered migrating Sea Trout (Salmo truter) and are within a Natura 2000 protection area under the 1992 EU Habitats Directive. The principle receptor for the purpose of the HIA is the surface water environment. Any future mining operations must be able to demonstrate that suitable management methods can be employed to mitigate against negative impacts.

Methodology

Impact management comprises several components; baseline characterisation, impact prediction, mitigation methods, and mine design. This paper focuses on the first three components although environmental considerations were incorporated into the mine design, for example:

• WRDs are located such that all seepage from PAF material and the majority from the NAF material is captured by pit dewa-

tering during operations or the pit lakes post closure;

- Expansion of the historical tailings site has been selected in favour of constructing a new facility; and
- The water management plan avoids any discharges of surface water to minor watercourses during mining.

WQO Standards

Site-specific Water Quality Objectives (WQOs) for river water quality were developed using the ANZECC methodology (ANZECC & ARM-CANZ, 2000). 'Trigger Values' (TVs) and 'Action Values' (AVs) were derived for each chemical parameter. AVs are based on toxicological data and if exceeded there is an expectation of immediate remedial work. Under the ANZECC method exceedances of TVs should act as a warning of potential future exceedances of AVs. TVs are defined based on statistical analysis of baseline stream water quality data. However, at the project site baseline water quality is generally very good and for some larger rivers the baseline data shows limited seasonal and interannual variation resulting in a low standard deviation within the data set. Hence, in many cases TVs were significantly lower than AVs whereby a relatively small increase in baseline concentrations would result in an exceedance of a TV. Consequently, TVs were viewed as an indicator of change from baseline conditions rather than a potential risk to aquatic life.

Baseline Characterisation

Within the study area there are no long-term flow or surface water level records. Therefore baseline surface water hydrology was assessed through analysis of regional stream flow data from Finland's environmental administration OVIA database, supplemented by on-site stream flow measurements. The analysis produced estimates of annual runoff, average monthly flow conditions, low flows and wetted area for the key rivers potentially impacted by the development.

Baseline surface water quality in rivers close to the development has been charac-



Fig. 1 Proposed Hannukainen site layout

terised through a monitoring program undertaken by the mine operator since mid-2007. Generally samples have been collected five times per year; monthly in the summer months and once in the spring and autumn. Sampling is not possible during the winter due to freezing of the rivers.

There has been very limited groundwater monitoring at the existing TMF. A multi-level monitoring network was designed and installed as part of the HIA study and provided the majority of the groundwater baseline data. A more established monitoring network exists at the historical mine site with piezometers installed in both the overburden and bedrock. Regular groundwater sampling and water level monitoring began in mid-2011.

Surface Water Flow Modelling

The combined impact on river flow due to changes to baseflow and changes to surface water runoff have been estimated for both the local and regional rivers. Changes to baseflow were generated by numerical groundwater modelling. It was assumed that the lost runoff volumes to each river were proportional to the lost catchment area. The changes in catchment area were assumed to impact stream flows in open water/non-winter months (May to October) due to decreases in surface runoff.

Groundwater Modelling

Groundwater level data and mapped wetlands were used to calibrate a 3-D numerical ground-

water model of the site area, constructed using MODFLOW-2005, a block-centred, finite-difference, groundwater flow model. The model was used to characterise the hydrogeological regime, including the interaction between groundwater and surface water bodies, and to estimate a water balance for the TMF ponds under different climatic conditions. Fractured zones were represented by zones of increased hydraulic conductivity.

Geochemical Modelling

Estimates of source term chemistry at the WRDs and TMF were determined through both geochemical mass balance calculations and thermodynamic equilibrium modelling using the USGS code PhreeqC version 2 (Parkhurst and Appelo 2012). Source term solution chemistry was then mixed with baseline groundwater quality, saturated minerals were allowed to precipitate and adsorption of metals to mineral phases was permitted to predict the solution chemistry discharged to the receiving watercourse.

A conservative mass balance approach was applied to predict metals concentrations within the local receiving rivers using Gold-Sim. This method is conservative in that it does not take into account processes such as mineral saturation, pH equilibrium, atmospheric gas equilibrium or attenuation through adsorption. Due to the short residence times and relatively low concentrations in the receiving watercourses, a mass balance approach is justified because it cannot be guaranteed that equilibrium will be reached or that precipitates will form a colloidal suspended load.

Water quality in the Muonionjoki at the proposed outfall was calculated using three methods:

- Box model: At the outfall where the effluent undergoes initial dilution.
- Plume model: Close to the outfall where the effluent has formed a plume but has not fully mixed across the river. This is modelled using a 2D advection-diffusion equation; and

• Complete mixing model: At a distance from the outfall when the effluent has fully mixed with the river flows. This is modelled using a conservative dilution modelling approach.

Upon cessation of mining the pits will be artificially flooded. Modelling incorporated a coupled mass balance – thermodynamic equilibration approach in which chemical loadings from various sources including high wall runoff, WRD seepage and precipitation were mixed.

Baseline Characterisation River Network

There are marked seasonal variations in flows within rivers close to the site (Fig. 2). High flows follow snow melt in spring (May and June) and low flows occur in winter (December to April) when precipitation is held within catchments as snow and ice. These seasonal variations affect the amount of natural dilution available in the river systems through the year.

Baseline water quality in one local river, the Niesajoki, is negatively affected by uncontrolled releases of surface water from ponds at the historical tailings pile to the river. Water quality improves downstream of the TMF, as shown by the nickel concentrations presented in Fig. 3.

Groundwater

Groundwater monitoring indicates that the groundwater surface is generally 0–25m below



Fig. 2 Typical annual flow hydrograph for the site (gauge number 65761 from OIVA database)



Fig. 3 Water quality downstream of the existing TMF, fitted to a log-normal distribution. FS13=North Pond, FS14=South Pond, FS15=Niesajoki mid-point, FS16=Niesajoki close to mouth, FS12=Niesajoki at mouth

ground surface (bgs) throughout the project site, broadly following topography, and the local groundwater system discharges to the wetlands and rivers, supporting base flows to these streams (Fig. 4). Geology at the site comprises intrusive igneous rocks, metasediments and metavolcanics overlain by Quaternary age glacial deposits with a measured thickness of up to 45m. Groundwater flow in the bedrock is primarily through open, connected fractures which persist to depths of at least 250 m.

Water quality is generally good however there is evidence of impact from the existing WRD and TMF characterised by elevated concentrations of sulphate, cobalt, copper and nickel. Suppressed pH (<6.5) was observed but since pH is often naturally low in northern Scandinavia this alone does not prove existing impacts; elevated sulphate is the strongest indicator.

Assessment of Potential Impacts Construction Phase

Construction of mine facilities will include excavation of new stream diversion channels, development of water impoundment dams and construction of other infrastructure including a pipeline to the Muonionjoki. There are no planned releases to the local river network during dewatering of the existing pits and therefore there are no predicted impacts on water quality or flow. If construction works are undertaken adhering to best practise, for example effective sediment control, it is anticipated that impacts on water quality in the local rivers will not be significant.

Operational Phase

There will be small (<5 % during an average year) decreases in flows in the rivers located downstream of mining infrastructure due to a decrease in baseflow and a reduction of catchment area flowing to the rivers. However, hydraulic calculations indicated that these changes will result in a negligible change in channel wetted area; important for the maintenance of aquatic life.

During the operational phase there will be no uncontrolled releases of surface water from the TMF and river flows immediately downstream of the facility may decrease by approximately 40 %. The magnitude of flow reduction



Fig. 4 Groundwater contours at the mine site under (a) baseline and (b) life of mine conditions



Fig. 5 Baseline and life of mine (LoM) flow in the Niesajoki River, downstream of the TMF

decreases with increasing distance from the TMF (Fig. 5).

The reduction of flows from the TMF should result in a marked improvement in the quality of water in the river. Elsewhere, modelling indicates that key parameter concentrations are predicted to remain within 16 % of baseline during the spring thaw, apart from chloride. During winter months exceedances of TVs for cadmium, chromium, mercury and uranium are predicted.

Discharge to the Muonionjoki will comprise less than 1 % of the baseline river flow and is not predicted to have a significant impact on flow. Modelling indicates that there will be a dilution zone downstream of the outfall within which there is a risk of AV exceedances for some parameters. For most parameters the main impacts are during winter months (Fig. 6) when flows in the river are at their lowest. The effluent plume is predicted to have fully mixed with river water within 1-2 km of the outfall. At this point modelling predicts no exceedances of AVs. However, exceedances of TVs for cadmium, cobalt, copper, molybdenum, nickel and uranium are predicted near the end of mine life.

Closure Phase

It is predicted pit lakes may overtop once fully recovered. There is negligible impact predicted on river flow. Calculations indicate that following the first over-spill of water to the rivers, TVs are predicted to be exceeded for a number of



Fig. 6 Plume prediction model for life of mine (Year 18)

key parameters. Copper predictions are predicted to exceed AVs under some flow conditions. Steady state predictions highlight the potential for exceedances of some AVs with exceedance of TVs for the majority of key parameters.

Upon closure, seepage from the tailings will continue to report to the TMF ponds and local rivers. Ultimately, water from the South Pond will be discharged directly to the Niesajoki without treatment. River flow rates would be expected to return close to present day conditions. The water quality of the Niesajoki is predicted to deteriorate due to this release, with exceedances of TVs for a number of parameters, and the potential for exceedance of AVs for copper.

Potential Mitigation Measures Operational Phase

Generally no mitigation is required for river flows, however flows immediately downstream of the TMF could be augmented using treated mine water or diverting natural catchments surrounding the TMF. At the Muonionjoki, potential mitigation options include improvements to proposed water treatment, optimisation of the site water management plan to reduce winter discharges, and engineering of the outfall. For example, a diffuser design would enhance mixing close to the outfall.

Closure Phase

There is predicted to be both groundwater and surface water discharge from the pit lakes and TMF site following closure of the mine and modelling has demonstrated potential detrimental impacts on the surrounding watercourses. Based on the current understanding and predictions the following options are being considered as long term solutions to potential water quality issues:

- Treatment of acidity in pit lakes through alkaline amendment (such as lime, CaO) addition;
- Treatment of the pit lake and TMF water at point of discharge with passive wetland, permeable reactive barriers and active systems being considered;
- Mitigation at source, for example addition of alkaline rock amendment (limestone, CaCO₃) to the PAF WRD to attenuate acidity or installation of a low permeability, oxygen limiting cover to PAF waste to decrease metals loading to the pit lakes; and
- Amending blasting strategies to ensure that waste rock fracturing is minimised.

Equally important to impact management methods are assessment criteria to quantify the success of mitigation.

It should be noted that a number of conservative assumptions have been made during water quality predictions including full mixing of the pit lakes, no sub-surface attenuation of solutes, and the use of static "NAG" testwork for prediction of WRD seepage. It is intended that water quality predictions will be updated as new information, such as fully matured kinetic test data, becomes available. Modelling of pit lake stratification is also planned to refine the pit lake water quality prediction.

Conclusions

This paper highlights the challenges and limitations of the methods used to characterise the baseline condition at Hannukainen and predict potential impacts of mining activities. It also underlines the multidisciplinary approach that is required for a study of this kind.

Generally there are limited impacts due to the mine on surface water flows in any of the rivers located immediately downstream of mining facilities. On cessation of mining WRD seepage will continue to flow into the pit voids, forming a point source rather than an uncontrolled diffuse source of seepage. This will aid post closure mitigation and seepage control. There is predicted to be both groundwater and surface water discharge from the pit lakes, therefore it is proposed that either long term active or passive treatment of pit lake discharge should be investigated to ensure discharge limits are achieved.

Acknowledgements

The authors thank SRK Consulting (UK) Limited and Kaya Consulting for their support of this submission, and Northland Mines Oy for permission to publish the findings of the study.

References

- ANZECC & ARMCANZ, 2000. Australian and New Zealand guidelines for fresh and marine water quality. National Water Quality Management Strategy Paper No 4, volume 1. Australian and New Zealand Environment and Conservation Council & Agriculture and Resource Management Council of Australia and New Zealand, Canberra, Australia.
- EU, 1992. Council Directive 92/43/EEC of 21 May 1992 on the conservation of natural habitats and of wild fauna and flora
- Parkhurst, D.L., Appelo, C.A.J. 2012. PhreeqC Version 2– A computer program for Speciation, Batch-Reaction, One Dimensional Transport and Inverse Geochemical Calculations. US Geological Survey.

Sensitivity of Database Selection in Modeling the Transport of Uranium

John J. Mahoney

Mahoney GeochemicalConsulting,892 S. Newcombe Way, Lakewood, Colorado, 80226, USA,jmahoney@mahoneygeochem.com

Abstract Reactions defined in geochemical databases can directly influence conclusions drawn from fate and transport models. Unfortunately, many of these "off-the-shelf" databases contain numerous and significant errors. An appreciation of the historical development of these databases can help in selecting realistic values, and produce more accurate models. Recently, errors in the diffuse layer database for uranyl sorption onto ferrihydrite have been identified and corrections published; but dissemination of this information has been limited and users must make corrections themselves. Comparisons between solute transport models using the older and revised databases result in significant differences, which can affect costs and performance criteria.

Keywords Uranium surface complexation, database, PHREEQC, PHAST for Windows, transport modeling

Introduction

In the 35 years since Donald Langmuir published his summary on uranium solution mineral equilibria (Langmuir 1978) there have been numerous changes to the distribution of the dissolved species and to the surface ionization and complexation models (SICM)that describe adsorption of uranium onto mineral surfaces such as hydrous ferric oxide (HFO). These changes produce significant differences in the modeled extent of adsorption of uranium, and the predicted mobility of uranium in the subsurface. Of notable importance is that because database derived differences can change retardation factors they can also alter model estimated amounts of uranium in a system.

Corrections to the Diffuse Layer Model

It was not until 1990, when Dzombak and Morel (1990)published their database compilation on the diffuse layer model, and their values were incorporated into the MINTEQA2 database (Allison *et al.* 1990) that the surface ionization and complexation model became widely accepted as an important attenuation process. Unfortunately, and in spite of the availability of data to prepare a robust set of diffuse layer model reactions for uranium adsorption onto HFO, Dzombak and Morel did not estimate parameters from published data. Rather they proposed a Linear Free Energy Relationship (LFER) to estimate surface complexation constants for uranyl sorption. Previously, Hsi and Langmuir (1985) had prepareda triple layer model (Fig. 1), and provided laboratory measurements that could have been used to define diffuse layer model surface complexation constants for uranyl sorption, but Dzombak and Morel took an alternative approach.

When compared to experimental data, it became apparent that the values obtained from the original D&M LFER were clearly wrong (Mahoney and Jakubowski 2008). The D&M LFER overestimated sorption for uranium by a factor of about 10 for non-carbonate systems. Furthermore, the failure of the Dzombak and Morel (1990) compilation to consider uranyl hydroxide or uranyl carbonate surface complexation reactions was another shortcoming.To be fair, it was never intended that their compilation should become the industry

_	Hsi a Langr FeO∵_U2 _(U02)3(OH (U02)3(OH +_U02(C03 +_U02(C03) +_U02(C1	nd nuir M JJO ₂ ⁺² OH) ⁺ FeO ⁻) ₅ ⁺ (FeO ⁻) ₃ -) ₅ ⁺ FeOH ₂) ₂ ⁻² FeOH ₂ CO ₃) ₃ ⁻⁴	Dzombak and Morel DLM 0.2+ sites/mol Hfo_SOUO ₂ + Hfo_wOUO ₂ + Bid	Waite <i>et al.</i> DLM 0.875+ sites/mol (P_sO)_2UO_ (P_wO)_2UO_ (P_wO)_2UO_2CO_3^- (P_wO)_2UO_2CO_3^-2no endate Complexes	te:	Manoney, Cadle and Jakubowski DLM 0.2 sites/mol Hfo_sOUO2* Revised D&M K Values added Hfo_wOUO2(CO3)2 ⁻³					
1975	1980	1985	1990	1995 200 Morrison <i>et al.</i> 0.1 sites/mol SOH_UO2(OH)3 SOH_(UO2)3(OH)8 ² no electrostatic term	00 2005 Wazne <i>et al.</i> DLM 0.875 sites/mol SO_UO ₂ ⁺ SO_UO ₂ CO ₃ ⁻ SO_UO ₂ CO ₃ ⁻²³	2010 Merkel e DLt 0.2 sites Hfo_sO Hfo_wOU D&M K	2015 <i>t al.</i> VI s/mol UUO ₂ ⁺ O ₂ ⁺ Kept values	Fig. 1 . Tim changes ir			
Langmuir, 1978 Database		Grenthe 1992 OECD NEA Database	1996 Ca ⁺² - CO ₃ ⁻² - UO ₂ ⁺² Complexes	Guillaumont 2003 OECD NEA v.2 Database	adde Hfo_wUO ₂ (Ci Hfo_wOHUO ₂ (a 0 ₃) ₂ - (CO ₃) ₂ -2	complexa solution co				

History of Uranium Surface Ionization and Complexation Model Database (Hydrous Ferric Oxide)

Fig. 1. Timeline showing the changes in uranium surface complexation models and solution complexation databases.

standard for uranium sorption, but it filled a need for a set of readily useable parameters to describe sorption of many trace metals, including uranium, and was in a database that had some apparent acceptance by researchers in the USEPA's Center for Exposure Assessment Modeling.

To correct some of these oversights, other groups performed additional laboratory work and published new models. Unfortunately, these models were constructed independently from the original D&M framework, which limited their utility in complicated problems where simultaneous (competitive) adsorption reactions might be critical to a better understanding of the dominant geochemical processes. The models were specific to uranium only, and other surface complexation reactions would require different model parameters. Morrison et al. (1995) used a smaller site density than defined by Dzombak and Morel (1990), and to simplify the computational load eliminated the electrostatic terms. Waite et al. (1994) and Payne (1999) produced excellent fits to their data, but they used a different site density and changed the surface hydrolysis reactions (pK_{a1}^{int} and pK_{a2}^{int}), preventing a direct import into the previously codified compilations in MINTEQA2 and PHREEQC. Wazne (2003) used the Waite *et al.* (1994) site density, but selected a different set of surface reactions. Even more recently, Merkel *et al.* (2008) used the original Dzombak and Morel (1990) uranyl surface complexes with two reactions for uranyl carbonate surface complexes. These reactions were listed in his textbook (2nd edition), but there was no discussion or documentation about the two additional surface complexation reactions involving carbonate.

Ultimately these parameters were corrected (Fig. 2), and the results published (Mahoney *et al.* 2009). The effort used PHREEQC (Parkhurst and Appelo 1999) coupled with UCODE (Poeter *et al.* 2005); and drew data from five different research groups that represented 14 different experimental conditions and 214 different data points. The following surface complexation reactions were selected to describe uranium (as uranyl) adsorption onto HFO, based upon constants in the WATEQ4F.DAT (first value) and the updated NEA databases:

- Hfo_sOH + UO₂⁺² = Hfo_sOUO₂⁺ + H⁺ Log K₁ = 3.735, NEA = 3.792
- $Hfo_wOH + UO_2^{+2} = Hfo_wOUO_2^{+} + H^{+}$ Log K₂ = 2.534, NEA = 2.507,

- Hfo_wOH + $UO_2^{+2} + CO_3^{-2} =$ Hfo_wOUO₂CO₃⁻ + H⁺ Log K_{Hfo_wOUO2CO3}⁻ = 9.014, NEA = 9.150
- Hfo_wOH + $UO_2^{+2} + 2CO_3^{-2} =$ Hfo_wOUO_2(CO_3)_2^{-3} + H^+ Log K_{Hfo_wOUO2}(CO_3)_{2-3} = 15.24, NEA = 15.28

In addition to the uranyl adsorption reactions, two additional reactions (Appelo *et al.* 2002) were added to the database. These reactions are defined below:

- $Hfo_wOH + CO_3^{-2} + H^+ =$ $Hfo_wOCO_2^- + H2O$ $Log K_{Hfo_wOCO_2^-} = 12.78$
- $Hfo_wOH + CO_3^{-2} + 2H^+ =$ $Hfo_wOCO_2H + H2O$ $Log K_{Hfo_wOCO_2H} = 20.37$

Other Database Updates

Around the same time as the revised surface complexation constants were published, there were several papers that further demonstrated the existence of divalent uranyl carbonate complexes, specifically $CaUO_2(CO_3)_3^{-2}$, $Ca_2UO_2(CO_3)_3^{\circ}$ and $MgUO_2(CO_3)_3^{-2}$ in solution (Dong and Brooks 2006). Updating the surface complexation database with the new constants tended to increase uranyl sorption in carbonate bearing waters. Including the ternary complexes generally lessened the extent of uranyl adsorption, so in calcite bearing systems there is often some offsetting.

Impacts to Solute Transport Models

In solute transport models, surface complexation is directly related to retardation of the solute. Consequently selection of database parameters will have a profound influence on model conclusions. Fig. 3 shows the results of a series of PHREEQC calculations for various SICM parameters under different scenarios. The figure shows uranium breakthrough curves using the PHREEQC transport model. There were 20 cells in the model and 80 shifts for a total of 4 pore volumes. The calculations



Fig. 2 Comparison of Dzombak and Morel (1990) uranyl sorption model (dashed lines) onto HFO with refit model of Mahoney et al. (2009) solid lines. Diamonds represent 0.15 g/L of HFO X's represent 1.0 g/L HFO. Total U was 1.0×10^{-5} mol/kg of water.

in Fig. 3 do not include calcium, so the ternary complexes are not considered. The original Dzombak and Morel (1990) parameters overestimated uranium surface complexation in non-carbonate bearing waters, (middle of the set of curves - solid lines). For comparison, models that use only the first two revised surface complexation constants (K_1 , and K_2) were prepared (dashed lines), those models reduced the amount of surface complexation and so in this transport model they show greater mobility and less retardation. However, most groundwaters contain carbonate and all four reactions plus the complexes Hfo wOCO2⁻and Hfo wOCO₂H are required. Inclusion of the updated surface complexation constants increases the overall retardation of uranium (short dashes). The two Hfo carbonate complexes compete for sites and reduce uranyl sorption slightly.

Other model scenarios are summarized in Table 1. Both open systems with fixed partial pressures and a closed system [calcite only, no fixed $CO_2(g)$] scenario were examined; some scenarios included calcite. To estimate the sensitivity of database assumptions on mobility, additional comparisons, with and without the



Fig. 3 Solute transport models (breakthrough curves) for uranium onto HFO using different SICM models and assumptions about the presence or absence of carbonate species.

ternary complexes, were also performed. Inclusion of the ternary complexes tends to decrease the retardation factor. Notice how greatly retardation values change up and down a column, as different database assumptions are evaluated.

Changes in retardation factors can produce another unintended consequence and in certain PHREEQC based models more uranium can be added to the modeled system than may have been intended. The "-equilibrate surface with solution" option in PHREEQC will add uranium to a surface until it is equilibrated with the defined solution. A comparison of uranium transport models showed that inclusion of the newer database assumptions decreased bulk distribution coefficients by a factor of 2.5. Specifically, a three dimensional transport model run in PHAST (Parkhurst *et al.* 2010) and using the original Dzombak and Morel (1990) parameters (WATEQ4F.dat database provided with version 2 of PHREEQC) without the ternary complexes calculated a distribution coefficient of 50. The program required that the surface contain 50 ppm for every 1 ppm of uranium in solu-

MODEL	No CO ₃ -2	Fixed pH =6 CO ₂ (g) =-3.5	.0 CO ₂ (g) =-2.0	Calcite Included No fixed CO ₂ (g)CO ₂ (g) =-3.5 CO ₂ (g) =-2.0						
D&M K ₁ K ₂	8.5	8.5	7.6	2.34 (1)	2.74 (1)	1.47 (1)				
Revised $K_1 K_2$	7.6	7.6	5.7	1.56 (1)	1.18 (1)	1.1 (1)				
$K_1K_2K_3K_4$	NA (7.6)	26	32	11.76 (1.7)	12.5 (2.74)	10 (4.1)				
K ₁ K ₂ K ₃ K ₄ HFO Carbonate	NA(7.6)	26	26	10.25 (1.7)	11.1 (1.96)	5 (1.1)				

Table 1 Retardation factors for different surface complexation model assumptions for different sce-narios. Values in parentheses represent NEA database with ternaries, the pH was allowed to float inthe calcite scenarios, values were around 7.9 to 8.1.

tion. Whereas, the same model based upon the four surface complexation constants plus the updated NEA database (Grenthe *et al.* 1992, Guillaumont *et al.* 2003) with the ternary complexes produced a distribution coefficient of 18. For evaluation of performance and cleanup costs these two different starting points will greatly impact any cost estimates and feasibility evaluations.

Conclusions

The importance in selecting database parameters that represents realistic quantifiable reactions cannot be underestimated. Geochemical modelers must understand the impact that selection of such reactions can have on model conclusions. In many cases, the selection of these parameters can have a much greater impact than defining other model conditions such as carbonate minerals and the partial pressure of carbon dioxide gas. Database selection will impact conclusions from solute transport models, and potentially affect the permitting of new facilities. This historical review has shown that the extent of uranium plume migration is not always caused by the geologic setting, but in some cases by historically changing database parameters.

References

- Allison JD, Brown DS, Novo-Gradac KJ (1991) MINTEQA2/PRODEFA2, a geochemical assessment model for environmental systems, Version 3.0 User's Manual: U.S. Environmental Protection Agency Report EPA/600/3-91/021, 106 p.
- Appelo CAJ, Van der Weiden MJJ, Tournassat C, Charlet L (2002) Surface complexation of ferrous iron and carbonate on ferrihydrite and the mobilization of arsenic. Environ. Sci. Technol., 36, 3096–3103.
- Dong W, Brooks SC (2006) Determination of the formation constants of ternary complexes of uranyl and carbonate with alkaline earth metals (Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺) using anion exchange method. Environ. Sci. Technol. vol. 40, 4689–4695.
- Dzombak DA, Morel FMM (1990)Surface complexation modeling – hydrous ferric oxide: New York, John Wiley and Sons, 393 p.

- Grenthe I, Fuger J, Konings RJM, Lemire RJ, Muller AJ, Nguyen-Trung C, Wanner H (1992) Chemical Thermodynamics of Uranium. 2004 reprint available from NEA OECD. 735 p.
- Guillaumont R, Fanghanel T, Neck V, Fuger J, Palmer D, Grenthe I, Rand M H (2003) Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium; Elsevier B.V. Amsterdam.960 p.
- Hsi CKD, Langmuir D (1985) Adsorption of uranyl onto ferric oxyhydroxides: Application of the surface complexation site binding model. Geochim. Cosmochim. Acta, vol. 49, 1931–1941.
- Langmuir D (1978) Uranium solution mineral equilibria at low temperatures with applications to sedimentary ore deposits. Geochim. Cosmochim. Acta, vol. 42(6), 547–569.
- Mahoney JJ, Cadle SA, Jakubowski RT (2009) Uranyl adsorption onto hydrous ferric oxide – a re-evaluation for the diffuse layer model database. Environ. Sci. and Technol. vol. 43, no. 24, 9260–9266. DOI 10.1021/es901586w.
- Mahoney JJ, Jakubowski RT (2008) Assessment of uranyl sorption constants on ferrihydrite – Comparison of model derived constants and updates to the diffuse layer model database. in Merkel, B.J. and Hasche-Berger, A., eds., Uranium, Mining and Hydrogeology; Springer, Berlin, p.919 – 928.
- Merkel BJ, Planer-Friedrich B (2008) Groundwater Geochemistry, a practical guide to modeling of natural and contaminated aquatic systems. 2nd Ed. Nordstrom DK, Springer, Berlin, 230 p.
- Morrison SJ, Spangler RR,Tripathi VS,(1995) Adsorption of uranium(VI) on amorphous ferric oxyhydroxide at high concentrations of dissolved carbonate(IV) and sulfur(VI). J. Contam.Hydrol.17, 333–346.
- Parkhurst DL, Appelo CAJ, (1999) User's guide to PHREEQE (version 2) – a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water Resources Investigation Report 99–4259, 312 p.
- Parkhurst DL, Kipp KL, Charlton SR, (2010) PHAST Version 2—A program for simulating groundwater flow, solute transport, and multicomponent geochemical reactions: U.S. Geological Survey Techniques and Methods 6–A35, 235 p.

- Payne TE (1999) Uranium (VI) interactions with mineral surfaces: controlling factors and surface complexation modeling. Ph.D. Dissertation, University of New South Wales, Sydney, NSW.
- Poeter EP, Hill MC, Banta ER, Mehl S, Christensen S (2005) UCODE_2005 and Six Other Computer Codes for Universal Sensitivity Analysis, Calibration and Uncertainty Evaluation; Techniques and Methods 6-A11; USGS: Reston, VA, 2005.
- Waite TD, Davis JA, Payne TE, Waychunas GA, Xu N (1994) Uranium(VI) adsorption to ferrihydrite: Application of a surface complexation model. Geochim. Cosmochim. Acta,57, p. 2251–2269.
- Wazne M, Korfiatis GP, Meng X (2003) Carbonate effects on hexavalent uranium adsorption by iron oxyhydroxide. Environ. Sci. Technol., 37, 3619–3624.

Neutralized Mine Water for Irrigation - Cost and Feasibility Study

Mosidi Makgae¹, Jannie Maree², John Annandale³

 ¹Environmental Geoscience Unit, Council for Geoscience, 280 Pretoria Road, Silverton, Pretoria, 0002, South Africa, mmakgae@geoscience.org.za
 ²Tshwane University of Technology, Private Bag X680, Pretoria, 0001, South Africa, mareej@tut.ac.za
 ³ Department of Plant Production and Soil Science, University of Pretoria, Hatfield, 0002, john.annandale@up.ac.za

Abstract The gold mines in South Africa produce about 345 ML of acid mine water. The purpose of this study was to identify cost effective solutions. The short term solution requires neutralization and metal removal to avoid negative environmental and health effects. The long term solution requires that surface water would not become salty from the discharge of saline mine water. For the short term solution, limestone/lime treatment was proposed.As a long term solution it was proposed to use neutralized mine water for irrigation. The irrigation option offers the benefit that the small volume of saline mine water will be kept away from the large volume of surface water destined for domestic use and normal irrigation. Through irrigation, 80 % of the mine water will be evaporated, resulting in the precipitation of gypsum as needle crystals in the soil.

Keywords neutralised mine water, irrigation, AMD treatment, Sequence Batch Process

Introduction

South Africa is well endowed with vast mineral resources and the wealth created through mining. In some areas these impacts have resulted in severe degradation of the quality of water. Water use in South Africa is dominated by irrigation, which accounts for around 62 % of all water used in the country, with domestic and urban use (including water for industrial use supplied by water boards) accounting for 27 % and mining, large industries and power generation accounting for 8 %. Commercial forestry plantations account for a little less than 3 % of water used by reducing runoff into rivers and streams. Agricultural activities also intercept rainfall and are not included in this breakdown.

Acid mine drainage (AMD) has for many years been a major environmental challenge associated with the mining industry, especially in the Western, Central and Eastern mining basins of Gauteng Province. The Western Basin AMD decants uncontrolled at a flow rate of 10– 60 ML/d. Similar situations exist in the Central Basin and in the Eastern Basin. In the Central Basin the water was at a depth of 540 m below the decant level at the time of writing, and rising at an average daily rate of 0.7 m. It is anticipated that decanting or overflow of acid mine water, at an expected rate of 60 ML/d, may start in 2013/14. The quality of this water is also acidic and saline, similar to the AMD decanting from the Western Basin. The immediate construction of a neutralisation plant is required for removal of free acid, metals and uranium, and for partial sulphate removal.

Many activities have been carried out by research organizations and industry to find a solution to the acid mine water problem. Fullscale limestone neutralization for free acid has been implemented on the West Rand with considerable cost savings when compared to other acid neutralisation processes. Pilot studies have also been completed on desalination using chemical processes. Freeze desalination could be a cost-effective solution for brine streams. A pilot plant has been assembled and can be inspected in operation at the Soshanguve Campus of the Tshwane University of Technology (TUT).

The Expert Team of the Inter-Ministerial Committee on Acid Mine Drainage investigated the matter in 2010 and recommended specific actions to further manage and control the AMD associated with the Witwatersrand mining boom (Expert Team of the Inter-Ministerial Committee under the Coordination of the Council for Geoscience 2011), recommended that acid mine water needs to be neutralized in the short term and for the long term that options be identified to prevent salinization of surface water.

The Department of Water Affairs (DWA) has appointed the Trans-Caledon Tunnel Authority (TCTA) to be responsible for the short term solution as required by the recommendations of the Inter-Ministerial Committee on Acid Mine Water (Creamer 2012). In June 2011, after a tender process, BKS and Golder Associates were appointed to develop a short-term plan to address the immediate concerns of the AMD problem. An urgent task was to neutralise the water decanting in the Western, Central and Eastern Basins (Creamer 2012). Owing to the huge threat posed by AMD, it was decided by TCTA to employ proven technology that uses limestone treatment for neutralisation of free acid, followed by additional lime treatment for removal of iron(II) and other (semi)-metals (Van Niekerk 2011). This approach has been applied widely for treatment of AMD (Aubé 2004). This treatment process (referred to as the 'High Density Sludge (HDS)' process) consists of a pH correction/sludge conditioning stage, a neutralisation/aeration stage, and a solid/liquid separation stage (Osuchowski 1992). A due diligence study of the Witwatersrand mining basins estimated the capital cost of AMD neutralisation plants for the three basins at a total of R924 m (million). As only R255 m. was approved for this project by Cabinet (Creamer 2012), ways of making up the shortfall of R669 m. should be identified, or, alternatively, options for reducing this high capital cost need to be investigated and applied.

DWA has appointed Aurecon to investigate a long term solution. Treatment targets that are targets for treated water quality will be site-specific and depend on a number of factors, including issues relating to protection of plant and equipment from corrosion, as well as protection of environmental values of receiving waters. In contrast with water-rich mining regions, South Africa not only faces high acidity and dissolved metal problems associated with AMD. The limited dilution potential associated with low rainfall exacerbates the contribution of salinity associated with AMD to the salinization of water resources. For example, effluents from gold mines contribute about 35 % of the salt load but only 6 % of the water flow at the Barrage in the Vaal River (the major water source of the industrial heartland of South Africa).

The aims of this investigation were to demonstrate the following: (i) Alkali cost for neutralization can be reduced by 50 % by using limestone for removal of free acid, iron(II), iron(III), aluminium(III), and lime for removal of the other metals present in low concentrations. Maree et al. (2013) demonstrated that the Sequencing Batch Reactor (SBR) is an improvement on the existing limestone neutralisation technology currently employed at several mines, especially when the focus is on Fe(II)-oxidation. (ii) Irrigation of crops with neutralized mine water where mine decant water offers a sustainable and cost-effective alternative to desalination as a long term solution.

The irrigation option is attractive as the relatively small volume of neutralized mine water (200ML/d), is kept away from the far larger volume of surface water which is used for domestic purposes (Rand Water produces 4 000 ML/d) and current irrigation in this region is roughly estimated at 10 000 ML/d).

Through irrigation, depending on prevailing weather conditions, cropping system selection and irrigation management, around 80 % of the mine water can be beneficially evaporated, resulting in precipitation in the soil, of 80 % of the gypsum in solution in the neutralised water. At an estimated average irrigation rate of 750 mm/year, an area of around 3.9 × 3.9 km will be needed for irrigation of 30 ML/d, and 10 \times 10 km for 200 ML/d (areas will depend on cropping system selection). The potential for use of gypsiferous water for crop irrigation was first evaluated in South Africa by Du Plessis (1983). Jovanovic et al. (2002) investigated crop response to irrigation with gypsiferous mine water, as well as the impact on soil and groundwater resources over more than 10 years in commercial scale field trials set up at several collieries on the South African Highveld. Sugar-beans, maize, wheat, potatoes and pastures were irrigated on virgin and rehabilitated land. Good crop yields were obtained, and, based on borehole measurements, groundwater impact was limited. It was concluded that irrigation with gypsiferous mine water is feasible and worth considering as part of the solution to South Africa's AMD problems (Annandale et al. 2011). Irrigation provides some flexibility, and cropping systems and irrigation practices can be designed to optimise water use, area needed for irrigation, gypsum precipitation, profit, or job creation.

The concern that leachate will affect groundwater can be addressed by careful site selection for irrigated fields, and if necessary, the installation of a drainage system. The collected leachate is to be treated, where necessary, with RO/Freeze desalination to recover clean water and salt. Possible scaling of the pivot system will be avoided using methods such as $BaCO_3$ treatment, diluting the neutralized water with desalinated water from the freeze desalination stage, or with fresh water. The volume needed for dilution will not exceed 10 % as it is only to ensure that the water is below the saturation level of gypsum.

This process configuration offers the following benefits: (i) Low initial treatment cost of acid water, as neutralization will only cost 46 % of that of the current operation. (ii) Irrigation of mine water will result in job creation and the generation of agricultural products. The big benefit of irrigation is that it can handle large volumes of water, and if carefully designed and well managed, should be able to pay for itself. Even if irrigation is subsidized to a degree through the supply of irrigation and storage infrastructure, the supply of some farming equipment, and the pumping of water, this is likely to be a relatively small cost compared to other treatment options. (iii) No need to contaminate large volumes of clean water with neutralized, saline mine water. (iv) No waste sludge due to sludge processing into raw materials and valuable by-products. (v) Limited pollution of groundwater. In most applications the proposed irrigation will be applied in areas where groundwater is already polluted. The hydro-geological setting will determine the approach to be followed to intercept and manage the leachate from the irrigated fields (e.g. minimizing the leachate to treat through interception and evaportranspiration with trees. freeze desalination or controlled release).

Methods

The following approach was followed to determine the capital and running costs associated with neutralization, needed to protect the environment from acid mine water in the short term, and irrigation, which can avoid salinization of surface water in the long term: (i) Prepare a process configuration for each option, (ii) Determine the capital cost for each option, (iii) Determine the running costs associated with each option and (iv) Identify whether there are any shortcomings that need to be addressed prior to full-scale implementation.

Discussion

In this study a cost effective solution was proposed for the AMD problem in Gauteng, South

Africa. The solution is based on neutralization with limestone and lime for cost effective removal of acid and metals, followed by irrigation to prevent salinization of surface water with neutralized mine water.

Neutralization

The plant design for neutralization includes the following stages: SBR, Clarifier, Limestone Handling and dosing system and chemical storage facility. The SBR is equipped with a compressor and fine bubble diffuser for aeration and a draught tube to mix the slurry contained in the reactor. Mine water, sludge and limestone slurry is first pumped into the SBR to allow acid neutralization, iron(II)-oxidation and some gypsum crystallization. Upon completion of iron(II)-oxidation, lime is dosed to precipitate metals and to allow further gypsum crystallization. This approach affords a lower alkali cost as limestone (CaCO₃) is used for neutralization of free acid (H₂SO₄).With the aid of aeration, removal of iron(II) as iron(III), and aluminium(III), which form the main dissolved cations of Witwatersrand AMD. Lime is used only for removal of metals such as manganese and magnesium. Reaction rates are related to the concentrations of the various reactants; the higher the concentrations, the faster the reaction rates. Benefits of the SBR system are, direct control of effluent quality and partial desalination down to sulphate levels lower than 2000 mg/L, through gypsum crystallization.

Upon completion of the neutralization, and oxidation reactions and gypsum crystallization, the bath content of the SBR is drained into a clarifier. Limestone (precipitated calcium carbonate, or milled limestone, both with a moisture content of 25 %) is stored in a V-shaped storage and dosing facility. A water jet is used to slurry the limestone to a solids content of 20 %, and dosed into the reactor. Limestone is available from the paper industry (SAPPI) or an alternative source will be mined limestone that is milled on-site or at the mine in a wet mill. Wet milling offers the benefit that the raw material can be transported in tipper trucks and will not need to be stored in silos. The estimated capital cost of this SBR treatment system amounts to R3.5 million per ML/d treatment capacity.

Quality of treated water

Table 1 shows the chemical composition of the feed and treated water after the various stages. The TDS of the feed water decreases from 4232 to 3779 mg/L after neutralization. The gypsiferous water is thus suitable for irrigation. Irrigation in combination with freeze desalination offers the benefit that no saline rich, neutralized mine water is discharged into rivers In fact, there is a good chance that any seepage will be limited to already polluted areas to a limited extent, which may negate the need for the final desalination step. The TDS of the leachate from the irrigation is calculated to be 8 295 mg/L, based on the assumption that 80 % of the water is evaporated during utilization through irrigation. This and even higher concentrations can be treated effectively through freeze desalination, if required.

Chemical, energy and labour requirements

Table 1 shows that a dosage of 1570 mg/L CaCO₃ will be needed for removal of free acid, iron(II), iron(III) and aluminium, followed by a low dosage of 97 mg/L lime for removal of manganese and other metals. Manganese removal may not be required which will allow further savings. The neutralized water that is saturated with gypsum will not be discharged into rivers or streams. It will mostly be evaporated and beneficially utilized through irrigation. Leachate could be intercepted and treated with freeze desalination as a further option if deemed necessary. Table 1 also compares the alkali cost of the current treatment process with the proposed treatment. The current alkali cost, where limestone is used for neutralization of only the free acid, amounts to R2.42/m³ (R26.4 million/year for 30 ML/d), compared to R1.27/m3 (R13.9 million/year)

Parameter		Future						Current	
						Freeze de-			
Chemical	Western &			Irrigation	Freeze de-	salination	Western &		
feed:	Central	CaCO3	Lime	leachate	salination	brine	Central	CaCO3	Lime
Flow (ML/d)	30.0	30.00	30.00	6.00	5.70	0.30	30		
Flow (m³/h)	1 250	1 250.00	1 250.00	250		13	1 250	1 250.00	1 250.00
Dosage (100%) (mg/L)		1 570.00	96.20					853.80	626.19
Stock solution (%)		15.00	10.00					20.00	10.00
Chemical dosage (m³/h)		16.33	1.57					6.66	10.23
Purity (%)		89.00	85.00					89.00	85.00
Utilization (%)		90.00	90.00					90.00	90.00
Actual dosage (mg/L)		1 960	126					1066	819
Usage (t/d)		58.8	3.8						
Price (R/t)		500	2 300			25.00		500	2 300
Cost (R/m ⁻)		0.98	0.29			25.00		0.53	1.88
Cost (R/manth)		904 272	1.27			25.00		496 222	2.42
Cost (R/month)		894 275	1 1 5 9 1 0 4			226 125		400 525	2 204 255
Cost (R/month)		10 721 272	2 167 055			226 125		5 0 2 5 0 7 1	2 204 255
Cost (R/year)		10/312/3	12 000 270			2 7 3 7 500		3 8 3 3 8 7 1	26 451 062
Evapration (%)			13 050 520	80.00		2737500			20 451 002
Capital cost (B/(ML/d))			3 000 000	00.00	20 000 000				
Capital cost (R/ha)			5 000 000	55 000 00	20 000 000				
Capital cost (R)			90 000 000	80 300 000	120,000,000				
Total Capital Cost (R)			50000000	00000000	290 300 000				
Total Capital Cost (R/(ML/d))					9 676 667				
Irrigation (mm/year)				750.00					
Recovery (%)						95.00			
Area (km ²)				14.60					
Area (ha)				1 460.00					
Cost ratio			0.53						1.00
Cost (R/year)									
Chemical usage (t/d)		58.80	3.77					31.98	24.56
Storage (t)		1 176.03	30.00					639.55	30.00
Sludge (mg/L)		1 593.84	260.00	9 900.00		114 815.0		144.44	1 709.40
Sludge (mg/L)			1 853.84	9 900.00		114 815.01			1 853.84
CaSO4.2H2O in leachate (as C	a)		55.02	874.51		54.44			
Na2SO4 in leachate (as Na)	-,			452.82					
MgSO4 in leachate (as Mg)				750.00					
Naci in leachate (as ci) Soluble salt (t/day):				150.00					
CaSO4 in leachate				17.84					
Na2SO4 in leachate				8.39					
MgSO4 in leachate NaCl in leachate				22.28					
Total				49.99					
pН	3	6.50	8.50	8.50			3	6.50	11.20
Total Acidity	1500	0.00	0.00	0.00	0.00		1500	716.20	0.00
Iron(II)	400	0.00	0.00	0.00	0.00		400	400.00	0.00
Iron(III)	C	0.00	0.00	0.00	0.00		0	0.00	0.00
Aluminium	50	0.00	0.00	0.00	0.00		50	0.00	0.00
Manganese	56	56.00	0.00	0.00	0.00		56	56.00	0.00
Magnesium	150	150.00	150.00	750.00	75.00	13 575.00	150	150.00	150.00
Sodium	110	110.00	110.00	550.00	55.00	9 955.00	110	110.00	110.00
Sulphate	3100	2 718.16	2 622.16	5 910.79	591.08	76 205.28	3100	3 100.00	2 622.16
Chloride	30	30.00	30.00	150.00	15.00	2 715.00	30	30.00	30.00
Alkalinity	C	70.00	100.00	100.00	10.00	100.00	0	70.00	100.00
Calcium	326	794.90	806.90	874.51	87.45	2 319.58	326	667.52	806.90
Free acid	506	0.00	0.00	0.00	0.00		506	0.00	0.00
TDS (mg/L)	4 2 3 2	3 901	3 779	8 295	830	104 830	4 232	4 556	3 779
TDS (t/day)			113	49.8	4.7				
TDS precipitated (t/day)		50.07		63.6					
Cations (+) (meq/L)	65.43	58.87	57.47	129.37	12.94	1 666.09	65.43	66.83	57.47
Anions (-) (meq/L)	65.43	58.87	57.47	129.37	12.94	1 666.09	65.43	66.83	57.47
Current met (med/L)	49.13	19.13	17.13	85.64	8.56	1 550.11	49.13	33.45	17.13
Gypsum ppt (mg/L SO4)				/ 200.00					
$Gypsum(t/a CaSO_4)$				10.00					
$Gypsum(t/a/nd SU_4)$				14.05					
Sypsum (ya/na CasO4)				14.00					

Table 1 Comparison of alkali cost and salt load to surface water between current and proposed treatment options

Item	Value
Flow (ML/d)	30
Profit (R/ha)	5 000
Area (km²)	14.6
Area (ha)	1 460
Profit (R/year)	7 300 000
Profit (R/(ML/d))	243 000

 Table 2 Estimated profit from irrigation

when limestone is also used for removal of iron(II), the main dissolved component in acid mine water.

Profits to be generated from the farming activities will depend on the cropping system selected, market forces, and overheads allocated to the farming operation. Conservatively, depending on cropping system selected and market forces, a profit of around R5000/ha is quite feasible. Table 2 shows that a profit of R5000/ha amounts to an income of R7.3 million per year or R243000 per ML/d for a 30 ML/d treatment facility. The main benefit associated with irrigation, however, is that of job creation and the relative savings when compared to existing alternative desalination technologies. This makes this a viable option even if no direct farming profit is generated.

Waste products and re-use potential

The following waste products/re-usable products will be produced from 30 ML/d: (i) 55.6 t/d gypsum, Fe(OH)₃, Al(OH)₃, MnO₂ and other metal hydroxides will be produced in the neutralization stage. Initially this sludge will be stockpiled in an open pit, but later will be processed to recover metals, sulphur and CaCO₃. Pilot studies are at an advanced stage where gypsum is reduced to CaS at 1050 °C. The CaS is converted to sulphur and CaCO₃. South Africa imports 3 million t/year of sulphur at a price of R2000/t. CaCO₃ is used for neutralization of acid water and as filler in the paper and pharmaceutical industries. (ii) 59.4 t/d gypsum (14.85 t/ha per year CaSO₄) will be precipitated in the soil during irrigation. Much research has been carried out where it has been demonstrated that many crops can be produced successfully using gypsiferous water. (iii) 49.9 t/d salts will leach through the soil to already polluted groundwater, or be collected by means of a drainage system. The 49.9 t/d salts will be made up of 17.8 t/d CaSO₄, 8.4 t/d Na₂SO₄, 22.3 t/d MgSO₄ and 1.5 t/d NaCl. If the leachate is collected and processed during freeze desalination, separate recovery of the various compounds will be possible at a later stage.

Capital cost of a 30 ML/d treatment facility

The capital cost for neutralization and irrigation is estimated at R148 million (R4.9 million per ML/d) for a 30 ML/d plant (Table 3), calculated as follows: (i) R90 million for limestone/lime treatment (R3 million per ML/d) (ii) R36.5million for the centre pivots. The Fig. was calculated from: R25 000/ha; a flow of 30 ML/d; irrigation or 750 mm/year; requiring an area of 14.6 km² or about 1500 ha. (iii) R6.8 million (R0.23 million per ML/d) for storage of water for an estimated 10 day requirement, as it is not possible to irrigate responsibly at a constant rate (Table 4). (iv) R13.5 million for farming equipment and soil conservation works on newly developed irrigation fields. (v) Ro.65 million for optimization studies - this will involve soil surveys to identify irrigable soil profiles, a geo-hydrological study to determine the fate of water and any solutes leaching from irrigated fields and to propose cost effective means of intercepting this water, dam design and placement, and the determination, through agricultural modelling, of ideal cropping systems and areas required to develop under irrigation to utilize the water available. (vi) If leachate is collected via a drainage system it can be treated with freeze desalination. The capital cost of such a system is estimated at R20 million per ML/d and the running cost at R30/m³. Such a system will only be considered if it appears to be needed. (vii) R43.8 million for a leachate system (R1.5 million per ML/d). Depending on the outcome of a soil and geo-hydrological survey, a

Item	Cost
Flow (ML/d)	30
Neutralization (R)	90 000 000
Centre pivot (R)	36 500 000
Storage (R)	6 851 000
Tractors and equipment (R)	13 500 000
Security	150 000
Studies (R)	650 000
Total cost (R)	147 651 000
Total cost (R/(ML/d))	4 922 000

 Table 3 Capital cost for neutralization, irrigation

 and storage for 30 ML/d

drainage system can be installed at a cost of R30 000 to R60 000/ha, but initial indications are that this will not be necessary.

The R4.9 million per ML/d (Table 3) compares very favourably with alternative treatment options. The capital cost of neutralization combined with reverse osmosis at the eMalahleni Treatment Works amounts to R25 million per ML/d.

Due to the low concentrations of sodium and chloride in the water from the Western and Central Basins, it may not be justifiable to attempt to prevent soluble sodium and chloride from leaching back into the already polluted aquifers. This will only be a feasible option if irrigation fields are carefully sited so that leachate returns to the polluted source water. However, if leachate has to be intercepted and treated, this can and will be done with a RO/freeze desalination plant that will be designed and optimised for the volume of water that needs to be treated. This is likely to add R1.5 million per ML/d, assuming a fourfold concentration of the neutralized water through irrigation. This is still significantly more cost effective than the RO option on the whole volume of neutralised water.

Conclusions

Two conclusions can be drawn from this work: (i) Limestone (calcium carbonate) can be used for complete removal of iron(II) in an SBR system within 90 min reaction time. Subse-

Parameter	Value
Flow (ML/d)	30
Storage period (days)	10
Free volume (%)	10
Volume (m3)	330 000
Excavation cost (R/m ³)	180
Soil to remove (m3)	15 000
Excavation cost (R)	2 777 000
Engineering cost (R)	2 777 000
Plastic area required (m ²)	10 000
Plastic liner price (R/m ²)	65
Plastic line cost (R)	648 000
Construction cost (R)	648 000
Storage pond cost (R)	6 851 000
Storage pond cost (R/(ML/d))	228 000

Table 4 Cost of storage (design included) of30ML/d for a period of 10 days

quently, lime can be used for complete removal of metals. The alkali cost for treatment of AMD from the Western Basin would amount to R2.80/m³ treated in the case of limestone/lime treatment, compared to R5.83/m³ treated if lime is used for both stages. (ii) The estimated capital cost for the SBR process amounts to R3.5 million per ML/d.

Acknowledgements

This work was made possible through the support of the following institutions/people: The South African National Research Foundation, which provided funding for Tshwane University of Technology projects on neutralization and sulphate removal through their Technology and Human Resources for Industry Programme (THRIP); and Tshwane University of Technology that provided substantial financial support for the Research Programme. Thanks to Prof. Fritz Carlsson for editing the manuscript.

References

Annandale JG, Beletse YG, Stirzaker RJ, Bristow KL (2011)

Managing poor quality coal-mine water: Is irrigation part of the solution? In: Observations on Environmental Change in South Africa, Larry Zietsman, (ed.) Sun Press, 174–177.

- Aubé B (2004) The science of treating acid mine drainage and smelter effluents. www.infomine. com/publications/does/Aube.pdf. [Accessed: 16.03.2007].
- Creamer T (2012) TCTA again warns of funding shortfall for acid water projects, Mining Weekly, 19 January 2012.
- Du Plessis HM (1983) Using lime treated acid mine water for irrigation. Water Science & Techology 15, 145-154.
- Expert Team, of the Inter-Ministerial Committee, under the Coordination of the Council for Geoscience (2010). Mine water management in the Witwatersrand Goldfields, with special emphasis on acid mine drainage. Report to the Inter-Ministerial Committee on Acid Mine Drainage, 21 October.

Jovanovic NZ, Annandale JG, Claassens AS, Lorentz SA, Tanner PD, Aken ME, Godgson FDI (2002) Commercial production of crops irrigated gypsiferous mine water, Water SA, 28(4), 413–421.

- Maree JP, Louw WJ, Carlsson, FHH (2013) Neutralisation treatment of AMD at affordable cost, Water SA, 39(2), (in press).
- Osuchowski R (1992) Advanced treatment of acid mine water, Technology SA, April, 9 11.
- Van Niekerk A (2011) Personal communication, 5 July 2011, Dr André van Niekerk, Divisional Director – Water Engineering, Golder Associates Africa (Pty) Ltd, PO Box 13776, Hatfield, 0028, South Africa.

Note

As irrigation will take place over already polluted groundwater the cost of the liner could be avoided.

US\$1 = R9.19 (18 April 2013)

The role of humic substances in metal attenuation in leachates emanating from abandoned gold tailings footprints

Taimos MAVUNGANIDZE, Hlanganani TUTU

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa, hlanganani.tutu@wits.ac.za

Abstract Mine leachates from gold tailings around Johannesburg, South Africa have been documented to contain a wide variety of trace elements. Natural wetlands occurring adjacent to most of the pollution sources have helped in attenuating these pollutants. In this work, we aimed at studying the role of humic substances in metal removal in these wetlands by assessing the isolated humic fractions (namely fulvic acids, humic acids and humin) and low molecular weight organic acids (LMWOAs). Metals held within the humic fractions were determined. The findings of the study revealed that a significant proportion of the metals were associated with fulvic and humic acids. This was higher than metal concentrations found to be associated with other phases.

Keywords mine leachates, gold tailings, humic substances, wetlands, low molecular weight organic acids

Introduction

Wetlands of the Witwatersrand Basin are mainly vegetated by reeds of the type Phragmites and Typha and their partially decomposed remains form the bulk of the organic matter (inset in Fig. 1). Wetland plants, including Phragmites australis, are tolerant of more extreme chemical conditions, such as elevated metals, nutrients, and organic carbon (Peverly *et al.* 1995). The high organic content in wetlands is mainly due to the decomposition of the plant material (Garnier-Sillam *et al.* 1999). Sulphate-reducing microorganisms (SRMs) play an important part in decomposing organic matter in wetlands. Huge expanses of wetlands, occurring mainly at inlets of dams, along streams and as buffers between tailings storage facilities (TSFs) and streams and dams (Tutu *et al.* 2008) form an important component of the catchment in the study area (Fig. 1).



Fig. 1 Generic model for water pollution and distribution pathways around gold mining activities (Tutu et al. 2008) Their role as sinks and mitigation zones for metals and other pollutants emanating from gold mining activities is fairly established (Tutu 2008; McCarthy and Venter 2006; Roychoudhury and Starke 2008). However, the role played by organic moieties in these important features has not been well researched. For instance, information regarding the most influential pools of these moieties that sequester metals is not available. To this end, this study has been pursued.

Materials and methods

The study site (Fig. 2) is located in the Central Goldfield (S26°13' E028°07'). The area features a stream (the Natalspruit) draining through a wetland. The wetland is located between the stream and an abandoned tailings footprint. On the footprint used to be a mixed tailings dump (*i.e.* a sand dump and a slimes dump) which was reprocessed around 2004. Since then, it was abandoned with little or no proper management to contain pollutants emanating from it. The pond also acts as a holding sink for polluted water which gradually drains out into the wetland and stream. Sediment samples were collected from four sites on the wetland using a hand-held auger (to depths of 90 cm).

Sediment samples were collected following recommended methods in literature (Hogan and Walbridge 2007). Recommended extraction protocols for humic substances in sediment samples were followed (Swift 1996) prior to determination of fulvic acids (FAs), humic acids (HAs), humin and low molecular weight organic acids (LMWOAs). Concentra-



Fig. 2 Aerial view of the study site

tions of carbon, nitrogen, hydrogen and sulphur were determined using the CHNS analyser (LECO) while LMWOAs were analysed using an ion chromatograph (Metrohm). The sediments were also digested in acid solutions in a microwave prior to metal determination. Metals in sediments and extracts of FAs and HAs were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES).

Results and Discussion

The results for the average elemental concentrations in various phases of all sediment samples are presented in Table 1. The % values have been calculated based on total elemental concentrations in sediments.

The results show that FAs complex around 55 % of the metals while HAs complex around 30 % of the metals. FAs complex more metals than HAs due to their lower molecular weight, higher oxygen contents, number of functional group and exchange capacity (Yamamoto *et al.* 2010; Fujisawa *et al.* 2012). The extractable organic matter (FAs and HAs combined) complexed >80 % of metal ions, showing the importance of this phase in attenuating metals.

The formation and distribution of extractable organic matter is important and some of the salient features related to this are presented and discussed briefly in the following section of the results.

The results for C/N ratios in the sediments are presented in Fig. 3. The trend shows a decrease in this ratio with depth in all the sample sites.

The C/N ratio is an indication of organic matter decomposition and stabilization. Most wetland plants typically have a C/N ratio of >50 (Nair *et al.* 2001). As the plant matter decays in the soil, CO_2 is evolved while N is retained. This results in a decreasing C/N ratio and the new lower C/N ratios suggest an increasing stabilization of the HSs with soil depth.

The results for the internal oxidation rates (ω) in the profiles are presented in Fig. 4.

Element distribution	Average concentrations of selected elements / mg kg ⁻¹																											
	AI	%	Bi	%	Ca	%	Co	%	Cr	%	Cu	%	Fe	%	Mn	%	Ni	%	Pb	%	S	%	Si	%	U	%	Zn	%
FAs	536.2	31	41.87	60	454.0	49	6.68	50	7.48	55	98.2	57	5484	55	91.73	53	42.6	47	8.07	42	1.22	0.3	46.39	neg	33.80	56	116.4	49
HAs	358.2	20	18.24	26	320.2	35	4.80	36	4.68	34	50.8	30	3191	32	64.26	37	28.5	32	6.13	32	1.81	0.5	23.93	neg	17.59	29	68.15	29
HSO and other phases	865.1	49	9.98	14	149.6	16	1.82	14	1.53	11	22.2	13	1239	13	16.81	10	19.2	21	4.98	26	367.9	99	3E+05	100	9.36	15	52.25	22
Soils	1760		69.09		923.8		13.3		13.7		171.2		9914		172.8		90.3		19.18		370.9		3E+05		60.75		236.8	

FAs – fulvic acids; HAs – humic acids; HSO – humin, silica and other phases; Soils – results for total concentrations after digestion

Table 1 Average concentrations of selected elements in extractable OM and pseudo-total concentrations for selected elements in sediments

The parameter ω (the degree of internal oxidation) is closely related to oxidation and degradation reactions. It is supposed that the degradation process involves the loss of CH₃ groups and partial oxidation, thus decreasing the number and length of aliphatic chains in the humic substance. High positive values of ω indicate a high degree of internal oxidation (Dębska 1997). According to literature, the atomic ratios O/C, O/H and ω indicate the degree of maturity of HSs (Gonet *et al.* 2010). From Fig. 4, ω showed that maturity of HSs increased with sediment depth.

The maturity of the HSs can also be tracked using LMWOAs. The results for these are presented in Tables 2 and 3. Thus, the low molecular weight constituents of the extractable OM presented in Table 1 can be characterized. The trend shows a general decrease in the concentration of LMWOAs with depth. However, concentrations of succinic and citric acids increased with depth, most likely as a result of their increasing carbon content (*i.e.* more humification).

The extent of aromaticity or aliphaticity been classified in Fig. 5. The results pointed to more samples having less aromaticity. This is consistent with the trend observed in Table 1 and could suggest that more metals are held in the less aromatic phases of HSs, namely fulvic acids. Thus, these acids exert a greater influence in metal sequestration.

Conclusion

The results have pointed to the superior role that humic substances, particularly fulvic acids play in metal sequestration in wetlands. Characterisation of the HSs revealed interesting trends that relate to their evolution and resultant properties and that can be used to pre-



Fig. 3 Variation of C/N ratios with sediment profiles



Fig. 4 Variation of ω with sediment depth for Humic Substances in SSP 3.

Soil depth

(cm)

Acetic

Maleic

	Concentration of organic acids at SSP 3												
Soil depth	Acetic	Oxalic	Malonic	Citric									
(cm)													
0	46.4	2.6	nd	nd									
15	94.2	6.1	8.6	16.8									
45	64.8	66.4	26.3	34.0									
75	20.6	25.7	32.1	80.4									

 Table 2 Variation of concentration of LMWOAs
 at SSP 3

75.4 0 nd 24.7 nd 15 150.7 15.1 65.3 44.5 105.3 24.8 28.4 16.2 45 75 45.6 60.5 9.1 3.6 Table 3 Variation of concentration of LMWOAs

at SSP 4

Succunic

Concentration of organic acids at SSP 4

(mg kg⁻¹ of dry soil)

Lactic

dict the metals likely to be distributed with them. For instance, LMWOAs were determined and these interact differently with various metals. This information is important for future studies that will focus on modelling the role of HSs in metal attenuation.

Acknowledgements

The authors thank the South African National Research Foundation for funding.

References

- Dębska B (1997) The effect of green manure on the properties of soil humic acids. In: Drozd J, Gonet SS, Senesi N, Weber J (Eds), The Role of Humic Substances in the Ecosystems and in Environmental Protection, Wrocław, Poland
- Fujisawa N, Fukushima M, Yamamoto M, Iwai H, Komai T, Kawabe Y, Liu D (2012) Structural alterations of humic acid fractions in a steel slag-compost fertilizer during fertilization. J Analytical and Applied Pyrolysis 95:126–133
- Garnier-Sillam E, Hariyento S, Bourezgui Y (1999) Humic substances in peats. Analysis 27(5):405-408





Gonet SS, Dębska B, Dziamski A, Banach-Szott M, Zaujec A, Szombathová N (2010) Properties of humic acids in soils under different management regimes.

In: Advances in Natural Organic Matter and Humic Substances Research 2010 Meeting of the International Humic Substances Society, Tenerife – Canary Islands, p 253–256

- McCarthy TS, Venter J (2006) Increasing pollution levels on the Witwatersrand recorded in the peat deposits of the Klip River wetland. South African J Science 102:27–34
- Nair VD, Graetz DA, Reddy KR, Olila OG (2001) Soil development in phosphate-mined created wetlands of Florida, USA. Wetlands 21(2):232-239
- Peverly JH, Surface JM, Wang T (1995) Growth and trace metal absorption by Phragmites australis in wetlands constructed for landfill leachate treatment. Ecological Engineering 5(1):21-35
- Roychoudhury AN, Starke MF (2006) Partitioning and mobility of trace metals in the Blesbokspruit: Impact assessment of dewatering of mine waters in the East Rand, South Africa. Applied Geochemistry 21(6):1044-1063.
- Swift RS (1996) Methods of soil analysis Part 3, Ch. 35, Chemical methods. Soil Sci. Soc. Am. Book Series: 5. Soil Sci. Soc. Am. Madison, WI, 1018 pp
- Tutu H, McCarthy TS, Cukrowska EM (2008) The chemical characteristics of acid mine drainage with particular reference to sources, distribution and remediation: The Witwatersrand Basin, South Africa as a case study. Applied Geochemistry 23(12):3666-3684.
- Yamamoto M, Nishida A, Otsuka K, Komai T, Fukushima M (2010) Evaluation of the binding of iron(II) to humic substances derived from a compost sample by a colorimetric method using ferrozine. Bioresource Technology 101(12):4456-4460.

Stream sediment geochemistry of the areas impacted by mining around Emalahleni (formerly known as Witbank), South Africa: Fingerprinting AMD potential point sources

Robert Netshitungulwana¹, B. Yibas², O. Novhe³, T. Motlakeng⁴

Council for Geoscience, Environmental Geoscience Unit, 280 Pretoria Rd, Silverton, 0184, South Africa, ¹robertn@geoscience.org.za, ²byibas@geoscience.org.za, ³onovhe@geoscience.org.za, ⁴tmotlakeng@geoscience.org.za

Abstract Emalahleni is located within the province of Mpumalanga, and is where most of the coal mining activities dominate the southern part of the Olifants catchment area. This paper presents the findings of the study of the severity of the mining impacts on the water resources and the ecosystem of the areas around Emalahleni, using SXRF, ABA, ICP-MS and IC analytical techniques. Based on 39 sediments samples, four AMD hotspots areas (PCA 1 to 4) were identified and fingerprinted using the Principal Component Analysis. The main pollution point sources were the coal mines (abandoned and operating) and the ferrochrome processing plant..

Keywords Stream sediments, AMD, Principal Component Analysis, Emalahleni, South Africa

Introduction

The subject of this study is a B1 sub - catchment of the primary Olifants River catchment. The Olifants River catchment has an area of approximately 87000 km² and is located in the northern part of South Africa straddling the border with Mozambique. It is one of the most polluted catchment in South Africa because of anthropogenic activities which include, coal mining activities in Emalahleni, industrial activities such as ferrochrome processing for vanadium extraction together with agriculture. The Council for Geoscience in collaboration with the Department of Mineral Resources launched a project to investigate the severity of the mining impacts on the water resources and the ecosystem of the country, using a catchment-based approach.

Stream sediments and water samples are used in this study for identifying the potential mine polluted areas with an objective of remediation/rehabilitating the impacted areas. Stream sediment geochemistry is commonly used for mineral exploration and in assessing the environmental concern areas. This is because sediments are sink of trace metals and can also act as a source of metals depending on the change of environmental conditions. In addition, stream sediment geochemistry can be used to estimate point source of contaminants that upon being discharged to surface waters are rapidly absorbed by particulate matter, thereby escaping detection by water monitoring (Forstner 2004, Salminen et al. 2005, Segura-Munoz et al. 2006). The screening study revealed anomalous values of Fe, Mn, Cr, Pb, Zn, U and Al in sediments in B1 catchment areas A and C. which forms part of the drainage area of the Emalahleni. The sediments from the screening level study revealed the sediments had a potential to generate acid (Netshitungulwana and Yibas 2012). Chrome signatures were thought to be associated with the processing of ferrochrome in and around the Witbank and Middelburg towns (Netshitungulwana and Yibas 2012).

According to Ashton *et al.* (2001), water bodies containing high levels of sulfate, iron, aluminium, cadmium, cobalt and radioactive elements such as uranium as those identified in the Olifants River catchment suggest that



contamination could be associated with mine polluted water, especially AMD. Surplus metals that escape to the environment as a result of mining or agriculture have devastating consequences including degrading the quality of water systems, destruction of heritage sites and endangering human health. McCarthy and Pretorius (2009) raised environmental concern for the future of the Witbank Coalfield once the coal reserves have been fully exploited. To date some of the abandoned mines are flooded and leaking acid water and the rivers are loaded with toxic metals in sediments and water.

Methods

A total of 39 stream sediment and 30 water samples were collected for various analyses and tests which include SXRF in chemical composition, ICP-MS and IC analyses of metal loadings of sediments, ICP-MS and IC cations and anions, XRD and SEM for mineralogical composition and, ABA for AMD potential assessment. ABA was done only on WB's samples. For sediments metal loadings, the data were plotted to understand the stream sediment compositional variation within the catchment and its relationship with the various mining activities in the catchment. Areas of elevated concentrations of selected metals are then identified for further investigations on environmental issues.

Results and Discussion

The entry of Al, Fe, Mn, Cu, Cr, V and As of the sediment chemistry to the Principal Component Analysis (PCA) has fingerprinted and discriminated the Emalahleni areas into PCA 1 to PCA 4 (Fig. 2).



Fig. 2 Area PCA1 to PCA4 discriminated by the Principal Component Analysis, the metals entered are Al, Fe, Mn, Cu, Cr, V and As.

Area PCA 1

The 14 samples collected from this area are distributed within the Brugspruit and Blesbokspruit rivers which are both tributaries to the Klipsruit River. The upstream activities include ferrochrome processing plant and abandoned underground coal mine. Based on acid base accounting results, the majority of the samples (except WB04, WB06 and WB07) is classified as potentially acid generating (Fig. 4). The acid potential of most of the samples exceeds the neutralization potential. The acid potential (AP) ranges from 1.2 kg CaCO₃/ton to 123.7 kg CaCO₃/ton, whereas neutralization potential (NP) ranges from -15.3 kg/ton CaCO₃ to 28.1 kg CaCO₃/ton. These samples show average paste pH value of 4.86, paste EC of 2613 and 1.09 % of sulfur content. The Paste pH and the EC indicate the status of the pore water which in this area is of low quality. This observation is further

supported by the high concentration of Mn, Pb, Mg, Na, Cd and SO_4^{2-} in the water samples which exceeds the South African drinking water quality and industrial limit guidelines. This result indicates that the previous water pollution control works constructed by the Department of Water Affairs (DWA) around 2004 following the report that AMD seeps from an abandoned mine into nearby Blesbokspruit and Brugspruit streams by Bell *et al.* (2002), does not seem to improve the situation.

Blesbokspruit

Samples collected upstream on the outflow side of the constructed AMD ponds on the Blekbokspruit have paste pH ranging from 2.83 to 3.16, paste EC range from 840 to 1171, total sulfur content range from 0.35 % to 0.4 % and have acid producing potential (Fig. 4). The downstream sediments show paste pH range from 4 to 5, paste EC range from 1934 to



Fig. 3 Principal Component Analysis, the metals entered are Cr, V, As, Zn, Cu, Ni and As.

2210, and total sulfur content range from 0.04 to 2.47 %, and have acid producing potential. For the water quality, the SO₄²⁻ concentration range from 459 mg/L to 3030 mg/L, which is above South African water quality guidelines for the domestic, industrial and irrigation uses (Fig. 2). Fe, Al, Mn and Mg are above the South Africa drinking water quality guidelines. The data suggest that Blesbokspruit stream water as well as sediments are severely contaminated and has not improved since Bell et al. (2002), reported the poor water quality status of the streams. The sediments are rich in Fe, Al, Mn, Cu, As, Cd and Pd metals. The acid generating potential sediments can be attributed to AMD sources that are situated upstream as a result of runoffs of coal spoils and precipitates. The sediments either generated AMD and released metals into the stream or are in the process of generating AMD and releasing metals. The relatively low concentrations of these metals downstream may be attributed to a possible adsorption of the metals into the wetland of the Blesbokspruit.

Brugspruit

Stream sediment samples collected upstream (WB11A) and downstream (WB11B) of the Brugspruit show sulfur content of 2.24 % and 0.05 %, paste pH values of 5.82 and 5.7, paste EC values of 262 and 6620. This data clearly shows the negative impact of the mining in the area. The samples with higher sulfur content show relatively low EC, whereas the samples with low sulfur content show higher paste EC, suggesting their current state in the oxidation and metal release processes. The high EC value reflects the upstream AMD sources. The elevated concentrations of Cr, Ni, V and As in Fig. 3 can be attributed to the Bushveld PGE mining, which is represented by the Vanadium processing plant. For the Bushveld PGE material,


Fig. 4 Acid Potential (AP) vs. Neutralization Potential (NP) graph for PCA 1 area indicating areas of likely acid generation and unlikely acid generation for open system; the line 1:1 means above this acidification is likely and 2:1 line means below this acidification unlikely.

the highest Cr, Ni and V concentrations in the sediments were 978, 430, 1738 mg/kg respectively with As concentrations range from 2 to 22 mg/kg. Poor water quality marked by $SO_4^{2^-}$ level of 362 mg/L in downstream sample is above the acceptable South African drinking water and above industrial category 3 quality standards. This reveals the severity of the pollution by mining activities of the Brugspruit. The main pollution sources are probably the coal mines (abandoned or operating) and the ferrochrome processing plant.

Area PCA 2 and 4

PCA 2 area is located within the Witbank Dam and PCA 4 in the southeast of the dam. The metal loadings in the sediments are marked by high levels of Al, Mn, Fe, As, Cu and radioactivity metals such as Pb, Th and U.

The water samples (MD24, MD25, MD30, MD31 and MD34) collected from within the dam have an average pH of approximately 7.5 and the SO_4^{2-} level range from 19 to 235 mg/L, with two samples above the current South Africa water quality drinking water and industrial category 3 quality guidelines.

Brown, (1997), observed that approximately 70–80 % of the SO_4^{2-} load in the Witbank Dam catchment emanates from diffuse sources and can be attributed to coal mining. This increase in diffuse pollution has resulted

in a gradual decline in water quality in the Witbank Dam catchment. Water quality in the dam itself has declined from 50 mg/L SO_4^{2-} and 100 mg/L TDS in 1997 to over 150 mg/L SO_4^{2-} and 400 mg/L TDS to date. The dam does not show any signs of improvement since 1997. The TDS value (calculated from the EC) from the 5 samples in the dam range from 438 mg/L to 540 mg/L, showing no signs of improvement since 1997. Pollution in the Witbank Dam emanate from the nearby coal mines (*e.g.* Area discriminated as PCA4), since SO_4^{2-} is a good indicator of salinity arising from this form of pollution.

Area PCA 3

PCA3 is an area downstream of the Witbank Dam (MD47, MD48 and MD49). The metal loadings on the sediments include Fe, Al, Mn, As, Cr, Cu and Mg. The water samples have SO_4^{2-} concentration range from 242 mg/L to 860 mg/L, which were found above the South African water quality drinking (MD47 and MD48) and industrial (MD49) guidelines. The metals of Mg, Mn, Pb, F, Cu, and Ca in the area were also found above the South African drinking aquatic ecosystem and industrial limit guidelines. The main pollution source in the area may be attributed to the coal mines upstream, and probably the coal mines west of the PCA3.

Conclusions

The use of stream sediment and water chemistry (ICP-MS, IC and ABA) of samples collected systematically upstream and downstream of potential pollution source mine infrastructures and metallurgical plants is found to be a useful tool to fingerprint and quantify the severity of pollution impacts. In this study, a pollution resulting from the coal mines and ferrochrome processing plants is clearly and characterised. Four impacted areas (hot spots) have been identified around Emalahleni area. The approach adopted herein suggests that the stream sediment chemical data can be accredited in characterising or fingerprinting impacted areas to an extent that liability in future can be apportioned. The main pollution point sources were the coal mines (abandoned or operating) and the ferrochrome processing plant located around the Emalahleni areas. For the affected areas, the SO₄²⁻ level exceeds that of the South Africa industrial and domestic water quality guideline, whereas Mg, Mn, Pb, F, Cu, and Ca were also found exceeding the aquatic ecosystem guideline.

Acknowledgements

The financial support provided by the Department of Mineral Resources, South Africa. We also like to thank the following sampling team, for their hard work during the early stages of this work: Mrs. M. Modiba, Mrs. M. Mdumela, Mr R. Lusunzi, Mr A. van Averbeke, Mrs. B. Mahlase, Mr G. Sandane, Mr J. S. Radebe, Mr M. E Nkosi, Mr J. Mathebula, Mr I. Phahlane and Mr K. Madikizela.

References

Ashton P, Love D, Mahachi H, Dirks P (2001) An overview of the impact of mining and mineral processing operations on water resources and water quality in the Zambezi, Limpopo and Olifants catchments in southern Africa, Contract Report of the Mining, Minerals and Sustainable Development (SOUTHERN AFRICA) Project, by CSIREnvironmentek, Pretoria, South Africa and Geology Department, University of Zimbabwe, Harare, Zimbabwe. Report No. ENV-P-C 2001–042. Xvi + 336 pp

- Bell FG, Bullock SET, Hälbich TFJ, Lindsay P (2001) Environmental impacts associated with an abandoned mine in the Witbank Coalfield, South Africa. International Journal of Coal Geology, Vol 45, 195–217
- Brown SAP (1997) The Witbank Dam catchment. In: Helmer R, Hespanhol (Eds), 1997 Water pollution control – A guide to the use of Water Quality Management Principles, United Nations Environment Program (UNEP), Case Study V.
- Forstner U (2004) Traceability of sediments analysis. Trends Analytical Chemistry 23 (3): 217–236.
- McCarthy TS, Pretorius K (2009) Coal mining on the Highveld and its implications for future water quality in the Vaal River system. International Mine Water Conference 19th – 23rd October 2009. Proceedings ISBN Number: 978-0-9802623-5-3 Pretoria, South Africa.
- Netshitungulwana R and Yibas B (2012) Stream sediment geochemistry of the Olifants catchment, South Africa: Implication for acid mine drainage. In: McCullough CD, Lund MA, Wyse L, 2012 International Mine Water Association Symposium, Bunbury, Western Australia, 257–264
- Salminen R, Batista MJ, Bidovec M, Demetriades A, De Vivo B, De Vos W, Duris M, Gilucis A, Gregorauskiene V, Halamic J, Heitzmann P, Lima A, Jordan G, Klaver G, Klein P, Lis J, Locutura J, Marsina K, Mazreku A, O'-Connor PJ, Olsson S, Ottesen RT, Petersell V, Plant JA, Reeder S, Salpeteur I, Sandström H, Siewers U, Steenfeldt A, Tarvainen T (2005) FOREGS Geochemical Atlas of Europe, Part 1 – Background information, methodology and maps. Geological Survey of Finland, Espoo, 525 pp. Also available at www.gtk.fi/ publ/foregsatlas/.
- Segura-Munoz SI, Adasilva Oliviery M, Nikaido T, Trelliato MB, Bocio A, Takayanagui AMA, Damingo JL (2006) Metals levels in sugarcane samples from an area under the influence of a municipal landfill and a medical waste treatment system in Brazil. Environmental International 32: 52–57

Use of an integrated source-to-receptor model to facilitate rapid assessment of water quality impacts during mine planning

Tina PINT, Peter HINCK

¹Barr Engineering Company, 4700 W. 77th Street, Minneapolis, Minnesota, USA, tpint@barr.com, phinck@barr.com

Abstract An integrated source-to-receptor model for assessing potential project-wide water impacts can save time and money by facilitating rapid evaluation of multiple design options. The proposed NorthMet Mine in northern Minnesota is presented as a case study for the benefit of using this approach. This modern mining operation will include a complex water management strategy designed to minimize potential impacts and make the mine more sustainable. An integrated source-to-receptor model was constructed for the mine site and used to evaluate various mine closure options during the mine planning process.

Keywords integrated mine water management, mine closure, water quality, predictions, Gold-Sim

Introduction

Mine water management is becoming more important as water quality regulations become increasingly stringent and water becomes increasingly scarce. Water plays an important role in most mining and extractive processes; it is used in mineral processing, for transportation of tailings or ore as slurry, for cooling, and for dust control (Nalecki and Gowan 2008). Water is also one of the primary mechanisms for transporting solutes from mine facilities to the environment. Defining and understanding how water is managed is critical during mine planning, operations, and reclamation.

In addition to the environmental aspects of water management, there are also economic incentives for mines to achieve a sustainable water balance. Operators need to insure that there is enough water for mineral processing throughout the year (including dry periods or times when water is frozen), yet having excess water can result in the need for additional treatment to minimize environmental impacts. Recycling water between various mine processes can minimize withdrawals and discharges, but complicate water management requirements. The combination of environmental, economic, social and engineering factors have resulted in increasingly complex mine water management strategies.

It has long been recognized that life-ofmine water management strategies should be considered in the mine planning process. Advanced planning for integrated mine water management can prevent expensive reclamation solutions (Sawatsky et al. 1998), and the use of predictive models to assess mine closure options is consistent with guidance for developing environmentally sound management plans (Eary et al. 2008). However, during the mine planning process, the water management strategy is often in flux. The potential for unacceptable water quantity or water quality impacts can drive changes in the mine plan to reduce potential water quality impacts or provide water treatment. As a result, the prediction of potential water quality impacts during mine planning is typically iterative and designed to explore the costs and effectiveness of various mitigation or treatment options. Having an integrated source-to-receptor water model during the mine planning process allows for the rapid assessment of mine plan

changes to the project-wide water balance and potential impacts to the environment. In addition, use of an integrated model reduces the risk of continuity (water and mass balance) errors compared to the typical compartmentalized modeling completed for many projects.

Background

Water quality modeling conducted for the proposed NorthMet Project is presented to demonstrate use of an integrated model for rapid assessment of various design options during the ongoing mine planning and environmental review process. The NorthMet Project is a proposed copper, nickel and precious metals mine located in northeastern Minnesota's Duluth Complex (Fig. 1), one of the largest undeveloped deposits of copper, nickel and other precious metals in the world (Eckstrand and Hulbert 2007). The NorthMet Project is currently undergoing environmental review, so the Project design presented here may change during the review process. It should be noted that model inputs have been developed to meet environmental agencies' requirements for estimating potential impacts. As currently proposed, approximately 32,000 tons (29,000 t) of ore per day will be mined via open-pit methods from two mine pits. Waste rock with the lowest sulfur content will be placed in a permanent surface stockpile at the mine site. Remaining waste rock will be temporarily placed in lined surface stockpiles and will be backfilled into the first mine pit (at the completion of mining in this pit) for long-term subaqueous storage. During reclamation, the permanent stockpile will be covered, the backfilled mine pit will be capped with a wetland, and the remaining mine pit will be allowed to flood.

Ore from the mine site will be transported approximately six miles (9.7 km) west to the plant site via rail, where it will go through crushing, grinding, flotation, and eventually hydrometallurgical processing. Tailings generated during the flotation process will be slurried to an existing, reclaimed taconite tailings basin for deposition. Reclamation of the tailings basin will include engineering controls designed to minimize oxygen and water penetration into the tailings as well as measures to collect and treat seepage emanating from the basin.

Evolution of the NorthMet Water Management Strategy and Modeling

The NorthMet Project is designed to re-use as much water as possible to minimize potential impacts to the environment, from both a water quantity and water quality standpoint. For example, during operations water generated at the Mine Site from pit dewatering and stockpile drainage will be treated and pumped to the Plant Site for use in processing. Then, during reclamation, water from the tailings basin will be treated and returned to the Mine Site to help expedite pit flooding, which will minimize the amount of time pit wall rock is exposed to the atmosphere and allowed to oxidize.

The proposed design of the NorthMet Project has changed several times throughout the mine planning and environmental review processes. Changes were made for both economic reasons (for example, changes in mine pit dimensions as additional information on



Wolkersdorfer, Brown & Figueroa (Editors)

the ore deposit became available) and environmental reasons (for example, changing the design of the tailings basin seepage capture system to increase effectiveness). In addition, the environmental review process requires the consideration of Project alternatives. This process resulted in the need for many iterations of water quality impact modeling. Each time the design of a feature changed, modeling was conducted to assess if the design change would potentially affect water quantity and quality. If the potential for impacts increased to an unacceptable level, additional engineering controls were added to the Project and the water impact modeling repeated.

Because of the interconnections between the various mine features, the change in the design of one feature had the potential to affect the water quality and quantity impacts associated with other mine features. For example, changing the type of cover used to reclaim a stockpile had the potential to affect:

- size of the wastewater treatment plant,
- flooding rate of the mine pit,
- potential water quality down gradient of both the stockpile and the mine pit,
- amount of tailings basin water that can be sent to the mine pit to expedite pit flood-ing, and as a result,
- potential water quality and quantity impacts associated with the tailings basin.

Initial water quality modeling conducted for the Project was performed using a series of stand-alone models, which required manual transfer of data between models. Separate models were constructed for the tailings basin pond, the tailings basin, mine pits, stockpiles, groundwater, surface water, and the wastewater treatment facilities. The manual transferring of data between models represented a high risk for error. To evaluate a change in the design of a mine feature, the various models needed to be re-run by multiple different modelers, which would often take days or weeks to complete. Having stand-alone models also made it difficult to assess whether mass was being conserved throughout the process and allowed for the possible double-counting of water as modelers attempted to make conservative assumptions with respect to various competing impacts.

Knowing that the mine plan was still changing and numerous options would need to be evaluated, the decision was made partway through the environmental review process to integrate the stand-alone models into source-to-receptor models for the Mine Site and the Plant Site. New models were constructed using the GoldSim modeling platform. The integrated GoldSim models can more rapidly assess potential water quality impacts, and have alleviated the concerns associated with data transfer among multiple models.

Following the conversion of the modeling to GoldSim, several different options were considered for operation, reclamation and longterm closure of the Project. For each option considered, the GoldSim model was run and the potential impacts to groundwater and surface water were assessed. Unlike previous modeling iterations conducted using the serious of stand-alone models, these various options were quickly assessed in a matter of days using the integrated model.

Comparison of Reclamation Scenarios

At one point in time, the proposed Project design resulted in increasing concentrations in the mine pit lake following reclamation. This design, presented here as the base model, included natural pit flooding, active treatment of the pit water during flooding, an engineered soil cover on the permanent stockpile, and a partial seepage containment system around the permanent stockpile. Knowing that increasing pit lake concentrations following reclamation may not be acceptable to the regulators or the public, three mine site reclamation scenarios were modeled to evaluate their effect on pit lake concentrations. Note that none of the scenarios presented here and examined in this intermediate modeling exercise are identical to the final design of the proposed NorthMet Project.

The three scenarios evaluated are as follows:

- Expedited Pit Flooding (Scenario 1) Ex-٠ pedited pit flooding in closure is a common strategy for mitigating loading from pit walls. However, expedited pit flooding results in less time available for active treatment of the pit water before discharge to the environment would occur. Several different options for pit flooding were considered for the NorthMet Project, including changing watershed areas via dike removal to direct more runoff to the pit and sending water from the tailings basin to the pit. This scenario looks at the option of routing up to 3,300 gpm $(0.21 \text{ m}^3/\text{sec})$ from the tailings basin to the pit to expedite the time it takes to flood the pit.
- Geomembrane Stockpile Cover (Scenario 2) – Engineered covers on waste rock stockpiles help to minimize the amount of infiltration that can contact the waste rock and mobilize solutes. The only permanent waste rock stockpile for the NorthMet Project was modeled with both an engineered soil cover (base model) and a geomembrane cover. The infiltration through the stockpile primarily influences the water quality of the downstream pit lake. This scenario includes the expedited flooding from Scenario 1.
- Stockpile Containment and Treatment (Scenario 3) – The base model includes a seepage containment system (cutoff wall with drain tile) constructed around three sides of the permanent stockpile in order to prevent seepage from flowing off-site. Water collected in the containment system is treated and discharged into the mine pit during flooding. The containment system was not originally planned to fully surround the stockpile, allowing

for stockpile seepage in the area without the containment system to flow into the mine pit. The option of extending this system around the entire stockpile was assessed to see how it would affect the treatment needs for the Project. This scenario includes the expedited pit flooding from Scenario 1 and a geomembrane cover on the permanent stockpile from Scenario 2.

The results of the water quality estimates for the base model and the three reclamation scenarios are shown in Figs. 2 and 3, which compare the modeled concentration of sulfate and nickel in the pit lake. Expedited pit flooding (Scenario 1) decreases the pit flooding time by approximately 30 years, from Year 95 under the base model to Year 65, and increases the modeled concentrations for sulfate and nickel in the pit lake at the end of flooding when pit water is expected to discharge to a local stream either naturally or, if necessary, via treatment. The modeled increase in concentrations is due to there being less time available for active treatment of the pit water prior to complete flooding. The long-term water quality approaches a similar steady state regardless of the pit flooding scenario. Stockpile reclamation with a geomembrane cover (Scenario 2) decreases the modeled concentrations in the pit lake at the end of flooding (Year 65) and more significantly in the long-term steady state condition. For these solutes there is very little difference in the modeled pit concentration with and without the extended containment system (Scenario 3), although pit concentrations are lower under this scenario.

The combination of expedited pit flooding and a geomembrane cover on the permanent stockpile results in pit lake concentrations that trend downward following reclamation, which was the desired outcome for the evaluation. Both of these options have been included in the revised mine plan for the Project. While extending the stockpile containment system is not predicted to significantly reduce pit lake concentrations of sulfate and



Fig. 2 Comparison of modeled pit sulfate concentrations for the base model and the three reclamation scenarios evaluate. Note that each modeled scenario assumes the inclusion of all previous scenarios.

Fig. 3 Comparison of modeled pit nickel concentrations for the base model and the three reclamation scenarios evaluated. Note that each modeled scenario assumes the inclusion of all previous scenarios.

nickel, this option has also been integrated into the revised mine plan because it should aid in the eventual transition of the Project from active to passive treatment, the discussion of which is beyond the scope of the evaluation presented here.

Summary and Conclusions

As regulatory pressure increases and water sources become scarcer, mine water management is becoming more critical. This often results in complex mine water management plans, which can be difficult and time consuming to assess. Developing an integrated sourceto-receptor water impact model early in the mine planning process can help facilitate rapid assessment of potential water quality and quantity impacts during mine planning. This approach was taken on the NorthMet Project, a proposed copper-nickel mine currently undergoing environmental review. The use of an integrated model allowed for rapid assessment of various options for mine site reclamation. In addition, having a single model, as opposed to separate models for mine features, groundwater and surface water, helped to insure mass conservation and prevented the double counting of water.

Acknowledgements

The authors thank Poly Met Mining Company for allowing us to present this work.

References

Eary LE, Jakubowski R, Eshleman J, Watson A, (2008) Applying numerical hydrogeochemical models as de-

cision support tools for mine closure planning. Tailings and Mine Waste '08, 221–231.

- Eckstrand OR, Hulbert LJ, (2007) Magmatic Nickel-Copper-Platinum Group Element Deposits. Mineral Deposits of Canada: A Synthesis of Major Deposit Types, District Metallogeny, the Evolution of Geological Provinces, and Exploration Methods: Geological Association of Canada, Mineral Deposits Division, Special Publication No. 5, 205–222.
- Nalecki P, Gowan M, (2008) Mine Water Management – Dynamic, Probabilistic Modelling Approach. International Mine Water Congress.
- Sawatsky LF, Beckstead G, Long D, (1998) Integrated mine water management planning for environmental protection and mine profitability. International Journal of Surface Mining, Reclamation and Environment Vol 12, Issue 1, p 37–39

Prediction of hydrogeochemical changes due to surface water seepage into 1B Mine Pool of Cape Breton, Canada

Chandra Devi Raman^{1,3}, Jessica MacSween¹, Joe Shea², Rajendran Kaliaperumal¹, Ken Oakes¹, Martin Mkandawire¹

¹Verschuren Centre for Sustainability in Energy and the Environment, Cape Breton University, P.O. Box 5300, 1250 Grand Lake Road, Sydney, Nova Scotia, Canada B1P 6L2, Chandra_Raman@cbu.ca ²Director Mine Water Management, Enterprise Cape Breton Corporation, P.O. Box 1750, 70 Crescent Street, Sydney, Nova Scotia, Canada B1P 6T7, joe.shea@ecbc-secb.gc.ca

³ Dr. Mahalingam College of Engineering and Technology, NPTC – MCET Campus, Udumalai Road, Pollachi – 642 003, Tamil Nadu, India, chandra@drmcet.ac.in

Abstract Since the 1B Mine Pool of the Sydney Coalfield in Nova Scotia was flooded in 1985, the mine water geochemistry has been evolving. The influence of surface water seepage into the colliery voids through the overlying geologic layers may alter hydrogeochemical dynamics and was thus simulated using FEFLOW model. Changes were predicted by time series analyses using weather data as well as different assumed seepage volumes and recharge rates. The preliminary simulation results confirm that infiltration might influence water head rise at the 1B mine pool, the formation and potential flow of contaminants in the 1B Mine Pool.

Keywords Groundwater-flow model, Sydney Coalfields, FEFLOW, mine water

Introduction

To develop an effective mine water management system for abandoned mines, it is necessary to consider all factors contributing to the current hydrogeochemical instability in the mine pools. One of the contributing factors to groundwater of hydrogeochemical dynamics is the interaction of surface water with the groundwater. Mostly the surface waters of concern are those that come from precipitation run-offs. In most cases, precipitation run-off from either rainfall or snow melting dissolve different chemical elements as they infiltrate different soil and geological formations into the groundwater aquifers. Consequently, the geochemistry of the groundwater may change and result into a chain of desorption and dissolution reactions that may lead to an increase in contamination of the groundwater. Further, the pressure exerted by the infiltrations may influence groundwater flow. Similarly, the infiltration of surface water into the mine pools may lead to contamination formations like

acid mine drainage. Therefore, the potential influence of surface water on the hydrogeochemical dynamics in flooded mine pools of abandoned mines of Sydney Coalfield in Cape Breton, Nova Scotia need to be considered as an integral component in the mine water management system.

It is in this context, that the project whose preliminary results are reported in this paper was conceived. The aim is to determine and predict the potential influence of the seepage of surface water on the ever changing hydrogeochemical characteristics of mine pools within the Sydney Coalfield. The Sydney Coalfield is located in the Maritimes Carboniferous Basin on the east coast of Cape Breton Island, Nova Scotia, Canada. For the current study, it is hypothesized that the seepage of surface water into the voids of collieries and its contact with the geology of mined region increases contaminant level and results in acid mine drainage. To test the hypothesis, the behavior of groundwater flow and pollution

transport in the 1B Mine Pool was simulated using 3D FEFLOW (Finite Element Subsurface Flow system) model. Using geochemical and weather data for Cape Breton as well as different assumed recharge rates of pools with seepage, the potential geochemical changes were predicted by time series analyses. The broader objective was to develop a three-dimensional (3D) model for mine water flow and transport of contaminants with a view to estimate their long-term impact on geochemical stability of the mine pools. Hence, this paper presents the preliminary FEFLOW modeling results of the hydrogeochemical changes and contaminant concentrations in the 1B Mine Pool, which are required for designing effective treatment and management strategies.

Methods

Description of study area

The current study concentrated on colliery No. 5 of the 1B Mine Pool, which is located beneath the communities of Glace Bay, Reserve Mines and Dominion, situated near the east coast of Cape Breton Island (Fig. 1). The 1B Mine Pool was chosen for the preliminary study because it is the largest of the three mine pools, while colliery No. 5 was chosen because it is located on land and has a high probability of benign influence with seepage surface water through the Phalen seam outcrop and into the bootlegs nearby. The No.5 colliery was depillared completely during the mining activities and part of the colliery collapsed accompanied by surface subsidence. The site receives annual precipitation in the form of rainfall and snow accounting for 85 % and 15 %, respectively (Shea 2008, 2009). The recorded mean annual precipitation for the Sydney area is 1504 mm per year (Environment Canada 2013).The study area covers 6.6 km² and the No.5 colliery was extended to a depth of 217.314 m, for the mining activities.

Subsurface profile of study area

The subsurface layers of different coal seams at depths are shown in Fig. 2. The 1B Mine Pool formed following the mining activities of within a gently folded structure, the Glace Bay Syncline and along the northward flanks of the Bridgeport Anticline (Shea 2010; Wolkersdorfer 2011). The mining occurred at three major coal seams namely the Emery, Phalen and Harbour, which are of different depths. The coal measures strata are of Carboniferous age, with the seams separated by sequences of sedimentary rock while the inter seam strata generally consists of mudstone, shale, siltstone, sandstone and traces of limestone. The No.5 colliery was mined only through the Phalen seam and no coal mining was done at the Harbour seam.

Modeling procedure

The conceptual model was developed based on surficial topography and subsurface profile exploration to understand the surface water seepage into the mining ground of the study area. The generated conceptual model is used to simulate a numerical 3D model using FE-FLOW Version 6.1. For the FEFLOW simulations, the study area was converted into a polygon,



Fig. 1 Location of study area above No.5 colliery



Fig. 2 Location of study area having Phalen Seam outcrop (Shea 2008)

and a mesh containing 23312 triangular-prism elements was generated (Fig. 3). The subsurface profile of the study area was designed to have four layers based on its geological background. The first layer contains elevation data on the topography of the study area, the second layer includes both the over burden and fractured rock layers, the third layer extends to the bottom of Phalen seam, and the last layer contains hard rock stratum.

For the simulation, the model was initially assumed as 3D unsaturated aquifer, which was later saturated variably during the simulation using Richard's Equation (1), which is incorporated directly in the FEFLOW procedure:

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial y} \left[k(w) \left(\frac{\partial p}{\partial y} + 1 \right) \right]$$
(1)

where, w is the volumetric aquifer water content changing with respect to time t; k is the permeability or hydraulic conductivity of the aquifer; p is the pressure head variation with respect to vertical elevation y.

Thus, transient flow was simulated based on the surface runoff due to precipitation. The boundary condition assumed absence of flow in and out of the aquifers. The fluid flow was monitored for 365 days, having an initial time step as 0.001 day. The inflow of water head due to the precipitation is assumed as 1504 mm/year and flows into the model from the topographic layer. The assumed permeability in the horizontal direction is 1 m/d and it is as-



Fig. 3 The finite elements generated for the study area

sumed greater in the vertical direction due to collapsed roof of No.5 colliery. The porosity of the unsaturated aquifer is assumed as 0.3, since the geological details of the study area includes only sedimentary rock types. The time stepping procedure is based on Adams-Bashforth/Trapezoid rule predictor-corrector, which is incorporated in FEFLOW Software.

Results and Discussion Surface runoff and potential infiltration into mines

In order to understand the surface runoff, modeling the exact topography of the study area is important. Based on the topography data and information about the study area, the simulation with FEFLOW predicts the direction of surface runoff to be northwards(Fig. 4 (a)).

The model acknowledges the possibility of surface runoff into the Phalen outcrop, the nearby bootlegs and the watershed of Cadegan Brook. Hence, the model suggests that the source of infiltration of surface runoff into the mine pool is likely to be through surface features shown in Fig. 4.

Saturation and hydraulic head isolines

Fig. 5(a) shows the saturation of the unconfined aquifer model, while Fig. 5(b) shows the hydraulic head isolinesafter365 days simulation. The model predicted maximum saturation locations that coincide with the area known as MacKay's corner. This area contains a natural wetland and is considered the main infiltration point of the 1B Hydraulic System (Shea 2008).

Therefore, this site in particular is suspected to be the source of precipitation run off infiltration into the No.5 colliery. The hydraulic head isolines predicted in wetland and water catchment area are lower because of surface water seepage into the subsurface and colliery (Fig. 5(b)).

Hydraulic and pressure heads

The predicted hydraulic head as well as the pressure created by the water percolation is





Fig. 5 (a)Saturation of the model at the end of 365 days (b) Hydraulic head – isolines at the end of 365 days

presented in Fig. 6. The model has predicted the hydraulic head based on the topographic layer and permeability of rock layers, showing the minimum value within the lowland drainage region (Fig. 6a). The pressure head varies as the water infiltrates into the subsurface layers of the model (Fig. 6b).

Underground velocity flow

The predicted flow direction of the model is shown in Fig. 7. The predicted flow velocity of the percolated water ranges between



Fig. 6 (*a*) *Hydraulic head at the end of 10th day – shows surface runoff and head of water percolated into ground; (b) Pressure variation along the layers at the end of 10th day*

0.005730 m/d to 0.68751 m/d. The flow of the percolated water varies based on the permeability of the aquifer and changing porosity during unsaturated to saturated condition. The computed precipitation net inflow rate of the model at the end of 365 days is 25437.9 m³/d (4667 USGPM). The simulated precipitation inflow of water into the subsurface has not included its loss during surface run off. In future modeling, these limitations will be taken into account when simulating the hydrogeochemical changes of surface water into No.5 colliery.

The preliminary numerical study shows that there is the greater possibility of precipitation runoff into No.5 colliery and nearby bootlegs, which shall increase the mine water head in the 1B mine pool and induces the mine hydrochemistry in the Phalen coal seam.

Conclusion

The preliminary results from the simulation revealed that percolation of surface runoff into the underground seam at No.5 colliery would indeed affect the hydrogeochemical stability of the mine water at 1B Mine Pool. The inflow rate of water is predicted as 4667 USGPM using numerical modeling and it is confirmed with the range of 1B Mine pool water capacity, which fluctuates 450 to 7000 USGPM during the year based on the precipitation events. The percolated water into the siltstone, shale, sandstone, mudstone rock layers and also on the Phalen coal seam may have the hydrogeochemical changes that would cause the acidic mine drainage at 1B mine pool. Further studies will be toward simulation of actual hydrogeochemical changes, including dissolution, desorption dynamics that may take place due to the inflow of precipitation into the rock layers and Phalen seam.

Acknowledgements

The authors thank Bob Bailey, Deanne von Rooyen, Ben Pickles, Kevin Driscoll – all of Cape Breton University – and Glenn Macleod of CBCL Ltd. for assistance in the project including mine data, geological issues and GIS. Chandra is specifically indebted to C. Ramaswamy, Ibrahim Alladin, Ranga Palaniswamy of Dr. Mahalingam College of Engineering and Technology (MCET), Pollachi, India and Allen Britten, Edwin MacLellan, Ross McCurdy of Cape Breton University (CBU), Syd-





ney, Canada for their support in MCET-CBU research collaboration activity.

References

- Shea J (2008) Innovative mine water management techniques for Submarine Coal, Nova Scotia, Canda. In: West Virginia Mine Water Drainage task Force Symposium, West Virginia, 1–20
- Shea J (2009) Mine Water management of Flooded Coal Mines in the Sydney Coal Fields, Nova Scotia, Canada. In: Wolkersdofer C (ed) International Mine Water Proceedings, Pretoria, South Africa. IMWA, 289–297
- Shea J (2010) Innovative management techniques to deal with Mine Water Issues in Sydney Mine Coal

Fig. 7 Predicted flow direction of the percolated water

Field, Nova Scotia, Canada. In: Mine Water and Innovative Thinking – International Mine Water Association Symposium, Cape Breton University, Sydney, 633–637

365 [d]

- Wolkersdorfer C (2011) Tracer Test in a Settling Pond: The Passive Mine Water Treatment Plant of the 1 B Mine Pool, Nova Scotia, Canada. Mine Water Environ 30 (2):105–112, doi:10.1007/s10230-011-0147-3
- Environment Canada (2013) National Climate Data and Information Archive (February 4th, 2013) http:// climate.weatheroffice.gc.ca/climateData/canada_e. html

Increasing ARD and rare earth metal concentrations in an alpine watershed

Garrett RUE¹, Caitlin CROUCH², Diane MCKNIGHT¹

¹Institute for Arctic and Alpine Research at the University of Colorado – Boulder, USA; ²Integral Consulting, Inc., USA

Abstract The coupled environmental impact of acid rock (ARD) and acid mine drainage (AMD) is a problem facing many waterways across the Rocky Mountains and throughout the world, particularly in areas of historic mining. Here we examine the Snake River watershed, located near the former mining boomtown of Montezuma, Colorado. Over the last three decades, researchers for numerous government agencies, the Institute of Arctic and Alpine Research, and graduate students from the University of Colorado have monitored changes in Snake River water chemistry and metal contamination present in its tributary streams.

Keywords rare earth, acid rock drainage

Extended Abstract The coupled environmental impact of acid rock (ARD) and acid mine drainage (AMD) is a problem facing many waterways across the Rocky Mountains and throughout the world, particularly in areas of historic mining. Here we examine the Snake River watershed, located near the former mining boomtown of Montezuma, Colorado. Over the last three decades, researchers for numerous government agencies, the Institute of Arctic and Alpine Research, and graduate students from the University of Colorado have monitored changes in Snake River water chemistry and metal contamination present in its tributary streams.

The Snake River watershed represents a unique water quality challenge because its headwaters are impacted by ARD, and downstream tributary inflows compound this with AMD. These acidic, metal-rich inflows create an acutely toxic environment for fish and most aquatic organisms. Long-term data sets of precipitation, temperature, river discharge at many sites throughout the Colorado Rockies show decreasing trends in summer flows (Rood *et al.* 2008) which correlate to other, more recent findings which highlight a snowpack that is melting 2–3 weeks earlier (Clow 2010). Using snow water equivalent measurements from SNOTEL sites nearest to the Snake River, a trend was shown between advancement of peak stream flow by an earlier melt season and rising metal concentrations in summer months (Todd et al. 2012). A 30-year water chemistry data set from the upper Snake River further show that fluctuations from 100-400 % of baseline are occurring during these low-flow months. Over the last 10 years, more frequent drought conditions and earlier occurrence of peak spring snowmelt have further reduced water quality during low-flow conditions. In addition to lower flows, changes in water chemistry have been driven by increased weathering rates of exposed sulfide minerals, resulting in decreased pH. The additional acid production has caused dissolution of metals from the host rock and enrichment of the stream with these solutes, which are mobilized greater distances down the reach.

Iron is the predominant metal present in the upper Snake River, but upon mixing with pristine neutral inflows precipitates as iron oxides (McKnight *et al.* 1988). Zinc, however, is less affected by this increase in pH and remains dissolved well downstream of the ARD and AMD sources. Of particular concern is that stream chemistry data has shown a four-fold increase in zinc concentrations in the last 10 years, with a transition from a steady linear increase over a previous 20-year record to that of an exponential trend (Crouch et al. 2012). More recent study of the upper Snake River and its contributing streams led to the discovery of rare earth metals in high concentrations. For example, neodymium is present in one particular tributary in levels as high as $120 \mu g/L$. Retesting of archived samples going back as far as the 1990s has confirmed a continued presence, proving an intriguing issue for further study. The hydrologic and geochemical changes observed in this watershed may have important implications for mitigation as well as remediation of mine sites

References

Clow D (2010) Changes in the timing of snowmelt and streamflow in Colorado: a response to recent warming. Journal of Climate.23(9), 2293–2306

- Crouch C, McKnight D, Todd A (2012) Quantifying sources of increasing zinc from acid rock drainage in an alpine catchment under a changing hydrologic regime. Hydrologic Process 1099–1085 doi: 10.1002/hyp.9650
- McKnight D, Kimball B, Bencala K (1988) Iron photoreduction and oxidation in an acidic mountain stream. Science 240:637–640.
- Rood S, Pan J, Gill K, Franks C, Samuelson G, Shepherd A (2008) Declining summer flows of Rocky Mountain Rivers; changing seasonal hydrology and probable impacts on floodplain forests. Journal of Hydrology 349, 397–410
- Todd A, Manning A, Verplanck P, Crouch C, McKnight D, Dunham R (2012) Climate-Change-Driven Deterioration of Water Quality in a Mineralized Stream. Joint study between the U.S. Geological Survey, IN-STAAR, and EPA. Environmental Science and Technology 46 (17), 9324–9332



Fig. 1 Site location





Attenuation Potential of Clay Liner Carbon-in-Leach Tailings Storage Facilities – A Case Study at Gold Fields Ghana Limited, Tarkwa Mine (GFGL)

M. A. SACKEY¹, G. K. ANORNU¹, Y. KUMAH¹, B. K. KORTATSI², Kofi Antwi Yeboah³

¹Department of Civil Engineering, KNUST, Kumasi ¹UMat –P.O. Box 237, Tarkwa Ghana ²CSIR-Water Research Institute, P. O. Box M32, Accra, Ghana ³Newmont Ghana Limited, Ahafo Mine

Abstract This study presents research findings on cyanide attenuation potential of the substrata material of Tailings Storage Facilities (TSF) at Gold Fields Ghana Limited (GFGL), Tarkwa Mine. The attenuation properties of the substrata considered and evaluated were hydraulic conductivity (K), permeability characteristics and geochemical properties; pH, Organic Matter Content (OMC), Cation Exchange Capacity (CEC), Iron Oxide and Anion Exchange Capacity (AEC). Substrata material samples were taken before and after an insitu cyanide leaching test at five locations in and around the three TSF; TSF 1, TSF 2 and TSF 3. Total and Weak Dissociable Cyanide (WAD) were analyzed after leaching test.

Keywords Tailings Storage Facility, hydraulic conductivity, permeability, geochemical, organic matter content, cation exchange capacity

Introduction

The environmental fate of free cyanide and metal-cyanide complexes have been under intensive investigation over the last three decades. Cyanide is naturally occurring and natural mechanisms exit both geochemically and biogeochemically exist to retard or attenuate its movement in subsurface, and to degrade its compounds into low-hazard reaction products such as nitrogen gas, ammonia, nitrate, and carbon dioxide. The attenuation capacity of subsurface earth materials can be measured, quantified, predicted, and most importantly can be enhanced by rather simple and inexpensive procedures. The fact that natural earth materials have quantifiable and predictable ability to remove contaminant trace elements from migrating seepage has been documented for more than ten years (Griffin 1976, Griffin 1977). According to Griffin (1976), the overall pollution from contamination sources could be reduced if liners of natural earth material were designed for lower hydraulic conductivities. According to Ghosh *et al.* (2006a), various factors effluence the cyanide cycle in the environment and it includes but not limited to pH, temperature, sunlight intensity and OMC of soils.

Study Area

The study area comprised of the TSF at GFGL with specific emphasis on he substrata. The facility is located in the Tarkwa Nsuem Municipality in the Western region of Ghana. Tarkwa is on latitude 5°15′ N and longitude 2°00′ W and located within the South Western equatorial climatic zone. This zone is described as a moist tropical climate characterised by high year round temperatures and rainfall pattern. Rainfall peaks is from April to June and October to November. Average rainfall over the last 50 years at the mine site is 1600 mm per annum. The average daily temperatures range from 24.5 °C to 27.8 °C with peak readings in the months from February to April (Arthur et al. 2004). The three TSF's (TSF 1, TSF 2 and TSF 3)

"Reliable Mine Water Technology"

Sample ID	nH	C.E.C	A.E.C	OMC	Fe ₂ O ₃
Sumple ID	PII	(meq/100 g)	(meq/L)	(%)	(ppm)
Station 1	4.5	2.01	1278.25	0.36	49.57
Station 2	4.5	2.89	1057.50	0.53	63.14
Station 3	4.8	2.34	881.25	0.78	66.43
Station 4	4.3	1.92	1057.50	0.43	22.86
Station 5	4.5	2.37	881.25	0.98	29.00

were substrata were the prime focus of the study.

Methodology

Field Leaching Test

Leaching test was carried out at five locations in the TSF basin. At each station, an auger drill was used to drill a hole to a depth of 1.5 m and fitted with a 2 m length Polyvinyl Chloride (PVC) pipe (101.6 mm diameter) which has been perforated. Four monitoring holes, at a distance of 3 m from the leaching point hole were also similarly constructed as the leaching point. A depth of 1.5 m was chosen to conform to the thickness of the clay in the TSF basin. Tailings slurry with 50 mg/L WAD concentration was introduced into the leaching points at the respective leaching sites, up to the 1.5 m level. Concentration of slurry conformed to GFGL mine limits for WAD in tailings discharged which averaged 48 mg/L from field sampling programme at various spigoting points.The leachates in the monitoring points at the respective leaching points were sampled and analyzed for Total and WAD cyanide after a month. Cyanide leachate in the monitoring holes surrounding the leaching points were sampled monthly and analyzed for WAD and Total cyanide. This was repeated over six month's period. Samples of the substrata were taken and analyzed to verify the impact of the leaching on the attenuation potential of the TSF clay liner.

Soil Sampling

A total of ten (10) clay soil samples were collected from the five leaching points in July 2010 prior to the leaching test. The same number of samples was taken in June 2011 to analyze for geochemical parameters after the leaching test. These disturbed clay samples of varied texture were taken from depths ranging from 1 to 1.5 m. The samples were coned and quartered on a clean polyethylene sample sheet and representative samples taken and transferred into a new, clean polyethylene sample bag. Samples earmarked for dry sieve analysis weighed 7 kg each, whiles that earmarked for hydrometer tests and geochemical tests weighed 1.5 kg each. The attenuation properties of the clay samples considered are the hydraulic conductivity, permeability characteristics and geochemical properties.

Results and Discussion Geochemical Parameters

Geochemical investigations carried out on clay samples collected from five identified sites showed the results of the geochemical parameters as presented in Table 1.

Hydraulic Conductivity (K), Permeability (k_i) and Porosity (n) of Soil Samples

The Alyamani and Sen (1993) empirical formula and relevant parameters derived from grain size analyses were used to determine the hydraulic conductivity of the clay samples collected from the five respective stations. The field calculated hydraulic conductivity values were in the range of 6.2×10^{-3} to 1.41×10^{-2} m/d with a mean value of 8.3×10^{-3} m/d which is presented in Table 2. The maximum value of *K* was obtained from clay sample from Station 3, whiles the minimum value of K was obtained from Station 5. Hydraulic conductivity values of silt, clay and mixtures of sand, silt and clay were in the orders of 10^{-2} and 10^{-4} m/d (Brassington 2007). Based on this

"Reliable Mine Water Technology"

Samp	ple ID	I _o (mm)	<i>d</i> ₁₀ (mm)	(1	d <i>50</i> mm)	K (m/day)	
Stati	ion 1	1.17×10^{-3}	4.1×10^{-3}	³ 5.34	× 10 ⁻²	7.5×10^{-3}	
Stati	ion 2	1.12×10^{-3}	4.1×10^{-3}	³ 5.40	0×10^{-2}	7.3×10^{-3}	
Stati	ion 3	2.17×10^{-3}	4.0×10^{-3}	3 4 88	10^{-2}	1.4×10^{-2}	
Stati	ion A	1.15×10^{-3}	4.1×10^{-3}	3 / 86	5×10^{-2}	6.7×10^{-3}	Table 2 Summary of Hy
Stati	ion 5	1.13×10^{-3}	4.1×10^{-2}	 3 1 4 6	2×10^{-2}	0.7×10^{-3}	draulia Conductivity of Clay
Stati	1011 3	1.11 × 10 °	4.0×10^{-5}	- 4.0c	5 × 10 ~	0.2×10^{-3}	araune conductivity of clay
				N	lean	8.3 × 10 ³	Samples
-	Sample ID	K (m/day)	Mea Dynar Visco	n mic sity	<i>K_i</i> , (m ²)		
_	Station 1	7.5 × 10 ⁻	³ 8.87 ×	10-1	7.72×10^{-10})-12	
	Station 2	7.3×10^{-1}	³ 8.87 ×	10-1	7.50×10^{-10})-12	
	Station 3	1.4×10^{-1}	² $8.50 \times$	10-1	1.39×10^{-1})-11	
	Station 4	6.7×10^{-10}	³ 8 90 ×	10 ⁻¹	6.91×10^{-10})-12	
	Station 5	6.7×10^{-10}	³ 8 50 ×	10-1	6.01×10)-12	Table & Fative atod Daves a
	Station 5	0.2 × 10	0.50 ×	10	0.10 × 10	-12	Table 3 Estimated Perme-
-			Iviea		0.4 <u>4</u> × 10		ability (Ri) of Clay Samples
No: of Sample	f Mea es d ₁₀ (m	n Mea m) <i>d₆₀(m</i>	m M (m) U = d	ean 1 ₆₀ /d ₁₀	n = 0	/lean 0.255(1 + 0.83 ^U)	Table 4 Estimated Mean
5	4.1×1	0^{-3} 7.8 ×	10 ⁻² 19.2	2069	0.	.2621	Dorosity (n) of Clay Samples
					Percenta	ge = 26.21 %	Forosity (II) of City sumples
Sample ID	e K (m/day) pH	C.E.C (meq/100g)	A.E.C (meq/L)	Total Cyanid (mg/L)	WAD e Cyanide (mg/L)	
Station	1 7.5 × 10	-3 4.5	2.01	1278.25	0.010	0.010	
Station	2 7.3×10	-3 4.5	2.89	1057.50	0.020	0.011	
Station	3 1.4×10	-2 4.8	2.34	881.25	0.030	0.010	
Station	4 6.7 × 10	-3 4.3	1.92	1057.50	0.010	0.010	Table 5 Summary of Major
Station	5 6.2×10	-3 4.5	2.37	881.25	0.010	0.010	Attenuation Properties

premise, the results can be said to be quite consistent with the hydraulic conductivity of clay. Permeability values (k_i) were calculated using Kresic (2007) equation. The k_i values as presented in Table 3, are very low ranging from 7.72 × 10⁻¹² to 1.39 × 10⁻¹¹ m² with a mean value of 8.42 × 10⁻¹² m².

The estimated mean porosity value as shown in Table 4 is 26.21 %. Comparing this value with standard porosity values for clay (\approx 26-68 %; Kresic 2007), and studies conducted by Barnie (2010), on similar clay materials in the Atankwidi sub-basin of the White Volta Basin in Ghana, where he had a mean porosity of 26.24 %, the obtained mean poros

ity value is consistent with clayey soils in Ghana.

Table 5 gives a summary of the major attenuation properties of the TSF sub-strata material that influences cyanide attenuation.

Cyanide decay analyses of the sub-strata material of the TSFs

Within a working radius of 3 m, the sub-strata material at the respective leaching sites returned average Total cyanide concentrations ranging from 0.01 to 0.03 mg/L and WAD cyanide levels ranging from 0.01 to 0.011 mg/L. No concentrations of Free, WAD or Total cyanide were detected in the drilled holes prior



Fig. 1 Hydraulic Conductivity Results from the respective stations

to the leaching test.WAD cyanide results from the leaching test falls within limits stipulated, for TSFs with planned measures for cyanide degradation, where concentrations range from \approx 1-10 mg WAD-CN/L (NICNAS, 2010). Moreover, the Total and WAD cyanide results falls within stipulated limits of EPA-Ghana, which states a Total and WAD cyanide limit of 1 mg/L and 0.6 mg/L respectively and hence, poses no threat to groundwater resource. However, the average cyanide detected with time at the five stations remained fairly constant as time increased.

Effect of hydraulic conductivity and permeability on cyanide attenuation

Total cyanide concentration from the leachate at Station 3 recorded the highest value due to the high hydraulic conductivity of the substrata. Clay material from Station 5 had the least hydraulic conductivity and attenuated 50 mg/L concentration of NaCN to 0.010 mg/L of Total cyanide and WAD cyanide respectively. Based on the geochemical results from the leaching stations, it was observed that clay material from Station 5 had unfavorable geochemical parameters which gave it a weak cyanide attenuation property. Such properties (881.25 are; least AEC meq/L), high CEC(2.37 meq/100 g) and low Iron-oxide content (29 ppm). However, it exhibited acidic (average pH is 4.5) values, high OMC (0.98 %), 0.010 mg/L Total and WAD cyanide concentration respectively. Clay material from Station 2 was able to attenuate the 50 mg/L NaCN to 0.020 mg/L of Total cyanide and 0.011 mg/L of WAD cyanide due to the fact that it was acidic (pH-4.5), had a high AEC (1057.50 meq/L) and high Fe-oxide content (63.14 ppm). The sample however, had the highest CEC (2.89 meq/100g) and low OMC (0.53 %), thereby rendering it ineffective in cyanide attenuation.Despite the fact that there was 0.01 mg/L of WAD cyanide in leachate samples of Station 3, Total cyanide values were the highest (0.030 mg/L) compared to leachate from Station 2 (0.020 mg/L) and Station 5 (0.010 mg/L). Although its clay material had the highest Fe-oxide content (66.43 ppm) and high OMC (0.78 %), the differences in cyanide attenuation was due to the fact that it had the least AEC (881.25 meq/L), high CEC (2.34 meq/100g) and had the highest pH (4.8).

Clay material from Station 4 attenuated both Total and WAD cyanide to 0.01 mg/L inspite of its low OMC (0.43 %) property and lowest Fe-oxide content (22.86 ppm). This could be attributed to the fact that clay material from Station 4 was highly acidic (4.3), had lowest CEC (1.92 meq/100 g) and high AEC of 1057.50 meq/L. Similarly, clay material from Station 1 also attenuated both Total and WAD

cyanide to 0.01 mg/L, though having the lowest OMC (0.36 %) and a relatively lower CEC (2.01 meg/100 g). The cvanide attenuation in Station 1 was due to the fact that Station 1 was acidic (4.5), had the highest AEC (1278.25 meq/L) and Fe-oxide content of 49.57 ppm. An assessment of the hydraulic conductivity, permeability and geochemical results of clay material from the five leaching sites with respect to the Total and WAD cyanide concentrations from their leachate, revealed that low hydraulic conductivity and a combination of low acidic pH, relatively high AEC and low CEC were the major attenuation properties that influenced cyanide attenuation (Fig. 1). This agrees with studies conducted by Dzombak et al. (2006a)

Significant variations were recorded in all the geochemical parameters in samples taken after the leaching test and these are the pH, AEC, CEC, Fe₂O₃ and OMC. pH decreased significantly for all the five leaching sites with values ranging from 3.0 to 3.4 and a corresponding increase in AEC ranging from a minimum value of 1650 ppm to a maximum value of 2116.67 ppm. According to finding by Dzombak et al. (2006); Ghosh et al. (2006a) the substrata material after the leaching test increased effectiveness of the attenuation potential of the clay material but considering the higher CEC and OMC. OMC for Station 5 reduced from 0.98 % to 0.79 % rendering it less effective in attenuating cyanide and other minerals. Fe₂O₃levels for Stations 1(14.5 %), 2 (60.9 %) and 3 (49.5 %) decreased after the test whiles that of Station 4 (27.3 %) and 5 (8.0 %) were elevated. The pH reduced after the test at all the five stations ranging from 3.0 to 3.4 comparing to preleaching pH range of 4.3 to 4.8. Stations 1 and 3 reduced by 33.3 % with Stations 2, 4 and 5 reducing by 24.4 %, 23.3 and 27.8 % respectively.

Conclusion

The following conclusions were deduced from the studies carried out;

Estimated mean porosity values of the substrata material of the TSF basin establishes it as clayey with further classification of silty

clay (TSF 1 and 2), laterite on slopes in TSF 3 and silty sand at low lying areas of TSF 3.

Mean calculated permeability and hydraulic conductivities of samples conforms to acceptable regulatory materials for the construction of tailings substrata. Station 5 exhibited the least attenuating geotechnical capabilities.

Confirmed geochemical parameters of the substrata effective in attenuating cyanide to tolerable and acceptable limits especially for stations 1, 2 and 3, with Station 5 being less effective.

The substrata material after the leaching test increased effectiveness of the attenuation potential of the clay material but considering the higher CEC and OMC. OMC for Station 5 reduced from 0.98 % to 0.79 % rendering it less effective in attenuating cyanide and other minerals.

pH for all the test stations became more acidic after the leaching test. Adsorption onclay particles and iron hydroxides can reduce metal and WAD cyanide concentrations. So can chemical reactions and ion replacement/exchange as the fluid infiltrates through the soil profile. Soils containing a clay component are especially effective in attenuating metals.

References

- Alyamani MS, Sen Z (1993) Determination of Hydraulic Conductivity from Grain-Size Distribution. Curves. Groundwater.Vol. 31, No. 4. 551–555.
- Barnie S (2010) Hydrogeological and Hydrochemical Framework of Groundwater for irrigation in the Atankwidi sub-basin of the White Volta Basin. MSc. Thesis (unpublished), Kwame Nkrumah University of Science and Technology, Kumasi, Ghana. Brassington, R. (2007). Field Hydrogeology.3rdEdition.John Wiley and Sons Ltd. United Kingdom.
- Brassington R (2007) Field Hydrogeology. 3rdEdition.John Wiley and Sons Ltd. United Kingdom.
- Dzombak DA, Ghosh RS, Young TC (2006) Physical– Chemical Properties and Reactivity of Cyanide in Water and Soil. In: Cyanide in Water and Soil. Chem-

istry, Risk, and Management. Dzombak, D.A., Ghosh, R.S. and Wong-Chong, G.M., (eds.), CRC Press, Boca Raton, Florida, USA, (2006), p. 61.

- Ghosh RS, Ebbs SD, Bushey JT, Neuhauser EF, Wong-Chong GM (2006a) Cyanide Cycle in Nature. In: Cyanide in Water and Soil. Chemistry, Risk, and Management. Dzombak, D.A., Ghosh, R.S. and Wong-Chong, G.M., (eds.), CRC Press, Boca Raton, Florida, USA, (2006), p. 225.
- Ghosh RS, Meeussen JCL, Dzombak DA, Nakles DV (2006c) Fate and Transport of Anthropogenic Cyanide in Soil and Groundwater. In: Cyanide in Water and Soil. Chemistry, Risk, and Management. Dzombak, D.A., Ghosh, R.S. and Wong-Chong, G.M., (eds.), CRC Press, Boca Raton, Florida, USA, (2006), p. 197.
- Griffin RA (1976) Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals: Part 1-Column Leaching and Field Verification, Ill. St.Geol. Surv. Envir. Geol. Notes No. 76, Urbana, Nov.1976.
- Griffin RA (1977) Attenuation of Pollutants in Municipal Landfill Leachate by Clay Minerals: Part 2-Heavy-Metal Absorption. Ill. St. Geol. Surv. Envir. Geol. Notes No. 79, Urbana, Apr. 1977.
- Kresic N (2007). Hydrogeology and Groundwater Modeling. Second Edition, CRC Press, Taylor & Francis Group, Boca Raton, USA, (2007), p. 807.
- NICNAS (2010), Sodium Cyanide, February 2010. Priority Existing Chemical Assessment Report No. 31. Sydney, Australia. Internet accessed on April 3rd 2010 at www.nicnas.gov.au

Cyanide Decay and Metal Speciation in Decant Ponds of Carbon-in-Leach Tailings Storage Facilities – A Case Study at Gold Fields Ghana Limited, Tarkwa Mine (GFGL)

M. A. Sackey¹, G. K. Anornu¹, J. S. Y, Kuma², B. K. Kortatsi³

¹Department of Civil Engineering, KNUST, Kumasi ²UMat –P.O. Box 237, Tarkwa Ghana; ³CSIR-Water Research Institute, P. O. Box M32, Accra, Ghana

Abstract The environmental fate of cyanide in gold processing tailing dams has raised concerns over the last two decades especially the presence of residual cyanide and metals which may lead to chronic groundwater contamination. Results from the TSFs at Gold Fields Ghana Limited (GFGL) Tarkwa Mine TSFs show that WAD and total cyanides for the two dams increased significantly with increase in depth of decant which is inversely proportional to pH of decant pond. Significantly, metal concentrations (Na, Fe, Cu and Mn) increased proportionally with depth in the decant pond and consistent metals identified in ore geochemistry and underdrainage sump.

Keywords Cyanide Decay, Geochemical, Total Dissove Solids (TDS), Weak Acid Dissociable (WAD), Tailings Storage Facility (TSF)

Introduction

Cyanide concentrations in the decant ponds vary with depth, season and temperature varies with respect to depth of burial and distance from the discharge point. Total cyanide is independent of depth although constraints like time lag may affect it, but that cannot be said about Weak Acid Dissociable (WAD) and free cyanide. The possibility that cyanide salt and complexes occur at depth is high and under anaerobic conditions in non-sterilized soil mediums it is converted to nitrates with the potential to migrate into the groundwater system. Free cyanide concentrations decay with increased depth of burial and this makes migration into the groundwater system difficult. Metals and other trace element concentrations may vary with depth due to association with cyanide. This study is to assess the decay and concentration of cyanide and metals at depth variations in the two tailings dams at GFGL and the associated impact on the immediate environment.

Study Area

The study area is the operating tailings dams of GFGL. It is located in the Western Region of Ghana at latitude 5°15′N and longitude 2°00′W. Tarkwaian formation in the concession is mined as ore and geological tests on the ore proves that there is no potential for acid generation due to high level of neutralizing minerals present in the rocks (Arthur et al. 2004). Gold is extracted from crushed ore using the cyanidation technique via a Carbon in Leach (CIL) plant and a heap leach facility. This generates on the average 900,000 m³ of tailings every month and is deposited in two clay lined TSF's (TSF 1 and TSF 2). The TSF site is generally underlain by Huni Sandstone with the south western boundary of the site by a ridge of Tarkwa Phyllite. In addition more recent Quaternary deposits formed by the fluvial system in the area overlie these.

Methodology

Sampling of the two TSF was carried out in three areas comprising the two supernatant

ponds (decants), three underdrainage sumps which collects seepages from the network of underdrainage pipes, slurry from spigotting points along the discharge pipeline. Profile depth sampling was carried out in the decant ponds on the TSF 1 and 2 respectively. Sampling regimes started from July 2010 to July 2011. Sampling locations were selected at random and accessed by a canoe. The depth sampler was used at 1.0 m interval and the contents emptied into a dark (500 mL) and 1000 mL sterilized sample bottles. A total of eighty-nine samples were taken at thirteen locations in the TSFs.

Results and Discussion Cyanide Decay with Depth

According to Botz et al. (1999), cyanidation of tailings disposed in a surface impoundment experiences a loss of cyanide due to natural degradation, frequently reducing the cyanide concentration to very low levels. Quantifying cyanide losses in terms of pond geometry, local weather conditions and feed solution chemistry has been largely empirical though in many cases mining operations rely on surface impoundments to reduce cyanide to below an internally regulated concentration or an effluent limitation. Cyanide, depending on the form and concentration tends to react readily with many other chemical elements and molecules to form, as a minimum, hundreds of different compounds (Flynn and Haslem 1995). Several of these compounds break down and are generally less toxic than the original cyanide. However, these compounds are known to be toxic to aquatic organisms, and persist in the environment for significant periods of time. In addition, there is evidence that some forms of these compounds can be accumulated in plant tissues (Eisler 1991) and may be chronically toxic to aquatic life; in fishes, micro vertebrates and invertebrates (Heming 1989). WAD and total cyanide levels at two monitoring locations in the decant ponds of TSF1 and TSF 2 increased significantly over depth of pond water (Fig. 1). The UNEP Baia Mare report (Moran 2002) indicates that elevated total cyanide concentrations were detected for hundreds of kilometers downstream, for up to four weeks after the Baia Mare spill. The report stated total cyanide in the Tisza River did not decompose quickly as expected or from studies carried out to date.

WAD and total cyanides for the two sampling location increased significantly with increase in depth of decant which is inversely proportional to pH of decant pond. pH of samples ranged from 9.5 to 10.0 for both sampling locations. According to Lighthall et al. (1987), the rate of natural degradation is a function of cyanide type and concentration, pH, temperature, bacteria, sunlight, aeration and pond conditions, such as area, depth, turbidity, turbulence and retention time. At sampling location PBM (TSF1), alkalinity increased from 9.8 to 9.9 over a depth of 5 m of decant pond and total cyanide increased proportionally from 0.36 mg/L to 1.11 mg/L. A similar trend was documented for WAD cyanide concentrations. Higher decant pond depth (10 m) monitored at location PAM (TSF2) with alkalinity increasing from 9.4 at 1 m to 10.0 at 7 m and declined to 9.9 at 10 m; returned elevated Total (from 0.1 mg/L to 0.28 mg/L) and Wad (0.01 to 0.17 mg/L) cyanides with increase in depth. Toxicity cyanide calculated from the difference in Total and WAD cyanide ranges from 0.04 to 0.16 mg/L and there is clear indication from



Fig. 1 Total and WAD Cyanide Levels at Depth

the sampling regime that cyanide concentrations increase with increase in depth which could be attributed to dissociation of cyanide metal complexes. Many aspects of the geochemical behavior and toxicity of complex mixtures such as tailings are poorly known. For example, mining literature frequently states that cyanide naturally breaks down quickly in the presence of sunlight, into relatively harmless, non-toxic substances (Botz *et al.* 1999).

Practically, there is a restriction on the depth of light penetration in the tailings decant pond due to high turbidity. According to Moran (2002), studies conducted over the last twenty years by various authors represent useful discussion on the presence and toxicity of cyanide forms on the environment. A report sponsored by the Mining and Cyanide Manufacturing Industries states: "Since cyanide oxidizes when exposed to air or other oxidants, it decomposes and does not persist. While it is a deadly poison when ingested in a sufficiently high dose, it does not give rise to chronic health or environmental problems when present in low concentrations" (Logsdon et al. 1999). This statement is misleading and presents a falsely benign picture.

Metals, Trace Elements, Physicals and Anions Concentration

According to Clarke *et al.* (1987), cyanide species may be considered to act chronically on the environment in three distinct ways. The first is to produce a direct and ongoing minor acute poisoning, resulting in chronic symptoms, including anomalies in the nervous system of many of the higher organisms. The second is by the formation as well as the action of

its compound thiocyanate in interfering with certain common metabolic pathways. Lastly, because cyanide (and thiocyanate) is capable of complexing metals contained in natural water supplies, organisms using this water could either be subjected to toxic doses of certain metals or deficiencies of others. The surplus could arise from metals being retained in solution in assimilable complexes (e.g. Cu), while deficiencies in naturally occurring trace metals could result from the retention of these in non-assimilable complexes (e.g. Fe, Cu, Mn, Mg). Variation of average pH with depth in the decant ponds is insignificant and pond ranges from 10.0 at 1 m to 9.9 at depth of 8 m as shown in Table 1. Average conductivity values increased with depth implying elevated Total Dissolved Solids (TDS) as a result of metalcomplex dissociation which releases metals into solution corresponding to WAD and total cyanide speciation levels at depth.

In analyzing the concentration of metals and trace elements in the decant pond of the tailings dams, reference was made to chemical and mineralogical characterization carried out on the tailings and whole ore samples (Anon 2011). Averaged multi-element analysis of decant pond at various depths shows variations with concentrations in the supernatant pond and tailings slurry at the spigoting points and significant metal/trace metals are Ca, Mg, Fe, Cu, Na, Mn and K (Table 2). Significant elements identified conform to both ore and tailings chemistry and geochemistry respectively.

Averaged Na, Mn, Ca, Fe, Cu and Mg concentrations increased significantly with increase in depth whiles K decreased (Figs. 2 and 3). Comparing the concentration of these elements in the decant pond to levels in the su-

Depth	pН	EC	TDS	NH ₃	SO ₄	PO ₄	Cl	NO ₃	NO ₂	•
(m)		(µS/cm)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	
1	10.0	1112	744	0.14	33.40	0.62	26.22	171.44	128.22	
2	10.0	1112	743	0.11	33.80	0.71	25.78	169.28	131.07	
3	10.1	1154	776	0.13	36.60	0.56	26.74	167.22	134.94	
4	10.0	1153	776	0.07	34.80	0.58	26.32	176.22	129.49	
5	10.1	1154	779	0.06	34.80	0.67	22.75	221.70	116.63	
6	10.1	1167	787	0.15	34.80	0.62	25.80	160.40	133.17	Δ
7	10.1	1170	788	0.10	37.67	0.66	27.80	177.63	141.87	П
8	9.9	1169	759	0.16	36.50	0.77	22.00	216.65	115.08	

Table 1 Mean Physical and Anion Levels in Decant Pond of TSF 1 and 2

Wolkersdorfer, Brown & Figueroa (Editors)

Depth	Ca	Mg	Fe	Cu	Ni	Mn	Pb	Zn	Na	K	Ag	As
m	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
1	10.4	0.40	1.66	0.67	0.02	0.48	0.09	0.03	177.6	23.34	0.01	0.03
2	10.8	0.40	1.50	0.70	0.03	0.41	0.11	0.03	178.2	24.66	0.02	0.03
3	10.7	0.39	1.91	0.81	< 0.02	0.57	0.17	0.02	180.4	20.84	0.02	0.03
4	10.6	0.43	1.92	0.79	< 0.02	0.55	0.27	0.02	180.9	19.00	0.01	0.03
5	10.3	0.41	2.16	0.84	< 0.02	0.72	0.10	0.02	183.3	20.75	0.01	0.03
6	10.0	0.43	2.15	0.83	< 0.02	0.73	0.15	0.02	184.3	20.68	0.01	0.03
7	11.3	0.53	2.37	0.83	< 0.02	0.86	0.16	0.02	184.2	20.73	0.02	0.03
8	13.3	0.68	2.50	1.01	< 0.02	1.29	0.17	0.06	185.5	22.12	0.01	0.04
SP	10.3	0.14	0.58	0.19	0.02	1.13	0.02	0.09	169.0	20.09	0.02	0.04
T1	12.5	0.15	0.75	0.96	0.03	1.25	0.02	0.01	210.8	15.07	0.02	0.04
T2	11.4	0.12	0.90	0.92	0.03	1.30	0.02	0.03	211.8	19.61	0.02	0.03

Table 2 Mean Metal andTrace Metal Concentrationsin Decant Pond of TSF 1 and2, Supernatant Ponds andUnderdrainages for TSF1and TSF2

Note; SP = Supernatant Pond, T1 = Tailings Slurry from TSF 1, T2 = Tailings Slurry from TSF 2

pernatant pond (supernatant tower), which was 22 m deep at the time of sampling and at the same level as the underdrainage channels. Metals identified in the decant pond, underdrainage sump and tailings slurry were Na and Mg with trace elements being Fe, Cu, Mn, As, Ni, Zn and Cr, whiles alkali metals identified were Ca and K. The average concentrations of Na, Mg, Mn, Fe, Ca, Cu and K increase with depth whiles Zn, As, Ni and Cr increased at 7 m (Figs. 2 and 3) The tailings geochemistry indicated that silica was dominant as well as the presence of Ca, Mg, Fe, Cu, Na, Mn and K. Significant metals and trace elements identified in the in the decant pond were consistent with that of ore geochemistry (Table 3), tailings and in the underdrainage system.

Conclusion and Recommendations

It has been reported in the literature that free cyanide in nature, breaks down completely to CO_2 or nitrated compounds, which is not often

Mineral SQ-XRD	Chemical Formula	WT (%)
Quartz	SiO ₂	87.96
Albite	Na(AlSi ₃ O ₈)	4.74
Talc	Mg ₃ (Si ₄ O ₁₀)(OH) ₂	2.65
Hematite	Fe_2O_3	2.57
Clinochlore/Chlorite	Mg ₂ Al ₃ (Si ₃ Al)O ₁₀ (O) _e	1.34
Annite	KFe ₃ AlSi ₃ O ₁₀ (OH) ₂	0.74

Table 3 Ore Geochemistry at GFGL

the case as demonstrated in this study. Compounds of metals do form and resist decomposition in natural environments for long periods of time. Cyanide compounds assumed to be "destroyed" or "not-present" are in fact present and continually emit harmfµL/toxic components.

Both WAD and total cyanide concentrations increase significantly with increase in depth in the decant pond and consistent in both TSF 1 and 2. Total cyanide ranged from 0.1 mg/L to 1.11 mg/L whiles WAD cyanide concentrations ranged from 0.01 mg/L to 0.93 mg/L.





Fig. 3 Mg Concentrations with Depth

pH in the decant pond, tailings slurry and underdrainage supernatant tower remains alkaline with values ranging from 9.4 to 10.6. Comparing this to the natural pH of groundwater (4.5 to 5.6) in the study area, an unsaturated interface is created which could lead to water movement from the facility into aquifers.

Ore and tailings geochemistry indicates that silica is dominant and the presence of Ca, Mg, Fe, Cu, Na, Mn and K in the tailings dam. Significant metals and trace elements from laboratory analysis is consistent in the four components of the study; ore, tailings slurry, decant pond and in the underdrainage system. Average metal concentrations increased in depth of decant pond. Significant increased in average concentrations of Ni, Zn, Cr and As were recorded at depths exceeding 7 m in the decant pond was recorded whiles Ag concentrations decreased over the same depth of decant pond. It can be concluded from the study that Ag complexes at depth due to reduced concentration at high depths of the decant pond

References

Botz MM, Mudder TI (1999) Modeling of cyanide degradation in tailings impoundments, SME Annual Meeting, March 1–3, 1999, Denver, Colorado.

- Clarke MC, Linkson PB (1987) The Toxicity and Degradation of Cyanide in Mine Tailings. Mining and Environment, A Professional Approach, National Conference, Brisbane. Pp 87-93.
- Eisler R (1991) Cyanide Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review: Contaminant Hazard Review report 23, U. S. Dept. Interior, Fish and Wildlife Service, Pp. 55.
- Flynn, C. M. and S. M. Haslem 1995, Cyanide Chemistry—Precious Metals Processing and Waste Treatment: U. S. Bur. Of Mines Information Circular 9429.
- Heming, TA, Blumhagen K A (1989) Factors Influencing Thiocyanate Toxicity in Rainbow Trout Salmo gairdneri: Bull. Environ. Contam. Toxicol. V. 43, P363–369.
- Logsdon MJ, Hagelstein K, Mudder TI (1999) The Management of Cyanide in Gold Extraction: International Council on Metals and the Environment, Ottawa, Canada.
- Lighthall PC, Bruce IG, McLeod HN (1987) Tailings Management for Cyanide Leach Gold Plant. Klohn Leonoff Ltd, Richmond, British Columbia.
- Moran RE (2002) De-Coding Cyanide, An Assessment of Gaps in Cyanide Regulation at Mines. A Submission to the European Union and the United Nations Environmental Programme.

Impact of temperature on weathering rates – a long-term kinetic study on waste rock from Bergslagen, Sweden

Lotta Sartz¹, Mattias Bäckström²

¹Bergskraft Bergslagen, Harald Olsgatan 1, SE-714 31 Kopparberg, Sweden, lotta.sartz@oru.se ²Man-Technology-Environment Research Centre, Örebro University, SE-701 82 Örebro, Sweden, mattias.backstrom@oru.se

Abstract To assess the impact of different climatic conditions four weathering systems with waste rock from Bergslagen, Sweden, were followed. Secondary weathering products (ferrous and ferric sulphates and (oxy)hydroxides) on pyrite surfaces can slow down oxidation rates. It was investigated if repeated freezing/thawing could have an effect on the stability of the secondary product layer. After 90 weeks of weathering, freezing/thawing had not enhanced weathering rates, not even in combination with warm, humid air. Highest weathering rates were unexpectedly found in a reference system constantly kept at room temperature, and not in the more forceful humidity cell system.

Keywords climate, prediction, acidity, pH, iron, mineralogy

Introduction

Acid rock drainage (ARD) is a large environmental problem, mainly arising from mining of sulphidic ore. When exposed to oxygen, some sulphide minerals, like pyrite (FeS₂), produce acid. Low pHs then promotes leaching of primarily iron and cationic trace elements like copper, zinc and lead and hence affects the surrounding environment by bringing these metals in solution (Chandra and Gerson 2010).

The shrinking-core model is widely used to describe reactions at a particle's surface. According to the model, a product layer forms around the core and the unreacted core shrinks while the product layer grows (Safari *et al.* 2009; Szubert *et al.* 2006). In the case of pyrite oxidation, a product layer consisting of ferrous and ferric sulphates and (oxy)hydroxides forms on the surface of the pyrite particle (fig. 1) and as the oxidation reaction proceeds, oxygen transport to the pyrite surface is retarded and hence slows oxidation rates (Jerz and Rimstidt 2004).

The aim of this study was to investigate effects from freezing and thawing on oxidation rates and more specifically: if the product layer formed is affected by physical weathering caused by repeated freezing/thawing cycles. A scenario of a crack in the product layer is illustrated in fig. 1, enabling exposure of unoxidized pyrite surfaces and accordingly further acid production. If the product layer is susceptible to break from the physical stress, more effects from freezing/thawing would be expected in regions with no permafrost but many freeze/thaw cycles in the spring. Re-



Fig. 1 Schematic illustration of the shrinking-core model and a crack in the product layer, enabling exposure of unoxidized pyrite surfaces and further acid production.

gional climate condition could therefore be a key parameter for ARD prevention and mitigation and in that case, it is important with climate specific test methods for accurate mine water chemistry prediction.

Materials and Methods

Waste rock used in the experiments was sampled at the historical mine site Ljusnarsbergsfältet in Kopparberg, approximately 200 km NW of Stockholm, Sweden. Collected rocks were crushed with a jaw crusher and then screened. A fraction of 1–4 mm were taken out and distributed into eight 250 g samples. Each 250 g sample was put in a 2 L plastic container, and was thereafter treated according to a weekly leaching scheme.

Waste rock

An ocular investigation of the material indicated that sulphides (pyrrhotite, pyrite, chalcopyrite and sphalerite) were present in all rocktypes but with different matrix and that about 60 % of the rocks had a matrix dominated by amphibole skarn, 35 % had a silicified matrix ("ore-quartize"), 4 % had a biotite-amphibole-skarn matrix and 1 % a biotiteflourite-amphibole skarn matrix. Results from XRD-analysis of the material are shown in Table 1 and elemental composition is shown in Table 2.

All systems were based on the standard protocol for humidity cell testing: weathering for six days followed by leaching with deionized water on the seventh day. Leaching schemes for the systems are shown in fig. 2. System (i) – (iii) started in January 2011, while system (iv) started in March 2012. All systems were run in duplicates

Climate chamber

The humidity chamber was constructed from three 2 L containers which had been cut off and piled on each other. The bottom container

Mineral	Formula	Weight-%
Quartz	SiO ₂	30.7
Pyrite	FeS ₂	12.3
Pyrrhotite	Fe ₇ S ₈	11.3
Magnetite	Fe ₃ O ₄	6.0
Hornblende	NaCa2(Mg,Fe,Al)5[AlSi6O22](OH)2	20.7
Phlogopite	K(Mg,Fe) ₃ [AlSi ₃ O ₁₀](OH,F) ₂	8.9
Spangolite	$Cu_6Al(SO_4)(OH)_{12}Cl^*3H_2O$	3.0
Sphalerite	ZnS	3.7
Chalcopyrite	CuFeS ₂	3.4

Table 1 Results from XRD analysis on the waste rock (weight-%). The sample was finely ground and examined with XRD with CuK. Concentrations were calculated by Rietveld analysis.

Element	%	Element	mg/kg	
Si	35	As	<0.3	
Al	4.6	Cd	7.3	
Са	6.8	Со	110	
Fe	33	Cr	400	
К	0.98	Cu	8000	Table 2 Elemental composi-
Mg	3.7	Ni	6.8	tion of the waste rock. Total
Mn	0.12	Pb	310	digestion in microwave oven
Na	0.17	S	104000	with nitric acia. Analysis nerformed with ICP-AES and
Р	0.02	Zn	3800	(ICP-SFMS.



Fig. 2 Leaching scheme for the four systems. All systems were run in duplicates. (i) weathering in room temperature (6 days), (ii) weathering in room temperature (3 days) alternated with freezing conditions, -20 °C (3 days), (iii) weathering in room temperature (3 days) alternated with humid air, 25 °C (3 days; standard humidity cell) and (iv) weathering at freezing conditions, -20 °C (3 days) alternated with humid air, 25 °C (3 days).

collected the fluid and had a hole that was fitted with a 4 mm hose to release air. The sample was placed in the middle container. For air/water to pass through the sample 20 4 mm holes were drilled in the bottom of the container. Under the sample in the bottom of the container was a filter that prevented the smaller particles from leaving the sample. The top container was used as a lid and air inlet. Humid air was obtained by deionized water heated by an immersion heater to 25 °C in a 10 L container. Air was pumped into the container, where it was divided into small bubbles. The humid air was led through a tube that went into the upper container of the humidity chamber and out through the hole in the lower container. System (iii) was exposed for dry air at room temperature for 3 days, thereafter the climate chamber for 3 days followed by leaching (following the standard protocol for humidity cell testing; fig. 2)

Freezing/thawing

Samples were frozen for 3 days at -20 °C and were then brought to room temperature (16 °C) or climate chamber for system (ii) and (iv), respectively, where they thawed and then stayed for 3 days, followed by leaching (fig. 2).

Reference system

Two reference containers were also rinsed and sampled weekly, system (i). In the reference test, the same kind of containers was used as in the previously described systems. The reference samples stayed at room temperature (16 °C) throughout the whole cycle, followed by leaching (fig. 2).

Leaching and Analytical

Samples were leached with 500 mL deionized water and the samples stayed immersed in the

System		Until week	36		Until week	Until week 90		
	рН	El. Cond.	Acidity	pН	El. Cond.	Acidity		
		(µS/cm)	(meq/L)		(µS/cm)	(meq/L)		
(i)-a	4.28	109	0.18	4.30	95.0	0.15		
(i)-b	4.18	117	0.18	4.19	109	0.16		
(ii)-a	5.04	31.7	0.04	4.87	52.0	0.04		
(ii)-b	5.02	29.2	0.03	4.85	52.6	0.05		
(iii)-a	4.61	76.9	0.11	4.56	80.5	0.11		
(iii)-b	4.44	90.9	0.14	4.44	78.3	0.12		
(iv)-a	3.38	81.1	0.06	-	-	-		
(iv)-b	4.62	54.8	0.05	-	-	-		

Table 3 Average values for pH, electrical conductivity (μS/cm) and acidity (meq/L) for the different systems. Until week 90 for systems (i)-(iii) and until week 36 for all systems.



Fig. 3 pH in systems (i)-(iv) plotted against weeks of weathering, a and b denote replicates of each system.

Fig. 4 Sulphate concentrations (mg/L) in systems (i)-(iv) plotted against weeks of weathering, a and b denote replicates of each system.

water for one hour. Samples were collected for analysis of pH, Eh, electrical conductivity, alkalinity/acidity, inorganic anions and major and trace elements.

Electrical conductivity, pH and redox potential were determined immediately after sampling using relevant electrodes. Alkalinity (end-point pH 5.4) and acidity were determined through titration with HCl and NaOH, respectively. Inorganic anions (chloride, fluoride and sulphate) were analysed with ion chromatography. Elemental analysis was performed using ICP-MS. Photographs were taken weekly in order to study the evolution of the secondary precipitates.

Results and Discussion

Average values for general parameters (pH, electrical conductivity and acidity) are shown in Table 3 and pH against week of weathering is shown in fig. 3. All three systems were run in duplicates and gave almost identical results After 36 weeks of weathering average pH in the different systems were 5.0; 4.0; 4.5 and 4.2 for systems (ii), (iv), (iii) and (i), respectively. After 90 weeks of weathering for systems (i) – (iii), average pH:s were generally the same as after 36 weeks.

Sulphate concentrations plotted against week of leaching is shown in fig. 4. It is obvious that the systems with highest pH (freeze treated systems, (ii) and (iv)) have the lowest



Fig. 5 Magnesium concentrations (μg/L) in systems (i)-(iv) plotted against weeks of weathering, a and b denote replicates of each system.

sulphate concentrations. Interesting to note is that the so called reference system (i) has lower pH (fig. 3, Table 3) and higher sulphate concentration than the humidity cell system (iii).

Molar ratios between sulphate and iron $(SO_4^{2^-}/Fe)$ were very close to two for systems (i) and (iii), *i.e.* in agreement with the stoichiometry for pyrite oxidation (Eq. 1; Li *et al.* 2007). This was not seen in the freeze treated systems ((ii) and (iv)), where $SO_4^{2^-}/Fe$ was > 2.

$$FeS_{2} + \sqrt[1]{4}O_{2} + \sqrt[7]{2}H_{2}O \rightarrow$$

Fe(OH)₃ + 4 H⁺ + 2 SO₄²⁻ (Eq. 1)

Calcium and magnesium are good indicators of weathering, through dissolution of buffering minerals like *e.g.* magnesite, calcite or magnesium silicates. Fig. 5 shows concentration of magnesium plotted against weeks of weathering. It again becomes apparent that the freeze treatments ((ii) and (iv)) has a lower degree of weathering than the two other systems. At this point of the experiment the results, somewhat surprisingly, point to higher degree of weathering in the reference system, *i.e.* the system standing on the bench at 16 °C, than in the humidity cell system.

Conclusions

It was suspected that the growth of secondary weathering products (ferrous and ferric sul-

phates and (oxy)hydroxides) on pyrite surfaces might slow down oxidation rates, but also that repeated freezing and thawing could have an effect on the stability of the secondary product layer (cracks, channeling and exposure of new pyrite surfaces). The 0.25 pH-unit difference between systems (iii) and (i) could be explained by formation of weathering products (more in system (iii) than (i)) in the initial stages of the experiment. Freeze treatment, however, did not have the suspected effect, not even in combination with humid, warm air (system iv). The experiments are nevertheless still running, giving information on the importance of climate specific test methods for mine water chemistry prediction.

Acknowledgements

The authors thank prospecting geologist Mr. Stefan Sädbom and Mr. Erik Larsson for assistance in sampling of the waste rock and weekly analysis of chemical parameters, respectively.

References

Chandra AP, Gerson AR (2010) The mechanisms of pyrite oxidation and leaching. Surf Sci Rep 65:293–315

Li J, Smart RSC, Schumann RC, Gerson AR, Levay G (2007) A simplified method for estimation of jarosite and acid-forming sulfates in acid mine wastes. Sc Total Environ 373:391–403 Jerz JK, Rimstidt JD (2004) Pyrite oxidation in moist air. Geochim Cosmochim Acta 68(4):701-714

Safari V, Arzpeyma G, Rashchi F, Mostoufi N (2009) A shrinking particle – shrinking core model for leaching of a zinc ore containing silica. Int J Miner Process 93(1): 79–83 Szubert A, Lupiński M, Sadowski Z (2006) Application of shrinking core model to bioleaching of black shale particles. Physichochem Probl Miner Process 40:211–225
Modeling Application in Evaluating Environmental Impact due to Phosphate Mining Activities

Xin Song¹, Gaston Leone²

¹100 Montgomery Street, Suite 300, San Francisco CA USA, xin.song@arcadis-us.com ²630 Plaza Drive, Suite 100, Highlands Ranch, CO USA, gason.leone@arcadis-us.com

Abstract This paper presents a modeling application to evaluate the environmental impact to water resources due to proposed phosphate mining activities. The proposed project has the potential to impact surface and groundwater resources due to metals and other constituents release into the environment. A numerical groundwater flow and solute transport model has been developed to support the water resource impact analysis for the project environmental impact statement. The results of this quantitative assessment played a fundamental role in preparing the environmental impact statement and assisted in the mine design for permitting.

Keywords Mining Modeling, Environmental Impact, Permitting, Groundwater, Surface Water

Introduction

The Blackfoot Bridge Project (the project) proponent proposed to develop an open pit mine in Caribou County, Idaho, to recover phosphate ore. The proposed mining activities have the potential to impact surface water and groundwater resources and release metals and other constituents into the environment; hence, the Pocatello Field Office of the U.S. Department of Interior, Bureau of Land Management (BLM) prepared an Environmental Impact Statement (EIS). The Idaho Department of Lands (IDL), the Idaho Department of Environmental Quality (IDEQ), and the U.S. Army Corps of Engineers (USACE) were cooperating agencies for the preparation of the EIS.

A numerical groundwater flow and contaminant fate and transport model has been developed to support the impact analysis for the EIS and to analyze the proposed project's compliance with applicable Clean Water Act provisions and state water quality standards. This paper describes the development of the groundwater flow and contaminant fate and transport model and its application to predict potential impacts to surface and groundwater resources as a consequence of the proposed mining activities. Specially, the Blackfoot River, located to the north of the project (Fig. 1), is designated as a Special Resource Water recognized as needing protection to maintain outstanding characteristics and current beneficial uses.

Site background and project summary

The proposed mine consists of an open pit that would be mined in three panels (North Pit, Mid Pit, and South Pit) and includes auxiliary mine facilities (Fig. 1). Mining activities are expected to occur over a 17-year period and include construction of overburden piles and ore stockpiles, pit backfilling, construction of water control ponds, construction of water management facilities, and reclamation of impacted areas.

General goals of this groundwater modeling are to: (1) simulate the pre-mining groundwater system and its interaction with surface waterbodies in the area that could be affected by the project and (2) serve as a tool for evaluating the potential impacts on surface and groundwater resources associated with the proposed mining activities. The specific objectives of the model for the EIS impact analysis are to: (1) estimate groundwater inflow and dewatering requirements (if needed) for the open pits, (2) predict potential changes in groundwater/surface water levels and quality during mining operations and after closure, and (3) estimate potential impacts to groundwater and surface water quality associated with leachate from mine facilities including open pits, backfills, external waste dumps, and ore stockpiles. In addition to the objectives stated above, the model is intended to be used as a decisionmaking tool that is updatable and can be used to evaluate project alternatives. Furthermore, it may be used to establish operational monitoring and compliance points, evaluate mitigation strategies, and determine practical compliance levels for constituents of concern in groundwater and surface water.



Fig. 1 Proposed Mine Facilities

Conceptual Site Geology and Hydrology

A generalized stratigraphic column of the project area is shown on Fig. 2. The stratigraphic section includes Quaternary-age alluvium, colluvium, and travertine deposits; Tertiary-age basalt flows, tuff, and rhyolite; and Mississippian- to Triassic-age sedimentary rocks, including sandstone, siltstone, shale, dolomite, and limestone.

The structural geology in the project area is very complex. The Aspen Range Fault is a major structural feature that discharges deeply circulating groundwater to a series of springs (such as Woodall Springs) and wetlands along the mountain front and has a significant influence on the regional groundwater flow near the project area. Rocks in the Mid Pit and South Pit are cut by a series of high-angle normal faults that strike northeast and generally dip north. Displacement of bedding along the faults is usually minor, with the exception of the Offset Fault. The Offset Fault separates the Mid Pit from the South Pit and displaces bedding on the south side of the fault about 300 m to the east.

Several streams and surface waterbodies occur within or near the project area (Fig. 1). The major surface water feature is Blackfoot River, which flows west along the northern property boundary.

Model code selection and model construction

The groundwater model was developed using the numerical code MODFLOW-SURFACT (HydroGeologic 1996), which is a comprehensive three-dimensional groundwater flow and solute transport modeling code based on the United States Geological Survey (USGS) modular groundwater flow code MODFLOW (Mc-Donald and Harbaugh 1988). MODFLOW-SUR-FACT is functionally identical to the standard MODFLOW code with several enhancements for improved handling of unsaturated cells and pumping wells. MODLFOW-SURFACT was selected because of its ability to handle steep hydraulic gradients and cell re-wetting, which



Fig. 2 Generalized Column and Stratigraphic Section of the Project Area

are anticipated to occur during mine inflow and pit dewatering simulations.

MODFLOW-SURFACT can simulate variably saturated groundwater flow and solute transport. Detailed descriptions of MODFLOW-SURFACT capabilities, mathematical formulation, and model verification are presented in its user's manual (HydroGeologic 1996). MOD-FLOW-SURFACT is also selected as the solute transport model because it uses state-of-theart numerical schemes for solving the transport equation. The Total Variation Diminishing flux limiting schemes included in the code are designed to provide accurate, physically correct, and strictly mass-conservative numerical solutions. An adaptive implicit scheme is used to minimize temporal discretization errors. The matrix equations resulting from the finite-difference approximations are solved using an efficient Orthomin matrix solver. The primitive mass-conservative form of the transport equation is used, providing strictly massconserved numerical solutions.

The model domain covers an area of approximately 70 km², which is large enough to

encompass the potential water resources impacts. The model domain extends approximately 10 km along the south-north axis. Along the west-east axis, the model domain extends approximately 8 km. The southeastern model boundary runs along the State Land Creek watershed divide. The boundaries of the model grid were set at a significant distance from the project area to minimize the influence of model boundaries on simulation results. The horizontal grid cell spacing was based on the size of the area of interest, the total area of the model domain, and the degree of accuracy and precision needed. The finitedifference grid is composed of 204 columns and 400 rows. There are 979,200 cells in the model, of which 937,800 are active. The model grid was refined to 15×15 m within the project area to more accurately simulate groundwater flow and solute transport. Grid spacing increases and reaches up to 230 m toward the model boundaries. The model domain is discretized into 12 layers that were considered necessary to represent the significant hydrostratigraphic units identified in the conceptual site model, as well as the development of the open pits. Model layers are generally not horizontal and represent multiple hydrostratigraphic units to incorporate the complex geology at the site. Model domain and boundaries conditions are shown in Fig. 3.

The model was initially calibrated to steady-state conditions. Additionally, two types of transient calibrations were performed: one based on seasonal variations in recharge and a second calibration based on the results of a recent aquifer test. Upon completion of the transient calibration, the steadystate model was re-run to confirm that a single set of input parameter values satisfies both the steady-state and transient targets.

Site-specific geochemical characterization studies for the Blackfoot Bridge project have been prepared to evaluate the geochemical characteristics and leaching behaviors of the overburden and ore that would be produced from the proposed mine. Columns were prepared to evaluate the potential release of metals and other constituents from the proposed mine facilities, and leaching tests were conducted over several leaching cycles to obtain leachate concentrations for all potential source areas. Representative samples were prepared for the following source areas (Fig. 1): North Pit Backfill, Mid Pit Backfill, South Pit backfill Northwest Overburden Pile (NWOP), EOP, EOP – segregated Meade Peak overburden and Ore Stockpile.

Selenium was selected as the contaminant of concern for the site. Nine columns were designed to evaluate the leaching characteristics of the run-of-mine rock in unsaturated overburden dumps (NWOP, EOP), backfills (North, Mid, and South Pits), stockpiles (Ore Stockpile). Additional columns were designed to evaluate the leaching characteristics of the saturated backfill that would be placed in the North and Mid Pits. The bottom of the South Pit is located above the regional water table; therefore, no saturated backfill is expected to develop after mining. Leachate concentrations were estimated for three pore vol-



Fig. 3 Model Domain and Boundary Conditions

umes for unsaturated source areas and nine pore volumes for saturated source areas.

Selenium leachate concentrations collected from unsaturated columns ranged between 0.002 mg/L at the Dolomite/Limestone and 1.361 mg/L at the unsaturated South Pit backfill source area for the first pore volume. The leachate concentration from the saturated column is significantly lower at 0.003 mg/L for the North and Mid Pits backfill source areas. which is below the applicable regulatory groundwater standard of 0.005 mg/L. The different leaching behavior of selenium in saturated versus unsaturated columns is likely reoxidation-reduction lated to different potential conditions in the two environments (Whetstone 2010). These results indicate that the most significant potential source of selenium contributing to loading in groundwater is leachate from unsaturated source areas. The actual amount of selenium potentially discharging to groundwater would also depend on the net percolation rate through each cover type applied over the source areas.

Three scenarios were evaluated using the constructed model: (1) Proposed Action, (2) Alternative 1A, and (3) Alternative 1B. Three types of cover systems were considered in the three scenarios: the Base Case cover system, the Simple 1 cover system, and the "Complex 2" GCLL cover system. The Base Case cover system design consists of 46 cm of topsoil and 1.2 m of chert. The Simple 1 cover system design consists of 46 cm of topsoil, 0.3 m of weathered alluvium, and 0.6 m of chert. The Complex 2 cover system design is comprised of 46 cm of topsoil, 0.3 m of weathered alluvium, a GCLL layer (sodium bentonite encased between a geotextiles and a synthetic laminate high-density polyethelene or polyvinyl chloride), and 0.3 m of weathered alluvium cover material. The Proposed Action cover involves placing the "Base Case" cover system over a total area of 187 ha, and the "Simple 1" cover system over 9 ha. Alternative 1A involves placing a combination of the "Complex 2" GCLL cover system over 127 ha and the Simple 1 cover system over the remaining 68 overburden pile ha. Alternative 1B consists of the same cover system as Alternative 1A does, except that it will replace the Simple 1 cover over the 48.5 ha of external overburden in the EOP with Complex 2 cover system, which results in covering the entire EOP with a GCLL cover.

The simulation results for Alternative 1 A are shown in Fig. 4 and Fig. 5. Fig. 4 presents the simulated maximum selenium plume in the groundwater due to the mining activities; and Fig. 5 shows the anticipated impact of selenium to the surface water in the vicinity of the project. Reach 1 concentrations reach the maximum after about 50 years and remain stable until year 248. Selenium concentrations at Reach 2 reach a plateau after approximately 250 years and remain stable for a long period of time. Selenium concentrations at Blackfoot River Reaches 1 and 2 are not expected to exceed 5 μ g/L. A sensitivity analysis was conducted to evaluate uncertainties related to two key parameters: the hydraulic parameters within the Wells Formation and the unsaturated and saturated source strengths.

Conclusion

Numerical modeling and quantitative analysis are necessary to facilitate mining activity evaluation and to mitigate unacceptable impacts



Fig. 4 Simulated Selenium *Extent in Alternative 1A*

Wolkersdorfer, Brown & Figueroa (Editors)





to ground and surface water resources. The numerical modeling analysis conducted in this study was able to evaluate project alternatives by quantifying the potential impact to groundwater and surface water resources in the vicinity of the project; hence, support the preparation of the EIS.

References

HydroGeoLogic, Inc. 1996. MODFLOW-SURFACT Software Version 2.2. Code Documentation Report. MacDonald, M.G. and Harbaugh, A.W. 1988. A modular three-dimensional finite-difference groundwater flow model: U.S. Geological Survey Techniques of Water Resources Investigations Book 6, chapter A1.
Whetstone Associates. 2010. Baseline Geochemical Characterization Study, Blackfoot Bridge Mine EIS. Prepared for U.S. Department of Interior Bureau of Land Management, Idaho Falls District, Pocatello Field Office.

Realistic simulation of acid mine drainage generation in the gold mines of the Witwatersrand, South Africa

S. Tlowana, H. Coetzee, M. Makgae

Council for Geoscience, 280 Pretoria Street, Silverton, Private Bag x112, Pretoria, 0001, Republic of South Africa, stlowana@geoscience.org.za

Abstract Acid mine drainage generated in Witwatersrand mines has been identified as an environmental challenge. Following the cessation of underground mining, interconnected mine voids have been allowed to flood, posing a threat to the environment when acidified water discharges into the shallow aquifers and surface streams. The voids include an upper aerated zone overlying a saturated zone. Sulphides exist in both environments, contributing to the total contaminant load. A kinetic experiment was undertaken to simulate these conditions and assess the relative contributions to the generation of AMD. Results confirm that AMD generation is retarded in a completely flooded environment.

Keywords Acid Mine Drainage, Witwatersrand, gold mines voids, pyrite, oxidation

Introduction

Gold mining in the Witwatersrand area started in 1886 and continued to date, with majority of the mines ceasing underground operations in the 1970s. During almost this entire period gold was mined in three main, different, areas namely: the Eastern Basin (Springs-Nigel area), the Central Basin (Johannesburg area) and the Western Basin (Krugersdorp-Randfontein area), while additional quantities were mined in later years. In all three basins mining was mainly undertaken underground via vertical and steep inclined shafts. As a consequence of these mining activities a significant amount of waste tailings and underground mine voids were produced. The cessation of mining and abandonment of mines resulted in mine voids being flooded, with the first discharge to surface occurring in 2002 in the Western Basin. A similar situation could occur in the Eastern and Central basins (Ramontia et al. 2011), unless adequate steps are taken to prevent this.

The geochemical interaction of the underground water with sulphide (mainly pyrite) bearing rock and waste tailings dumps in the presence of oxygen generates acidic mine water which has a significantly high metals and salt load. The oxidation of iron pyrite (FeS₂) and the release of acidity into waters flooding underground mining voids has been described elsewhere (Singer and Stumm 1970, Tutu *et al.* 2008).

Rationale

Since the underground mine voids in the Witwatersrand gold mining basins are rapidly flooding with water, there are concerns regarding the fate of the mine water that is being generated. Two opinions regarding the management of this problem have been expressed:

- 1. The mine water should be pumped out and be treated for discharge purposes in which case the walls of the mine voids with pyritic rock will be further exposed to oxygen.
- 2. The mine voids should be allowed to flood with water which will be devoid the oxygen and oxidation of the pyritic rock will be limited.

This experiment therefore aims to simulate these two scenarios and to understand which of the two options above generate better quality mine water. It was decided to carry out column leach experiments simulating the two conditions and results are presented in this paper.

Materials and methods

A two column experiment was set up in a way to resemble saturated and unsaturated underground mine void conditions. Approximately 8 kg of a pyrite bearing rock was acquired from one of the Witwatersrand Western Basin mines and stored in a sealed plastic container to protect the material from oxidation. The sample was crushed to a particle size of 100 % <4 mm and split into equivalent portions using a ten way rotating splitter. Portions of the materials were analysed for mineralogy, metals and total sulphur content. These results are illustrated on Table 1, 2 and 3.

Two columns made of Perspex and of identical dimensions 50 mm internal diameter (*i.d*) and a height (*h*) of 480 mm, C_A and C_B were packed with 1272 g and 1278 g of the split material respectively. Each column was inoculated with 500 mL of AMD sample acquired from a shaft which was discharging AMD to the surface. The AMD was inoculated into the columns to introduce iron oxidizing bacteria (*Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*) to the sample in order to achieve optimum oxidation conditions. The columns were left to incubate for a period of 192 hours.

Deionised water was used as a leachant and delivered into the columns using a peristaltic pump as the driver at a speed of 3 revolutions per minute (rpm) through 0.51 mm i.d polyvinylchloride pump tubing. One column (C_A) was run in an upward flow configuration, allowing the packed pyritic ore sample to be completely covered in leachant simulating the saturated zones in the underground mine environment. The second column ($C_{\rm B}$) was run from top to bottom with an air inlet allowing oxygen to ingress the column. The column was not allowed to flood, resembling the unsaturated zones in the upper part of the underground mine environment. The first leachate was collected over a period of seven days and mainly comprised the AMD that was inoculated. The two columns were continuously leached for 22 weeks at a rate of around 0.45 L/week with leachate collection and analysis performed every seven days. The leachates were syringe filtered using 0.45 µm hydrophilic filter discs. The leachates were then analysed for pH, electrical conductivity (EC), dissolved metals and anions. The leachate solutions were acidified with three to five drops of 3M Nitric acid (HNO₃) prior to dissolved metals analysis.

Results and discussion

The mineral composition results illustrated in Table 1 indicate that the predominant component is quartz with a 80 % weight fraction, followed by pyrophyllite at 12 % and pyrite at 9 %. Mineral composition and the total sulphur results of 4.32 wt. % is a good indication that the material is a good source of sulphide for AMD studies.

X-Ray Fluorescence (XRF) results presented on Tables 2 and 3 confirms that the material contains predominantly quartz and has a potential to release significantly high con-

Mineral	Composition (weight %)	Mineral	Composition (weight %)	Table 1 X-Ray Diffraction (XRD) mineralogical deter-
Quartz	74	Jarosite	1	mination on the pyrite bear-
Pyrophyllite	12	Plagioclase	1	ing ore sample was per- formed and the results are
Pyrite	9	Mica	1	listed below expressed in
Kaolinite/Chlorite	2			weight %.

the pyrite

Element	Concentration (ppm)	Element	Concentration (ppm)	Element	Concentration (ppm)	
As	107	La	129	Pb	58	
Ba	68	Мо	6.3	Rb	5	
Bi	4.1	Nb	12	Sc	8	
Се	228	Nd	73	Se	4.4	
Со	91	Ni	80	Sm	10	<i>Table 2</i> XRF trace elements determination on the pyrite
Cr	509	V	29	Sr	57	bearing sample was per-
Cu	45	Y	12	Та	3.2	formed and the results are
Ga	6.5	Zn	35	Th	34	listed below expressed in
Hf	18	Zr	664	U	83	weight ppm.
Element	Concentration	(weight %)	Element	Concentrat	tion (weight %)	
SiO ₂	80.01		CaO	<0.01		
Fe_2O_3	8.87		Na ₂ O	< 0.01		
Al_2O_3	4.89		MnO	0.002		
TiO ₂	0.41		MgO	<0.01		
K ₂ O	0.11		P ₂ O ₅	0.05		determination on pyrite
Cr_2O_3	0.073					bearing rock

centrations of metals such as As, U, Ni, Co, Al, Zn, Cr and Zr into the water through leaching.

The weekly SO₄²⁻ loads, cumulative loads and the leachate pHs for the two columns are graphically illustrated on Fig. 1. Metal and sulphate concentrations, pH, EC and volume results of the leachate analyses from the column leach experiments, for a period of 22 weeks, are provided in Table 4.

Results for the two columns for week o showed high values for EC, metal and sulphate concentrations and pH values lower than 3 followed by sharp decreases and increase respectively. This is due to the AMD aliquot that was inoculated into the columns.

From weeks 4 to 22 the EC, metals and sulphate concentrations for column CA showed a steady decrease and increasing pH. This is indicative that pyrite oxidation and associated acid generation is inhibited. Column CB results showed steady increases in EC, metal and sulphate concentrations and a decrease in pH from weeks 4 to 18. From week 19, column B results showed a sharp increase in EC, metals and sulphate concentrations and sharp decreases in pH with values well below 2.5. The results for column C_B showed that there is acid generation from pyrite oxidation and release of metals into the water.

Conclusion

The purpose of this study was to assess the quality of the mine water produced in the saturated and the unsaturated areas in the underground mine voids in Witwatersrand gold mining area and whether the water should be pumped out or be left to continue flooding to displace oxygen and thereby limit acid generation through oxidation of the pyritic rock. The study revealed that the oxidation of pyrite in the flooded (saturated) zones is severely retarded with pH values above 4.5 and reduced salt loads, however in aerated (unsaturated) zones, pyrite is oxidised and produces a leachate with pH values of below 2.5 and high EC, salt and metal loads. This information can

Weekly load, cumulative load of SO $_4{}^{2 \cdot}\,$ and leachate pH from columns C $_A\,$ and C $_B\,$ for 22 weeks



Figure 1 A graphical illustration of weekly load and cumulative load of $SO_4{}^2$ and leachate pH for column C_A and C_B for 22 weeks.

Week	Column	0	1	2	3	4	5	6	7	8	9	10	11
Al (mg)	CA	136.5	147.7	11.7	3.1	0.999	0.601	0.214	0.170	0.000	0.337	0.223	0.191
(8)	C _B	316.0 2.40	4.27	1.77	0.278	0.116	0.115	0.236	0.388	0.000	2.987	1.191	0.644
Co (mg)	Св	5.28	0.215	0.0214	0.010	0.012	0.011	0.013	0.013	0.000	0.057	0.005	0.009
(mg)	CA	2.57	0.868	0.077	0.034	0.000	0.000	0.003	0.000	0.000	0.000	0.000	0.000
cu (ing)	Св	6.83	0.936	0.212	0.017	0.003	0.000	0.002	0.000	0.000	0.086	0.012	0.000
Fe (mg)	C _A	/33.3	834.1 46.40	22 52	28.56	6.40 11.96	2.61	5.81	6.49	2.92	1.44	0.650	0.440 2 5 1
	CA	18.36	19.53	1.51	0.550	0.158	0.066	0.029	0.027	0.020	0.028	0.018	0.016
Mn (mg)	CB	39.17	0.887	0.180	0.074	0.074	0.064	0.060	0.063	0.046	0.099	0.037	0.023
Ni (mg)	CA	4.09	4.82	0.488	0.198	0.066	0.035	0.022	0.025	0.000	0.027	0.000	0.000
(8)	C _B	10.33	0.695	0.176	273.8	0.044	0.040	0.045	0.048	0.039	0.215	0.060	0.038
SO42· (mg)	Св	11758	428.7	103.3	81.19	126.8	65.87	88.96	62.65	112.0	293.9	210.5	182.6
7n (mg)	CA	0.756	1.05	0.369	0.274	0.188	0.215	0.229	0.192	0.000	0.324	0.237	0.188
zn (ng)	Св	1.60	0.000	0.527	0.000	0.153	0.172	0.237	0.177	0.000	0.433	0.212	0.158
рН	CA	2.90	3.04	3.52	3.39	3.11	2.59	3.28	3.28	3.27	3.29	3.33	3.39
	C _B	2.85	3.50 4280	3.00	3.79	571	3.09	3.38	3.24	3.08	3.19	278	276
EC (µS/cm)	Св	8690	347	273	225	230	241	310	350	403	484	408	382
Vol (mI)	Ca	240	740	400	480	420	450	400	460	400	530	450	420
voi (iiiL)	Св	660	1640	800	430	460	465	400	410	400	520	450	420
Week	Column	12	13	14	15	16	17	18	19	20	21	22	Σ
Week	Column C _A	12 0.187	13 0.194	14 0.188	15 0.227	16 0.041	17 0.000	18 0.027	19 0.022	20 0.030	21 0.090	22 0.049	Σ 302.8
Week Al (mg)	Column C _A C _B	12 0.187 0.683	13 0.194 14.60	14 0.188 0.847	15 0.227 0.701	16 0.041 0.322	17 0.000 0.110	18 0.027 0.120	19 0.022 10.119	20 0.030 3.374	21 0.090 2.948	22 0.049 1.067	Σ 302.8 362.93
Week Al (mg) Co (mg)	Column CA CB CA	12 0.187 0.683 0.005 0.016	13 0.194 14.60 0.006 0.278	14 0.188 0.847 0.004 0.027	15 0.227 0.701 0.004 0.022	16 0.041 0.322 0.003 0.012	17 0.000 0.110 0.004 0.007	18 0.027 0.120 0.004 0.006	19 0.022 10.119 0.004 0.650	20 0.030 3.374 0.004 0.810	21 0.090 2.948 0.004 0.750	22 0.049 1.067 0.005 0.502	Σ 302.8 362.93 5.15 8.86
Week Al (mg) Co (mg)	Column C _A C _B C _A C _B	12 0.187 0.683 0.005 0.016 0.016	13 0.194 14.60 0.006 0.278 0.049	14 0.188 0.847 0.004 0.027 0.025	15 0.227 0.701 0.004 0.032 0.030	16 0.041 0.322 0.003 0.013 0.000	17 0.000 0.110 0.004 0.007 0.000	18 0.027 0.120 0.004 0.006 0.000	19 0.022 10.119 0.004 0.650 0.000	20 0.030 3.374 0.004 0.810 0.000	21 0.090 2.948 0.004 0.759 0.000	22 0.049 1.067 0.005 0.592 0.000	Σ 302.8 362.93 5.15 8.86 3.67
Week Al (mg) Co (mg) Cu (mg)	Column CA CB CA CB CA CB CA CB	12 0.187 0.683 0.005 0.016 0.016 0.033	13 0.194 14.60 0.006 0.278 0.049 1.62	14 0.188 0.847 0.004 0.027 0.025 0.131	15 0.227 0.701 0.004 0.032 0.030 0.186	16 0.041 0.322 0.003 0.013 0.000 0.014	17 0.000 0.110 0.004 0.007 0.000 0.000	18 0.027 0.120 0.004 0.006 0.000 0.000	19 0.022 10.119 0.004 0.650 0.000 4.932	20 0.030 3.374 0.004 0.810 0.000 1.50	21 0.090 2.948 0.004 0.759 0.000 0.749	22 0.049 1.067 0.005 0.592 0.000 0.492	Σ 302.8 362.93 5.15 8.86 3.67 17.76
Week Al (mg) Co (mg) Cu (mg)	Column CA CB CA CB CA CB CA CB	12 0.187 0.683 0.005 0.016 0.033 0.400	13 0.194 14.60 0.006 0.278 0.049 1.62 5.12	14 0.188 0.847 0.004 0.027 0.025 0.131 2.14	15 0.227 0.701 0.004 0.032 0.030 0.186 6.16	16 0.041 0.322 0.003 0.013 0.000 0.014 4.96	17 0.000 0.110 0.004 0.007 0.000 0.000 5.10	18 0.027 0.120 0.004 0.006 0.000 0.000 4.81	19 0.022 10.119 0.004 0.650 0.000 4.932 3.66	20 0.030 3.374 0.004 0.810 0.000 1.50 2.02	21 0.090 2.948 0.004 0.759 0.000 0.749 4.81	22 0.049 1.067 0.005 0.592 0.000 0.492 5.20	Σ 302.8 362.93 5.15 8.86 3.67 17.76 1742.7
Week Al (mg) Co (mg) Cu (mg) Fe (mg)	Column CA CB CA CB CA CB CA CB CA CB	12 0.187 0.683 0.005 0.016 0.033 0.400 3.53	13 0.194 14.60 0.006 0.278 0.049 1.62 5.12 83.12	14 0.188 0.847 0.004 0.027 0.025 0.131 2.14 12.71	15 0.227 0.701 0.004 0.032 0.030 0.186 6.16 15.51	16 0.041 0.322 0.003 0.013 0.000 0.014 4.96 3.15	17 0.000 0.110 0.004 0.007 0.000 0.000 5.10 1.08	18 0.027 0.120 0.004 0.006 0.000 0.000 4.81 2.50	19 0.022 10.119 0.004 0.650 0.000 4.932 3.66 147.8	20 0.030 3.374 0.004 0.810 0.000 1.50 2.02 2.24.0 2.24.0	21 0.090 2.948 0.004 0.759 0.000 0.749 4.81 193.2	22 0.049 1.067 0.005 0.592 0.000 0.492 5.20 161.7	Σ 302.8 362.93 5.15 8.86 3.67 17.76 1742.7 2690
Week Al (mg) Co (mg) Cu (mg) Fe (mg) Mn (mg)	Column CA CB CA CB CA CB CA CB CA CB CA CB	12 0.187 0.683 0.005 0.016 0.033 0.400 3.53 0.014 0.021	13 0.194 14.60 0.006 0.278 0.049 1.62 5.12 83.12 0.022 0.107	14 0.188 0.847 0.004 0.027 0.025 0.131 2.14 12.71 0.021 0.025	15 0.227 0.701 0.004 0.032 0.030 0.186 6.16 15.51 0.019 0.027	16 0.041 0.322 0.003 0.013 0.000 0.014 4.96 3.15 0.014 0.014	17 0.000 0.110 0.004 0.007 0.000 0.000 5.10 1.08 0.013 0.013	18 0.027 0.120 0.004 0.006 0.000 4.81 2.50 0.010 0.012	19 0.022 10.119 0.004 0.650 0.000 4.932 3.66 147.8 0.010 0.227	20 0.030 3.374 0.004 0.810 0.000 1.50 2.02 224.0 0.010 0.045	21 0.090 2.948 0.004 0.759 0.000 0.749 4.81 193.2 0.010 0.022	22 0.049 1.067 0.005 0.592 0.000 0.492 5.20 161.7 0.010 0.231	Σ 302.8 362.93 5.15 8.86 3.67 17.76 17.42.7 2690 40.47 42.42
Week Al (mg) Co (mg) Cu (mg) Fe (mg) Mn (mg)	Соlumn Са Св Са Св Са Св Са Св Са Са Са	12 0.187 0.683 0.005 0.016 0.016 0.033 0.400 3.53 0.014 0.031 0.000	13 0.194 14.60 0.006 0.278 0.049 1.62 5.12 83.12 0.022 0.197	14 0.188 0.847 0.004 0.027 0.131 2.14 12.71 0.021 0.035 0.023	15 0.227 0.701 0.004 0.032 0.030 0.186 6.16 15.51 0.019 0.027 0.000	16 0.041 0.322 0.003 0.013 0.000 0.014 4.96 3.15 0.014 0.014 0.014 0.014	17 0.000 0.110 0.004 0.007 0.000 0.000 5.10 1.08 0.013 0.012 0.000	18 0.027 0.120 0.004 0.006 0.000 4.81 2.50 0.010 0.012 0.000	19 0.022 10.119 0.004 0.650 0.000 4.932 3.66 147.8 0.010 0.227 0.000	20 0.030 3.374 0.004 0.810 0.000 1.50 2.02 224.0 0.010 0.045 0.000	21 0.090 2.948 0.004 0.759 0.000 0.749 4.81 193.2 0.010 0.033 0.000	22 0.049 1.067 0.005 0.592 0.000 0.492 5.20 161.7 0.010 0.021 0.000	Σ 302.8 362.93 5.15 8.86 3.67 17.76 1742.7 2690 40.47 42,43 9.82
Week Al (mg) Co (mg) Cu (mg) Fe (mg) Mn (mg) Ni (mg)	Column CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CA CB CA CB CA CB CA CB CA CB CA CB CA CA CB CA CA CB CA CA CB CA CA CB CA CA CB CA CA CB CA CA CB CA CA CB CA CA CB CA CA CB CA CA CB CA CA CB CA CA CB CA CA CB CA CA CB CA CA CB CA CA CB CB CA CB CB CA CB CB CA CB CB CA CB CB CA CB CB CB CA CB CB CB CA CB CB CB CB CB CB CA CB CB CB CB CB CB CB CB CB CB CB CB CB	12 0.187 0.683 0.005 0.016 0.016 0.033 0.400 3.53 0.014 0.031 0.000 0.054	13 0.194 14.60 0.006 0.278 0.049 1.62 5.12 83.12 0.022 0.197 0.027 1.14	14 0.188 0.847 0.004 0.025 0.131 2.14 12.71 0.021 0.025 0.023 0.083	15 0.227 0.701 0.004 0.032 0.030 0.186 6.16 15.51 0.019 0.027 0.000 0.095	16 0.041 0.322 0.003 0.013 0.000 0.014 4.96 3.15 0.014 0.016 0.000 0.046	17 0.000 0.110 0.004 0.007 0.000 5.10 1.08 0.013 0.013 0.012 0.000 0.027	18 0.027 0.120 0.004 0.006 0.000 4.81 2.50 0.010 0.012 0.000	19 0.022 10.119 0.004 0.650 0.000 4.932 3.66 147.8 0.010 0.227 0.000 1.88	20 0.030 3.374 0.004 0.810 0.000 1.50 2.02 224.0 0.010 0.045 0.000 1.39	21 0.090 2.948 0.004 0.759 0.000 0.749 4.81 193.2 0.010 0.033 0.000 1.13	22 0.049 1.067 0.005 0.592 0.000 0.492 5.20 161.7 0.010 0.021 0.000 0.852	Σ 302.8 362.93 5.15 8.86 3.67 17.76 1742.7 2690 40.47 42.43 9.82 18.47
Week Al (mg) Co (mg) Cu (mg) Fe (mg) Mn (mg) Ni (mg)	Column CA CB CA CB CA CB CA CB CA CB CA CB CA	12 0.187 0.683 0.005 0.016 0.016 0.033 0.400 3.53 0.014 0.031 0.001 0.054 129.7	13 0.194 14.60 0.006 0.278 0.049 1.62 5.12 83.12 0.022 0.197 0.027 1.14 178.0	14 0.188 0.847 0.004 0.027 0.131 2.14 12.71 0.021 0.023 0.023 0.083 83.91	15 0.227 0.701 0.004 0.032 0.030 0.186 6.16 15.51 0.019 0.022 0.000 0.000 0.095 76.46	16 0.041 0.322 0.003 0.013 0.000 0.014 4.96 3.15 0.014 0.014 0.016 0.014 3.15 0.014 0.016 0.000 0.004 31.88	17 0.000 0.110 0.004 0.007 0.000 5.10 1.08 0.013 0.012 0.000 0.027 76.27	18 0.027 0.120 0.004 0.006 0.000 4.81 2.50 0.010 0.012 0.000 0.012 0.000 77.38	19 0.022 10.119 0.004 0.650 0.000 4.932 3.66 147.8 0.010 0.227 0.000 1.88 1.88 27.47	20 0.030 3.374 0.004 0.810 0.000 1.50 2.02 224.0 0.010 0.045 0.000 1.39 44.08	21 0.090 2.948 0.004 0.759 0.000 0.749 4.81 193.2 0.010 0.033 0.000 1.13 68.93	22 0.049 1.067 0.050 0.592 0.000 0.492 5.20 161.7 0.010 0.021 0.000 0.852 16.82	Σ 302.8 362.93 5.15 8.86 3.67 17.76 1742.7 2690 40.47 42.43 9.82 18.47 11729
Week Al (mg) Co (mg) Cu (mg) Fe (mg) Mn (mg) Ni (mg) SO4 ² ·(mg)	Column CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB	12 0.187 0.683 0.005 0.016 0.016 0.33 0.400 3.53 0.014 0.031 0.0054 129.7 181.4	13 0.194 14.60 0.006 0.278 0.049 1.62 5.12 0.022 0.197 0.022 0.197 1.14 178.0 700.3	14 0.188 0.847 0.004 0.027 0.025 0.131 2.14 12.71 0.021 0.035 0.023 0.023 18.91	15 0.227 0.701 0.004 0.032 0.030 0.186 6.16 15.51 0.019 0.027 0.000 0.095 76.46 122.6	16 0.041 0.322 0.003 0.013 0.000 0.014 4.96 3.15 0.014 0.016 0.000 0.014 8.15 3.15 3.15 3.15 3.188 84.44	17 0.000 0.110 0.004 0.007 0.000 0.000 5.10 1.08 0.013 0.013 0.012 0.000 0.027 39.96	18 0.027 0.120 0.004 0.005 0.000 0.000 0.000 0.000 0.010 0.012 0.0010 0.012 0.000 0.77.38 67.18	19 0.022 10.119 0.650 0.650 0.650 0.000 4.932 3.66 147.8 0.010 0.227 0.000 1.88 27.47 785.7	20 0.030 3.374 0.004 0.810 0.000 1.50 2.02 224.0 0.010 0.045 0.000 1.39 44.08 1152	21 0.090 2.948 0.004 0.759 0.000 0.749 4.81 193.2 0.010 0.033 0.000 1.13 68.93 1100	22 0.049 1.067 0.005 0.592 0.000 0.492 5.20 161.7 0.010 0.021 0.000 0.852 16.82 1015	Σ 302.8 362.93 5.15 8.86 3.67 17.76 1742.7 2690 40.47 42,43 9.82 18.47 11729 18949
Week Al (mg) Co (mg) Cu (mg) Fe (mg) Mn (mg) Ni (mg) SO4 ²⁻ (mg) Zn (mg)	Column CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB	12 0.187 0.683 0.005 0.016 0.013 0.033 0.400 3.53 0.031 0.031 0.031 0.000 0.57 129.7 181.4 0.200	13 0.194 14.60 0.006 0.278 0.049 1.62 5.12 83.12 0.022 0.197 0.027 1.14 178.0 0.250	14 0.188 0.847 0.004 0.027 0.025 0.131 2.14 12.71 0.021 0.035 0.023 0.038 83.91 185.9 0.262	15 0.227 0.701 0.004 0.032 0.030 0.186 6.16 15.51 0.0127 0.000 0.095 76.46 0.000 0.022 0.000	16 0.041 0.322 0.003 0.013 0.000 0.014 4.96 3.15 0.014 0.016 0.000 0.014 3.15 3.15 3.15 3.188 84.44 0.000 0.022	17 0.000 0.110 0.004 0.007 0.000 5.10 1.08 0.013 0.012 0.0027 39.96 0.000 0.000	18 0.027 0.120 0.004 0.005 0.000 0.000 0.000 0.000 0.001 0.010 0.012 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000	19 0.022 10.119 0.004 0.650 0.002 4.932 3.66 147.8 0.010 0.227 0.000 1.88 27.47 785.7 0.000 0.577	20 0.030 3.374 0.004 0.810 0.000 1.50 2.02 224.0 0.010 0.045 0.045 0.045 0.045 0.045 1.39 44.08 1152 0.000	21 0.090 2.948 0.004 0.759 0.000 0.749 4.81 193.2 0.010 0.033 0.000 1.13 68.93 1100 0.000	22 0.049 1.067 0.005 0.592 0.000 0.492 5.20 161.7 0.010 0.021 0.000 0.852 16.82 1015 0.000	Σ 302.8 362.93 5.15 8.86 3.67 17.76 1742.7 2690 40.47 42,43 9.82 18.47 11729 18949 4.73
Week Al (mg) Co (mg) Cu (mg) Fe (mg) Mn (mg) Ni (mg) SO4 ²⁻ (mg) Zn (mg)	Column CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CA CB CB CA CB CB CA CB CA CB CB CA CB CB CA CB CB CA CB CB CA CB CB CA CB CB CA CB CB CB CA CB CB CB CA CB CB CB CB CB CB CB CB CB CB CB CB CB	12 0.187 0.6683 0.005 0.016 0.013 0.033 0.400 3.53 0.031 0.031 0.034 0.054 129.7 181.4 0.200 0.272 2.34	13 0.194 14.60 0.006 0.278 0.042 5.12 83.12 0.027 1.14 178.00 0.250 0.773 2.20	14 0.188 0.847 0.004 0.027 0.0131 2.14 12.71 0.035 0.035 0.023 0.083 83.91 185.9 0.262 0.221 2.32	15 0.227 0.701 0.004 0.032 0.186 6.16 15.51 0.0127 0.000 0.095 76.46 0.000 0.000 0.000 0.000 0.000 0.000 2.52	16 0.041 0.322 0.003 0.013 0.000 0.014 4.96 3.15 0.016 0.000 0.016 0.000 0.046 31.88 84.44 0.000 0.000 0.000 0.000 0.297	17 0.000 0.110 0.004 0.007 0.000 5.10 1.08 0.012 0.000 0.027 76.27 79.96 0.000 0.001 0.001 0.000 0.000 0.000 0.001 0.002 0.001 0.001 0.001 0.001 0.002 0.000 0.002 0.000 0.000 0.000 0.002 76.27 0.000 0.000 0.000 0.000 0.002 76.27 0.000 0.000 0.000 0.000 0.002 76.27 0.000 0.000 0.000 0.000 0.002 76.27 0.0000 0.00000 0.00000 0.0000 0.0000 0.000000 0.0000 0.0000 0.0	18 0.027 0.120 0.004 0.006 0.000 4.81 2.50 0.012 0.000 0.012 0.000 77.38 0.000 4.05	19 0.022 10.119 0.004 0.650 0.000 4.932 3.66 147.8 0.010 0.227 0.000 1.88 27.47 785.7 0.000 0.401	20 0.030 3.374 0.004 0.810 0.000 1.50 2.02 224.0 0.010 1.50 2.02 224.0 0.045 0.045 0.045 0.045 0.000 1.39 44.08 1152 0.000 0.349 4.01	21 0.090 2.948 0.004 0.759 0.000 0.749 4.81 193.2 0.010 0.033 0.000 1.13 68.93 1100 0.000 0.245	22 0.049 1.067 0.005 0.592 0.000 0.492 5.20 161.7 0.010 0.021 0.000 0.852 16.82 1015 0.000 0.184	Σ 302.8 362.93 5.15 8.86 3.67 17.7.6 17.42.7 2690 40.47 42.43 9.82 18.47 11729 18949 4.73 6.19
Week Al (mg) Co (mg) Cu (mg) Fe (mg) Mn (mg) Ni (mg) SO4 ^{2.} (mg) Zn (mg) pH	$\begin{array}{c} \textbf{Column} \\ \textbf{C}_A \\ \textbf{C}_B \\ \textbf{C}_A \\ $	12 0.187 0.6683 0.005 0.016 0.033 0.033 0.034 0.031 0.031 0.032 0.031 0.031 0.031 0.031 0.032 0.034 0.0354 129.7 181.4 0.2000 0.272 3.24	13 0.194 14.60 0.006 0.278 0.049 1.62 5.12 83.12 0.027 0.197 0.027 1.14 178.00 0.250 0.773 3.39	14 0.188 0.847 0.004 0.027 0.0131 2.14 12.71 0.035 0.023 0.023 0.023 0.023 0.023 0.023 0.023 0.023 0.023 0.023 0.023 0.023 0.023 0.023 0.262 0.221 3.05	15 0.227 0.701 0.004 0.032 0.186 6.16 15.51 0.027 0.000 0.095 76.46 122.6 0.000 0.000 3.53 3.02	16 0.041 0.322 0.003 0.013 0.010 0.014 0.014 0.014 0.014 0.014 0.014 0.014 0.014 0.016 0.000 0.046 31.88 84.44 0.000 0.000 0.000 3.90	17 0.000 0.110 0.004 0.007 0.000 0.000 0.000 0.012 0.012 0.000 0.027 76.27 39.96 0.000 0.000 0.000 0.000 4.09 3.27	18 0.027 0.120 0.004 0.006 0.000 0.000 0.481 2.50 0.012 0.012 0.000 0.000 0.000 77.38 67.18 0.000 0.000 4.000 0.000 3.30	19 0.022 10.119 0.004 0.650 0.000 4.932 3.66 147.8 0.010 0.227 0.000 1.88 27.47 785.7 0.000 0.472 4.01 2.36	20 0.030 3.374 0.004 0.810 0.000 1.50 2.02 224.0 0.010 0.045 0.000 1.39 44.08 1152 0.000 0.349 4.01	21 0.090 2.948 0.004 0.759 0.000 0.749 4.81 193.2 0.010 0.033 0.000 1.13 68.93 1100 0.000 0.245 4.42 2.26	22 0.049 1.067 0.005 0.592 0.000 0.492 5.20 161.7 0.010 0.021 0.000 0.852 16.82 1015 0.000 0.184 4.69 2.24	Σ 302.8 362.93 5.15 8.86 3.67 17.76 1742.7 2690 40.47 42,43 9.82 18.47 11729 18949 18949 4.73 6.19
Week Al (mg) Co (mg) Cu (mg) Fe (mg) Mn (mg) Ni (mg) SO4 ²⁻ (mg) Zn (mg) pH	$\begin{array}{c} \textbf{Column} \\ \textbf{C}_{A} \\ \textbf{C}_{B} \\ \textbf{C}_{A} \\ \textbf{C}_{A} \\ \textbf{C}_{B} \\ \textbf{C}_{A} \\ C$	12 0.187 0.6683 0.005 0.016 0.033 0.034 0.031 0.031 0.031 0.031 0.031 0.031 0.031 0.031 0.032 0.031 0.031 0.032 0.034 0.030 0.054 129.7 181.4 0.200 0.272 3.24 3.02 255	13 0.194 14.60 0.006 0.278 0.049 1.62 5.12 83.12 0.027 1.14 178.0 0.250 0.773 3.39 2.89 327	14 0.188 0.847 0.004 0.027 0.131 2.14 12.71 0.035 0.023 0.023 0.083 83.91 185.9 0.262 0.221 3.28 3.05 297	15 0.227 0.701 0.004 0.032 0.186 6.16 15.51 0.027 0.000 0.095 76.46 122.6 0.000 0.000 3.02 148	16 0.041 0.322 0.003 0.013 0.004 0.014 0.014 0.014 0.016 0.0016 0.000 0.046 31.88 84.44 0.000 0.000 0.000 3.97 3.00 130.6	17 0.000 0.110 0.004 0.007 0.000 0.000 0.000 0.012 0.012 0.000 0.027 76.27 39.96 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.001 0.004 0.007 0.004 0.007 0.004 0.007 0.004 0.007 0.004 0.007 0.004 0.007 0.000 0.002 76.27 39.96 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.027 76.27 39.96 0.0000 0.0000000 0.0000 0.0000 0.00000000	18 0.027 0.120 0.004 0.006 0.000 0.001 0.000 0.010 0.012 0.000 0.000 0.010 0.010 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 1.22.3	19 0.022 10.119 0.004 0.650 0.000 4.932 3.66 147.8 0.010 0.227 0.000 1.88 27.47 785.7 0.000 0.472 4.01 2.36 129.1	20 0.030 3.374 0.004 0.810 0.000 1.50 2.02 224.0 0.010 0.045 0.000 1.39 44.08 1152 0.000 0.349 4.01 2.15 124.4	21 0.090 2.948 0.004 0.759 0.000 0.749 4.81 193.2 0.010 0.033 68.93 1100 0.000 0.245 4.42 2.26 100.1	22 0.049 1.067 0.005 0.592 0.000 0.492 5.20 161.7 0.010 0.021 0.000 0.852 16.82 1015 0.000 0.184 4.69 2.24 82.7	Σ 302.8 362.93 5.15 8.86 3.67 17.76 1742.7 2690 40.47 42,43 9.82 18.47 11729 18949 4.73 6.19
Week Al (mg) Co (mg) Cu (mg) Fe (mg) Mn (mg) Ni (mg) SO4 ² · (mg) Zn (mg) pH EC (µS/cm)	$\begin{array}{c} \textbf{Column} \\ \hline \textbf{C}_A \\ \hline \textbf{C}_B \hline \textbf{C}_B \\ \hline \textbf{C}_B \hline \textbf{C}_B \\ \hline \textbf{C}_B \hline \textbf{C}_B \\ \hline \textbf{C}_B \hline \hline \textbf{C}_B \\ \hline \textbf{C}_B \hline \hline \textbf{C}_B $	12 0.187 0.663 0.005 0.016 0.033 0.400 3.53 0.014 0.030 0.054 129.7 181.4 0.200 0.272 3.24 3.02 255 384	13 0.194 14.60 0.006 0.278 0.049 1.62 5.12 83.12 0.022 0.197 0.027 1.14 178.0 700.3 0.250 0.773 3.39 2.89 327 1410	14 0.188 0.847 0.004 0.027 0.131 2.14 12.71 0.023 0.023 0.023 0.083 83.91 185.9 0.262 0.221 3.05 297 517	15 0.227 0.701 0.004 0.032 0.186 6.16 15.51 0.019 0.027 0.000 0.095 76.46 122.6 0.000 0.000 3.02 148 472	16 0.041 0.322 0.003 0.013 0.014 4.96 3.15 0.014 0.000 0.044 31.88 84.44 0.000 0.000 3.97 3.00 130.6 466	17 0.000 0.110 0.004 0.007 0.000 0.000 0.000 0.000 0.013 0.013 0.012 0.000 0.027 76.27 39.96 0.000 0.000 0.000 0.000 0.000 30.90 122.1 336	18 0.027 0.120 0.004 0.006 0.000 0.001 0.010 0.010 0.010 0.010 0.010 0.010 0.010 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 1.22.3 282	19 0.022 10.119 0.004 0.650 0.000 4.932 3.66 147.8 0.010 0.227 0.000 1.88 27.47 785.7 0.000 0.472 4.01 2.366 129.1 2066	20 0.030 3.374 0.004 0.810 0.000 1.50 2.02 224.0 0.010 0.045 1.39 44.08 1152 0.000 0.349 4.01 2.15 124.4 3480	21 0.090 2.948 0.004 0.759 0.000 0.749 4.81 193.2 0.010 0.033 68.93 1100 0.000 0.245 4.42 2.26 100.1 3630	22 0.049 1.067 0.005 0.592 0.000 0.492 5.20 161.7 0.010 0.021 0.682 16.82 1015 0.000 0.184 4.69 2.24 82.7 3210	Σ 302.8 362.93 5.15 8.86 3.67 17.76 1742.7 2690 40.47 42,43 9.82 18.47 11729 18949 4.73 6.19
Week Al (mg) Co (mg) Cu (mg) Fe (mg) Mn (mg) Ni (mg) SO4 ² -(mg) Zn (mg) pH EC (μS/cm) Val (ml.)	$\begin{array}{c} \textbf{Column} \\ \textbf{C}_A \\ \textbf{C}_B \\ \textbf{C}_A \\ $	12 0.187 0.683 0.005 0.016 0.033 0.0400 3.53 0.014 0.030 0.054 129.7 181.4 0.200 0.272 3.24 3.02 255 384 420	13 0.194 14.60 0.006 0.278 0.049 1.62 5.12 83.12 0.022 0.194 178.0 700.3 0.250 0.773 3.39 2.89 327 1410 420	14 0.188 0.847 0.004 0.027 0.025 0.131 2.14 12.71 0.021 0.033 0.033 0.043 83.91 185.9 0.262 0.221 3.28 3.05 297 440	15 0.227 0.701 0.004 0.032 0.300 0.186 6.16 15.51 0.019 0.027 0.000 0.095 76.46 122.6 0.000 3.02 148 472 450	16 0.041 0.322 0.003 0.013 0.000 0.014 0.014 0.016 0.000 0.014 0.016 0.000 0.004 31.88 84.44 0.000 0.000 3.97 3.00 130.6 466 420	17 0.000 0.110 0.004 0.007 0.000 0.000 0.000 0.001 1.08 0.013 0.012 0.000 0.000 0.0027 76.27 39.96 0.000 0.000 4.09 3.27 122.1 336 430	18 0.027 0.120 0.004 0.006 0.000 0.001 0.010 0.012 0.010 0.012 0.000 0.000 0.000 0.000 0.000 7.38 67.18 0.000 4.05 3.30 122.3 282 450	19 0.022 10.119 0.004 0.650 0.000 4.932 3.66 147.8 0.010 0.227 0.000 1.88 27.47 785.7 0.050 0.472 4.01 2.36 129.1 2066 380	20 0.030 3.374 0.004 0.810 0.000 1.50 2.02 224.0 0.010 0.045 0.000 1.39 44.08 1152 0.000 0.349 4.01 2.15 124.4 3480 3480	21 0.090 2.948 0.004 0.759 0.000 0.749 4.81 193.2 0.010 0.033 0.000 1.13 68.93 1100 0.000 1.13 68.93 1100 0.245 4.42 2.26 100.1 3630 3630 3630 450	22 0.049 1.067 0.005 0.592 0.000 0.492 5.20 161.7 0.010 0.021 0.000 0.852 16.82 1015 0.000 0.184 4.69 2.24 82.7 3210 480	Σ 302.8 362.93 5.15 8.86 3.67 17.42.7 2690 40.47 42.43 9.82 18.47 11729 18949 4.73 6.19

Table 4 Weekly leachates volumes, pH, EC and volume corrected mass loads of constituents for
columns C_A and C_B for a period of 22 weeks.

be used to assist decision making regarding the flooding of the Witwatersrand mines, however a decision cannot be made solely based on the results of these reactions. There are other factors that must be taken in to consideration when deciding to flood or pump the water in the Witwatersrand mine voids. Factors as reported by Ramontja *et al.* (2011) such as:

Flooding risks

- pollution of shallow groundwater resources required for agricultural use
- impact on the underground infrastructure due to their proximity to urban areas
- seismic activity
- the rate of seepage
- potential subsidence

Decant of AMD to the environment risks

- impact on ecological systems
- localised flooding of low lying areas
- impact on major river systems
- estimated water volume

Other factors such as the interaction of generated AMD with dolomitic rock strata and water that has being in contact with dolomitic rock strata prior to interacting with the sulphide rock must also be taken into consideration.

Acknowledgements

We thank the Council for Geoscience for financing the project and the Environmental Geosciences Unit staff for all the support and for reviewing this manuscript.

References

Blowes DW, Ptacek CJ, Jambor JL, Weisener CG (2003) The geochemistry of acid mine drainage. Treatise on Geochemistry 9: 149–204

- Edwards KJ, Gihring TM, Banfield JF (1999) Seasonal variation of microbial populations and environmental conditions in an extreme acid mine drainage environment. Applied and Environmental Microbiology 65(8): 3627–3632
- Fowler TA, Holmes PR, Crundwell FK (2000) On the kinetics and mechanisms of the dissolution of pyrite in the presence of *Thiobacillus ferrooxidans*. Hydrometallurgy 59: 257–270
- Hobbs PJ, Cobbing JE (2007) A hydrogeological assessment of acid mine drainage impacts in the West Rand Basins, Gauteng Province, CSIR/THRIP, Pretoria, CSIR/NRE/WR/ER/2007/C: 59
- Malmström ME, Gleisner M, Hebert RB (2006) Element discharge from pyritic mines tailings at limited oxygen availability in column experiments. Applied Geochemistry 21: 184–202
- Ramontja T, Coetzee H, Hobbs PJ, Burgess JE, Thomas A, Keet M, Yibas B, van Tonder D, Netili F, Rust UA, Wade P, Maree J (2011) Mine Water Management in the Witwatersrand Gold Fields With Special Emphasis on Acid Mine Drainage Inter-Ministerial-Committee on Acid Mine Drainage, Pretoria: 146
- Schoonen M, Elsetinow A, Borda M, Strongin D (2000) Effect of temperature and illumination on pyrite oxidation between pH 2 and 6. Geochemical Transactions 1: 23
- Shrenk MO, Edwards KJ, Goodman RM, Hammers RJ, Banfield JF (1998) Distribution of *Thiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*: Implications for generation of acid mine drainage. Science 279: 1519–1522
- Singer PC, Stumm W (1970) Acid mine drainage: The rate determining step. Science 20: 1121–1123.
- Singer PC, Stumm W (1968) Kinetics of the oxidation of ferrous iron. Second Symposium on Coal Mine Drainage, Pittsburgh: 12–34
- Tutu H, McCarthy TS, Cukrowska E (2008) The chemical characteristics of acid mine drainage with particular reference to sources, distribution and remediation: The Witwatersrand Basin, South Africa as a case study. Applied Geochemistry 23: 3666–368

Selenium in Mine Waters: A Review

Bartholomew WARREN

Queen's University, 99 University Ave., Kingston, Ontario, K7L 3N6, Canada, 11bw5@queensu.ca

Abstract Selenium (Se) has a role as both a nutrient and a toxic substance. Diverse in its compounds and oxidations states, Se research spans fields including, but not limited to: geology, chemistry, biology, and toxicology. Many of these fields of research are important from a mining perspective. From information about the origin of Se at a mine site, reactions which may release it to the environment, reactions and interaction with organisms, beneficial or toxic effects on those organisms, transfer through the food chain, and how this relates to treatment and legal requirements, Se research is a diverse field. This paper serves as a review of selenium research relevant to the mining industry, from the perspective of mine waters. The review focuses on the areas of Se geochemistry, biology, toxicity, treatment and advances in analytical methods.

Keywords bioavailability, toxicity, speciation, treatment

Introduction

Selenium is a naturally occurring metalloid element, essential to human and animal health in trace amounts but harmful in excess. Selenium's role in human physiology has been found to include the prevention of atherosclerosis, some cancers, arthritis, diseases of accelerated aging, central nervous system pathologies. male infertility, and altered immunological function (Lyn Patrick 2004). Of all the elements. Se has one of the narrowest ranges between dietary deficiency and toxic levels (Fordyce 2006).

Selenium exists in four oxidation states: 2^- , 0, 4⁺, and 6⁺. In aqueous environments Se is most often found as oxygenated anions, selenite (SeO₃²⁺) and selenate (SeO₄²⁺).In reducing environments selenium exists as selenites and elemental selenium Se⁰, both insoluble. Selenium is also incorporated into various organic Se compounds (Fordyce 2006). Knowledge of the different chemical forms and their environmental and biomedical distribution is important because of the dependence of bioavailability and toxicity on speciation (Dauchy *et al.* 1994).

Lemly (2004) suggests one of the primary human activities responsible for the mobiliza-

tion of Se in the environment is the mining, processing, and combustion of coal for electric power generation. Lemly (2004) further stated that on a total mass basis, the Sudbury ore deposits in Canada are one of the largest source of Se in North America. Although this statement was based upon old data, it illustrates the importance of Se in various settings. Selenium is found in all types of natural materials on earth including rocks, soil, waters, air, and plant and animal tissues. In general Se concentrations in rocks are low; magmatic rocks average 10-50 ppb. Sedimentary rocks are highest in Se. Shales are generally between 500 and 28,000 ppb, though some black shales are over 600,000 ppb. Some phosphatic deposits contain as much as 300,000 ppb. Coal and other organic rich deposits typically contain 1,000-20,000 ppb. The worldwide average in soils is 400 ppb. Some high Se soils from the Great Plains in the U.S. have 6,000–28,000 ppb and have led to a toxic response in several domestic animals (Fordyce 2006, Burau 1985).

Bioavailability and the food chain

Although much focus is currently on Se toxicity and increased concentrations due to human activity, Se deficiency in animals is

very common around the globe and many western countries adopt Se supplementation programs (Fordyce 2006). It is therefore important to understand both concentration and bioavailability. A general characteristic of Se that can be used to predict bioavailability is its oxidation state; Se⁴⁺ and Se⁶⁺ are more soluble, mobile and bioavailable than Se^o and Se²⁻ (Ryser et al. 2006). Other bioavailability determining factors include the pH, redox conditions, soil texture, mineralogy, organic matter content and the presence of competitive ions (Fordyce 2006). Uptake of Se into the food chain is also dependent on local flora. Some plants are Se accumulators and can absorb more than 1000 mg kg⁻¹, whereas non-accu- $< 50 \text{ mg kg}^{-1}$ mulators usually contain (Fordyce 2006). The balance is further complicated by biological processes that can release Se into the atmosphere in a volatile form; a potentially important source for the atmospheric enrichment of Se is natural biomethylation (Dauchy et al. 1994). Production of a variety of volatile methyl selenides have been confirmed in rats, fungus, and a variety of plants (Dauchy et al. 1994). Along with the complexities of how Se travels through an ecosystem is the complexity of how uptake and concentration of Se in an organism actually affects that organism's health. In 1996, bioaccumulation at levels exceeding published toxic thresholds was found in fish from the Elk Valley with apparently no ill effects (McDonald and Strosher 2000).

There have been many advances to our understanding of processes related to Se in the environment in recent years. A study of select reclaimed coal mine soils (Sharmasarkar and Vance 2002) found that selenite sorption was always greater than selenate sorption. Linear correlations of the adsorption parameters with different soil characteristics can be utilized to determine Se retention behavior in mine environments (Sharmasarkar and Vance 2002). Using our growing knowledge of the physical, chemical and biological interactions of Se, some biological processes are coming to light. For instance, knowing how much Se microorganisms take up based upon environmental levels and how Se travels through the aquatic food chain, it has been shown that using local food chain data modeling can predict Se concentrations in tissue of trout (Orr *et al.* 2012). This modeling can explain why differences in the food chain, such as a different diet of the same species of fish in different areas, can lead to different fish tissue Se levels in water with equal Se concentrations.

Toxicity

Debate and research around the topic of Se toxicity continues. There is inherent variability in Se toxicity that can be attributed to its interaction with other trace elements, different bioaccumulation potential in lotic and lentic ecosystems, and differences in sensitivity among species (Wayland and Crosley 2006). Elevated Se levels are no guarantee of a harmful reaction. Bujdos et al. (2005) found that plants in a contaminated study area were higher in Se concentration than outside the contaminated area, but were not hazardous and therefore posed no poisonous risk to other organisms. The results of individual studies that form the basis for many guidelines have also been called into question. Brix et al. (2000) claims the U.S. Fish and Wildlife Service (USFWS) thresholds for fish tissue appear overly conservative and do not appear to be adequately supported by the scientific literature. It is likely that the matter will not be resolved without further independent studies. Brix et al. (2000) further states "in several cases, the USFWS interpretation of the studies on which the thresholds are based are contrary to our interpretation, that of the U.S. EPA, and the authors that published the study."

The interaction of Se with other elements makes the toxicity issue a complicated one. Other elements can reduce the toxic effect of Se and if other toxic elements are present, concentrations of Se that would otherwise be toxic may be beneficial. The protective effect of Se against mercury toxicity and vice versa has

been observed in a number of different organisms(Cuvin-Aralar and Furness 1991). Although the benefits of Se in an equal molar ratio with mercury have been established. Ouedraogo and Amyot (2013) note that selenium to mercury molar ratio is not yet a widely accepted tool in mercury risk assessment. It has also been shown that Se toxicity may be alleviated by other trace elements (Wayland and Croslev 2006). The ecotoxicological complexities of this element dictate that thorough, well-designed assessments of effects, or lack thereof, are required in each instance of Se contamination before decisions can be made regarding remediation and management (McDonald and Strosher 2000).

Treatment

The key to successful treatment of selenium contaminated water is to reduce selenite to selenite (Sheoran and Sheoran 2006). Millimolar levels of selenite can be removed from waters quickly and efficiently by sodium sulfide (Pettine *et al.* 2012).

In cases where conditions permit, a more passive treatment system is often preferred. In pilot wetlands testing, cattails and saltmarsh bulrush have been shown to be efficient at removing Se from the water column (Huang *et al.* 2012).

Work by Knotek-Smith et al. (2006) supports an approach for remediation of Se-impacted soils using accelerated microbial reduction via nutrient amendment in concert with an iron amendment to enhance more stable mineralization. From association with pyrite, to adsorption characteristics on iron compounds, the geochemistry of Se is largely controlled by that of iron, with which Se is closely affiliated (Howard 1977). Iron-selenide and iron-selenite compounds are resistant to leaching by infiltration waters; thus coupling organic amendment and iron metal may be a preferred treatment technology for longer term stabilization of Se in contaminated soil environments, especially those not exposed to surface weathering (Knotek-Smith et al. 2006).

Analytical methods

As it is important to know both concentration and speciation of Se even when it exists in miniscule quantities, research has worked to lower detection limits and improve speciation techniques. "The fact that the lower limit of detectablility of our analytical method is not sufficient to indicate exactly the content of many of the Se-poor ores, precludes the drawing of any firm conclusions with respect to them." (Hawley and Nichol 1959). Though detection limits have improved many orders of magnitude since Hawley and Nichol (1959) had a stated lower detectability limit of 15 ppm, improvements are still needed and being made. Hydride generation atomic adsorption spectrometry using multi commutated flow analysis for the hydride generation has been shown to achieve a detection limit of 0.08 ppb, while providing low reagent and sample consumption (Piston et al. 2012).

Another recent method of Se speciation involving magnetic nanoparticle adsorption coupled with ICP-MS is rapid and sensitive (Huang *et al.* 2012).Selenite is adsorbed to the nanoparticles and can then be removed from the solution using a magnetic field.

Ryser *et al.* (2006) used micro-X-ray absorption near-edge structure spectroscopy for Se speciation. This method is able to determine speciation in solid samples on micron scale areas of a sample or map an area for speciation by location in the sample. Atomic adsorption spectroscopy with hydride generation (AAS-HG) and ion chromatography (IC) are both used for selenite/selenate speciation (Sharmasarkar *et al.* 1998).

Interest in increasingly lower concentrations of Se has kept pace with developments in modern analytical instruments, such that extraction and preconcentration processes are needed for the determination and speciation of Se in many cases (Najafi *et al.* 2012). Some thermodynamic data on Se compounds and species is available for modeling purposes; however, in reviewing thermodynamic data Seby *et al.* (2001) states that several values for selenide and selenate are reported but they are not always in agreement. More data is needed to predict what species may be present under given conditions.

Recent developments

The state of Kentucky recently changed regulations governing Se concentrations. The new regulations increased the limits on acute levels from 20 to 258 µg/d and changed the way the chronic standard is to be measured. Chronic level regulation uses a threshold Se concentration, which, if exceeded mandates fish tissue sampling is conducted (Payne 2013).

Similarly the state of West Virginia passed a bill requiring a Se concentration threshold be set and fish tissue monitoring conducted if that threshold is exceeded. The West Virginia bill also mandates a monitoring plan to include selenium chemical speciation (Phillips *et al.* 2013).

Conclusions

Many advances have been made to our understanding of Se. Detection limits are now lower than 1 ppb and speciation is becoming faster and more accurate (Piston et al. 2012). Understanding of important biological processes including how Se travels through the food chain and differences in toxicity among organisms continue to improve (Orr et al. 2012). Another area of toxicity which is being further explored is the interaction of Se with other elements. Some treatment methods which may be preferred, including passive wetlands based systems, have shown good initial results (Huang et al. 2012). Regulations continue to adapt and change, showing what seems to be balance protecting the environment while trying to set realistic expectations of companies and protecting economic interests (Payne 2013).

Acknowledgements

The author thanks Dr. Heather Jamieson for comments and editing suggestions, as well as Cortney Palleske for grammatical edits and input

References

- Brix, K. V., D. K Deforest, A. Fairbrother, WJ. Adams. Critical review of tissue-based selenium toxicity thresholds for fish and birds. British Columbia Mine Reclamation Symposium. Williams Lake: The technical and research commitee on reclamation, 2000. 220– 230.
- Bujdos, M., A. Mul'ova, J. Kubova, J. Medved. Selenium fractionation and speciation in rocks, soils, waters and plants in polluted surface mine environment. Environmental geology, 2005: 353–360.
- Burau, Richard G. Environmental chemistry of selenium. California agriculture, 1985: 16–18.
- Cuvin-Aralar, MA. Lourdes A., Robert W. Furness. Mercury and selenium interaction: a review. Ecotoxicology and environmental safety, 1991: 348–364.
- Dauchy, X., M. Potin-Gautier, A. Astrue, M. Astrue. Analytical methods for the speciation of selenium compounds: a review. Analytical chemistry, 1994: 792–805.
- Fordyce, Fiona. Selenium geochemistry and health. Symposium on Medical Geology. Stockholm: Royal Swedish Academy of Sciences 2006.
- Hawley, J. E., Ian Nichol. Selenium in some canadian sulfides. Economic Geology 1959: 608–628.
- Howard, J. Hatten. Geochemistry of selenium: formation of ferroselite and selenium behavior in the vicinity of oxidizing sulfide and uranium deposits. Geochimica et Cosmochimica Acta 1977: 1665–1678.
- Huang, Chaoshang, *et al.* Highly sensitive method for speciation of inorganic selenium in environmental water by using mercapto-silica-Fe₃O₄ nanoparticles and ICP-MS. Analytical Methods 2012: 3824–3829.
- Huang, Jung-Chen, Elodie Passeport, Norman Terry. Development of a constructed wetland water treatment system for selenium removal: use of mesocosms to evaluate design parameters. Environmental science and technology, 2012: 12021–12029.
- Knotek-Smith, Heather M., Don L. Crawford, Gregory Moller, Rachel A. Henson. Microbial studies of selenium-contaminated mine site and potential for onsite remediation. Industrial microbiology biotechnology, 2006: 897–913.
- Lemly, A. Dennis. Aquatic selenium pollution is a global environmental safety issue. Ecotoxicology and environmental safety, 2004: 44–56.

Lyn Patrick, ND. Selenium biochemsitry and cancer: A

reveiw of the literature. Alternative medicine review, 2004: 239–258.

- McDonald, Leslie E., Mark M. Strosher. Selenium in the Elk River Basin, British Columbia – A review of findings and discussion of implications for assessment and management. British Columbia mine reclamation symposium. Williams Lake: The technical and research commitee on reclamation, 2000. 160–173.
- Najafi, Nahid Mashkouri, Hamed Tavakoli, Yaser Abdollahzadeh, Reza Alizadeh. Comparison of ultrasound-assisted emulsification and dispersive liquid-liquid microextraction methods for the speciation of inorganic selenium in environmental water samples using low density extraction solvents. Analytica Chimica Acta 2012: 82–88.
- Ouedraogo, Ousseni, Marc Amyot. Mercury, arsenic and selenium concentrations in water and fish from sub-saharan semi-arid freshwater reservoirs (Burkina Faso). Science of the total environment, 2013: 243–254.
- P. L. Orr, C. I. E. Wiramanden, M. D. Paine, W. Franklin, C. Fraswer. Food chain model based on field data to predict westslope cutthroat trout (oncorhynchus clarkii lewisi) ovary selenium concentrations from water selenium concentrations in the Elk Valley, British Columbia. Environmental toxicology and chemistry, 2012: 672–680.
- Payne, Randall G. Update to Kentucky Water Quality Standards for Protection of Aquatic Life: Acute Selenium Criterion and Tissue-Based Selenium Chronic Criteria. government, Frankfort, Kentucky: Kentucky Cabinet for Energy and Environment 2013.
- Peterson, Erica. WFPL news. april 4, 2013. www.wfpl.org/ post/kentucky-releases-revised-selenium-proposalminimal-tweaks (accessed april 10, 2013).
- Peterson, Erica. WFPL news. april 10, 2013. www.wfpl. org/post/legislative-committee-advances-new-sel-

enium-regulations-despite-confusion-concerns (accessed april 10, 2013).

- Pettine, Maurizio, Francesca Gennari, Luigi Campanella, Barbara Casentini, Dario Marani. The reduction of selenium(IV) by hydrogen sulfide in aqueous solutions. Geochimica et Cosmochimica Acta 2012: 37–47.
- Phillips, *et al.* H. B. 2579. government, Legislature of West Virginia 2013.
- Piston, Mariela, Javier Silva, Ramiro Perez-Zambra, Isabel Dol, Moises Knochen. Automated method for the determination of total arsenic and selenium in natural and drinking water by HG-AAS. Environmental geochemistry and health, 2012: 273–278.
- Ryser, Amy L., Daniel G. Strawn, Matthew A. Marcus, Sirine Fakra, Jodi L. Johnson-Maynard, Gregory Moller. Microscopically focused synchrotron X-ray investigations of selenium speciation in soils developing on reclaimed mine lands. Environmental science and technology, 2006: 462–467.
- Seby, F., M. Potin-Gautier, E. Giffaut, G. Borge, O. F. X. Donard. A critical review of thermodynamic data for selenium species at 25 °C. Chemical Geology 2001: 173–194.
- Sharmasarkar, S., G. F. Vance, F. Cassel-Sharmasarkar. Analysis and speciation of selenium ions in mine environments. Environmental geology, 1998: 31–38.
- Sharmasarkar, Shankar, George F. Vance. Selenite-selenate sorption in surface coal mine environment. Advances in environmental research, 2002: 87–95.
- Sheoran, A. S., V. Sheoran. Heavy Metal removal mechanism of acid drainage in wetlands: A critical review. Minerals Engineering 2006: 105–116.
- Wayland, Mark, Robert Crosley. Selenium and other trace elements in aquatic insects in coal mine-affected streams in the rocky mountains of Alberta, Canada. Environmental contamination and toxicology, 2006: 511–522.

Application of Column Leaching Tests to Predict Seepage Water Quality from Waste Rock in the Southeast Idaho Phosphate District

Christa Whitmore¹, Mary Kauffman², Scott Effner³

¹Whetstone Associates, Inc., 104 W. Ruby Avenue, Gunnison, CO 81230, cwhitmore@whetstoneassociates.com ²U.S. Forest Service, Caribou-Targhee National Forest, 1405 Hollipark Dr., Idaho Falls, ID 83401, mkauffman@fs.fed.us

³Whetstone Associates, Inc., 104 W. Ruby Avenue, Gunnison, CO 81230, seffner@whetstone-associates.com

Abstract Evaluation of waste rock seepage chemistry is a key component of baseline characterization work for phosphate mine permitting in southeast Idaho. Column leaching studies provide insight into chemical processes in waste rock dumps and pit backfills and can be used to predict metal mobility. This information can be used to improve the design and environmental performance of waste rock disposal facilities. This paper presents recommendations for development of a standard column testing method that will help ensure that leaching tests provide comparable data consistent with observed seepage chemistry from full-scale mine facilities in the Southeast Idaho Phosphate District.

Keywords seepage chemistry, column leaching tests, Southeast Idaho Phosphate District

Introduction

The Southeast Idaho Phosphate District is an active mining area with currently operating and historic mines. Mining has typically been from the surface, with overlying lithologies and inter-burden deposited as external piles, pit backfill, or valley fill. Mining-related impacts have included increased concentrations of constituents of potential concern (COPCs) including selenium, cadmium, manganese, nickel, sulfate, and zinc in groundwater and surface water. Selenium has been the primary COPC due to high concentrations in waste rock seepage and notable environmental impacts to fish and mammals. Cadmium, manganese, nickel, sulfate and zinc also have significant mobility in waste rock seepage.

Column leaching studies have been used to provide information about the potential for metals mobility of waste rock for five mining projects in the district. The testing methodology has varied from site to site and has evolved with increased understanding of the chemistry and issues associated with phosphate mine rock seepage. Variables in the testing methodologies have included sample composition (mixed versus monolithologic), water:rock ratio, degree of saturation, solution application rate, and introduction of air or biota. Data from column leaching tests have been used to develop selective handling and placement strategies for waste rock, to evaluate the need for engineered covers and seepage collection systems for disposal facilities, and as source term inputs for predictive models of contaminate fate and transport.

Development of a standard column testing method will provide consistency in data that are used to predict seepage chemistry and will provide guidelines for the how data are generated to support mine planning and permitting. This paper reviews column testing programs that have been completed in the Southeast Idaho Phosphate District and compares the results to observed seepage chemistry from mining-impacted sites. Recommendations are also provided for a standardized column testing procedure to ensure that comparable data are available to evaluate the environmental performance of planned waste rock disposal facilities.

Constituents of Concern in the Southeast Idaho Phosphate District

Mines in southeast Idaho produce phosphate ore from the Meade Peak Member of the Phosphoria Formation. Waste rock associated with the ore includes marine shales and siltstone that have the potential to leach selenium, cadmium, sulfate, manganese, nickel, zinc, and other constituents at levels of regulatory concern (Maxim 2002a and 2005, Herring 2004, Whetstone 2010a). Selenium has been of primary concern in the district and has been implicated in livestock deaths and deformities in wildlife (Presser et al. 2004). Seepage from mining has also resulted in wide-spread contamination of surface water and groundwater in the Blackfoot River watershed (Hamilton et al. 2004).

Processes that Affect Selenium Mobility in Waste Rock Seepage

Selenium mobility in seepage from waste rock dumps and pit backfills is affected by redox conditions, pH, microbial activity, and sorption. Reduced forms, including selenide (Se²⁻) and elemental selenium (Se^o), are relatively insoluble and have low environmental mobility (Seed et al. 2000). Exposure of waste rock to atmospheric conditions can oxidize selenide and elemental selenium into the more mobile forms, selenite (SeO₃^{2–}) and selenate (SeO₄^{2–}), which are easily transported in groundwater and surface water. Redox reaction rates for selenium can be rapid and are strongly affected by microbial processes (Pickering et al. 1995, Beauwens et al. 2005). Sorption to clay, carbonate minerals, organic compounds, and oxyhydroxides of iron, manganese, and aluminum may also affect the mobility of selenium in water (Hayes et al. 1987, Balistrieri and Chao 1990, Rajan 1979). The mobility of other COPC-

sin water is affected by the same processes to differing degrees.

Regional Waste Rock Seepage Chemistry

Seepage water quality data for 12 phosphate mining sites in southeast Idaho have been compiled to provide a baseline for comparison of leaching data from column tests. The data span 12 years (1997 through 2008) and include analyses for selenium, cadmium, nickel, manganese, and zinc. Observed COPC concentrations in waste rock seepage are summarized in table 1.

Regional data indicate that selenium concentrations in waste rock seepage vary by more than five orders of magnitude (<0.0001 to 13.3 mg/L). This wide range is attributable to compositional and chemical variability of waste rock and other factors including facility construction (e.g. backfills vs. eternal dumps, plug dumping vs. end dumping), meteoric water infiltration rates, oxygen availability, and degree of saturation. Individual seeps also exhibit seasonality with selenium concentrations that vary by more than two orders of magnitude (Whetstone 2010b). The highest selenium concentrations are typically observed in the spring. Other COPCs exhibit similar variability in concentration over a narrower range.

Given the observed range of concentrations in waste rock seepage, selection of a single value or narrow range of values that represent the average concentration of COPCs is problematic. The mean selenium concentration for the seepage data (n = 278) is 0.70 mg/L. The median value is 0.12 mg/L and the geometric mean is 0.10 mg/L. Because the highest selenium concentrations in seepage typically occur during high infiltration conditions (spring snow melt) and represent a disproportionally large percentage of the seepage volume, it is likely that a relatively broad range centered on the mean(0.7 mg/L)provides the best estimate of regional selenium concentration in seepage. Concentrations for other COPCs have similar seasonal patterns.

	Sulfate	Cadmium	Manganese	Nickel	Selenium	Zinc
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Ballard					0.44 - 0.44	
Champ'					0.0149 - 0.041	0.004
Conda ¹	30 - 540	0.00006 - 0.01	0.005 - 0.04	0.003 - 0.31	0.0041 - 4.0	0.001 - 0.59
Dry Valley ¹	220 - 3,170	0.0001 - 0.08	0.002 - 4.8	0.0005 - 4.0	0.0023 - 0.18	0.007 - 17
Enoch Valley					0.002 - 0.3	
Henry					0.001 - 0.001	
Mountain Fuel ¹					0.0005 - 0.34	
North Maybe ¹					0.0336 - 0.49	
S. Rasmussen Ridge ¹	270 - 1,200	0.0008 - 0.014		0.02 - 1.0	0.048 - 0.75	0.04 - 3.0
Smalm Comma ¹	24.7 1 120	0.0001 0.02	0.005 2.4	0.005 0.17		0.001 -
Smoky Canyon	24.7 - 1,120	0.0001 - 0.02	0.005 - 2.4	0.005 - 0.17	0.0003 - 13.3	0.43
WooleyValley ¹					0.0028 - 1.4	
Conda ²	260 - 353	0.00002 -	0.05 - 0.07	0.01 - 0.05		0.009 -
		0.006			0.0098 - 0.35	0.23
Henry ²	66-76	0.0004 - 0.003	0.027 - 1.5	0.005 - 0.04	0.00028 -	0.002 -
					0.00065	0.01
Maybe Canyon ²					0.64 - 1.5	
Smoky Canyon ²					0.07 - 2.35	
Ballard ³	27 - 905	0.0001 - 0.0003	0.006 - 1.98	0.02 - 0.02	0.03 - 1.94	0.01 - 0.01
Dry Valley ³	526 - 957	0.003 - 0.62	0.34 - 2.4	0.07 - 2.2	0.0001 - 0.0567	0.16 - 20
Maybe Canyon ³					0.0019 - 9.85	
Smoky Canyon ³	1,484 - 1.666	0.0836 - 0.172	0.0058 - 0.0108	0.449 - 0.916	0.299 - 1.06	3.85 - 4.54

Notes: 1 = Seeps, 2 = Under Drains, 3 = Saturated Backfill Source: Whetstone 2010b

Previous Column Leaching Tests for Phosphate Mine Rock in Southeast Idaho

Column leaching studies have been completed for five mines in the district over the past decade. Common aspects of most column testing programs include water:rock ratios of less than 0.5:1 and solution contact periods of a week or more. Variables in column construction have included sample size and composition, particle size, column size, degree of saturation, inoculation with bacteria, water:rock ratio, air cycling, and solution application rates. Columns have been prepared to test both single and mixed rock material. Monolithologic columns have provided information about COPC mobility from specific units that are amenable to selective handling. They also provide data that can be used to evaluate changes to the mining plan. Mixed rock columns provide a closer analog to the complex chemical reactions that occur in waste rock piles. They have typically been constructed to reflect the average composition of specific facilities. Columns have been operated under saturated, unsaturated, and variably saturated conditions. Operational pa**Table 1** Observed Concentra-tions of Selected Elements inSeepage from PhosphateMine Rock.

rameters for columns are summarized in table 2.

As indicated earlier, particle size has varied in previous phosphate mine rock columns. Leached rock has included hand-broken or jawcrushed core screened to 100 % passing ³/₄-inch and finer cuttings from air-reverse and sonic drilling. A study of the available reactive surface area for different particle sizes was completed by Whetstone (2010a). The study involved adsorption of a monolayer of nitrogen gas to the solid material using Brunauer, Emmett, and Teller (BET) testing. The mass of sorbed nitrogen was used to calculate the surface area of the solid based on the interatomic spacing of the gas monolayer. The results of the analysis indicate that reactive surface area is a function of the grain size of the sedimentary rocks rather than the size of the clasts. This suggests that leachates should not be particularly sensitive to the gross particle size of the packed material provided that the sizing is small enough to prevent preferential flow within the columns. As a general rule, the column diameter should be at least four times greater than the largest particle (Potter

	SC, Panels B & C	SC, Panels F & G	NRRM	DVM, South Ext.	BFBM
# of Columns	9	25	11	2	13
Column Diameter	6"	4" - 6"	6"	6"	6"
Sample Mass	5 kg	5 - 22 kg	5 kg	25 - 45 kg	20 kg
Monolithologic Columns	8 unsat.	13 unsat. 8 variable	11 unsat.		
Mixed Comp. Columns	1 unsat.	2 unsat. 2 partial		1 sat. 1 unsat.	9 unsat. 4 sat.
# of Cycles	10	5-20	10	10 - 13	11 - 19
Cycle Length	4 - 8 days		4 - 6 days	3 - 4 weeks	19 days
Innoculation	yes	23 of 25	no	no	no
Aeration Cycle	1 - 2 days	2 - 3 days	1 - 2 days	no	3 days
Application Rate (mL/hr)	30 - 100	15 - 22	30	15	15

Notes: SC = Smoky Canyon, DVM = Dry Valley Mine, NRRM = North Rasmussen Ridge Mine, BFBM = Blackfoot Bridge Mine

Table 2 Summary of Operational Parameters for Column Leachate Tests.

1981,Cathles and Breen 1983). Previous testing in the district has used column diameters greater than eight times the largest particle.

Columns have been operated under unsaturated, variably saturated, and saturated conditions. Time series plots for leachates from unsaturated columns show pronounced washout curves for selenium and other COPCs that decrease to low asymptotic levels during latecycles. Saturated columns have lower initial release rates for selenium for the same rocks, while other elements such as manganese show increased mobility (Whetstone 2010a). The column study prepared for the Blackfoot Bridge Mine paired unsaturated and saturated columns of identical mixed-rock composition. The range of concentrations for selected COPCs for the unsaturated and saturated columns are presented in table 3. Saturated leachates also have higher dissolved carbon dioxide concentrations which are interpreted to indicate increased microbial activity (Whetstone 2010a). Work by Lisa Kirk of Enviromin Inc. suggests that naturally occurring bacteria of the genus Dechloromonas are responsible for selenium reduction and reduced selenium mobility in saturated column leachates (Kirk *et al.* 2009, Kirk *et al.* 2010). Columns that were inoculated with cultured bacteria had similar release characteristics for other COPCs as non-inoculated columns.

Despite the variability associated with previous column testing methods, effluents from the first 1 or 2 cycles have generally provided reasonable models of COPC concentrations in seepage from field-scale facilities (Whetstone 2010b). Selenium releases in firstcycle leachates from unsaturated columns have ranged from 0.11 to 9.32 mg/L and have mean and median values of 1.36 and 0.89 mg/L, respectively. This range is compared to a mean selenium concentration of 0.70 for field observed seepage. Other COPCs are similarly comparable. The range of COPC concentrations in first cycle column leachates for the Blackfoot Bridge Mine (table 3) can be compared with ranges for seepage from fieldscale facilities presented in table 1.

Conclusions

Standardization of column testing methods for phosphate waste rock in southeast Idaho

	Sulfate mg/l	Cadmium mg/l	Manganese mg/l	Nickel mg/l	Selenium mg/l	Zinc mg/l
Unsaturated Mixed Rock	629 - 1340	0.0014 - 0.0064	0.54 - 0.72	0.06 - 0.16	0.74 - 2.5	0.02 - 0.29
Saturated Mixed Rock	234 - 609	0.0015 - 0.0042	1.07 - 2.18	0.05 - 0.29	0.001 - 0.008	0.01 - 0.45

 Table 3 Observed First Cycle Leachate Concentrations of Selected Elements in the Blackfoot Bridge
 Column Test.

will facilitate comparison between mining sites and improve confidence in predictions of COPC mobility in seepage. It is recommended that both monolithologic and mixed rock columns be prepared to characterize new waste rock disposal facilities. Monolithologic columns provide information that can be used to evaluate selective handling strategies and changes to mining plans and should be prepared for each rock type that comprises 5 % or more of the material balance. Mixed rock columns are a better analog of the complex reactions that occur in heterogeneous dumps and backfills and can be used to calibrate equilibrium-based mixing models of monolithologic leachates. Mixing models may be prepared to evaluate the inevitable differences between planned and constructed facilities.

The operating condition of the columns (saturated vs. unsaturated) should be selected to model the site-specific environment. Unsaturated columns should be prepared for materials that will be stored above the water table in external piles, pit backfills, and valley fills. If any portion of a facility extends below the water table, a saturated column should be prepared. Other factors, such as plans to infiltrate dewatering water through pit backfill, should be considered when planning saturated vs. unsaturated columns. Continuation of the variably saturated column testing method is not recommended because of difficulty in interpreting the results. However, the method may be applicable to evaluate attenuation of COPC concentrations under specific circumstances.

The authors have a preference for larger columns over smaller columns and recommend that leaching tests be performed in sixinch diameter columns packed with 20 kg of material. This size is large enough to accommodate samples that represent the run-ofmine composition of modeled facilities, but small enough that sufficient material is usually available from exploration boreholes that were used to define the ore body. The packed material should be sized to 100 % passing ³/₄inch mesh, but should not be overly disaggregated if possible.

Although bacteria mediate redox reactions involving selenium and other COPCs, inoculation of the columns is not recommended. Bacteria are known to be naturally present in phosphate mine waste rock and flourish in the columns under favorable (saturated) conditions. Regulatory agencies have expressed concerns regarding the feasibility of collecting, identifying, and culturing representative populations of bacteria in inoculants. Monitoring of constructed facilities to determine if biologic communities reflect those in the columns is also problematic.

Standardization of the solution application rate, length of leaching cycle, water:rock ratio, and air cycle is also recommended. Infiltration rates in field-scale facilities are often more than an order of magnitude less than in columns. The head solution application rate should therefore be as low as practical. Experience indicates that accurate application of 15 mL/h is achievable with readily available metering pumps. This application rate provides for a 19-day leaching cycle to generate approximately 5 L of effluent. For unsaturated columns, each cycle includes 14 days of solution application, a two day drain-down period, and a three dayaeration period. Saturated columns include a 14-day solution application period and a five day reaction period.

Finally, it is recommended that columns be operated for a minimum of five cycles. Observed wash-out curves for COPCs from previous tests typically become asymptotic by the fifth cycle as processes within the columns approach quasi-equilibrium. However, additional cycles may be required to provide documentation of steady-state release rates.

References

BalistrieriLS, ChaoTT (1990) Adsorption of Selenium by

Amorphous Iron Oxy-Hydroxide and Manganese Dioxide. Geochimica et CosmochimicaActa, vol. 54, 739–751 Beauwens T, De Cannière P, Moors H, Wang H, Maes M (2005) Studying the Migration Behavior of Selenate in Boom Clay by Electromigration. Engineering Geology, v. 77, 3–4, 285–293

Cathles L, Breen K (1983) Removal of Pyrite from Coal by Heap Leaching. University Park: Pennsylvania State University, p. E1

Hamilton S, Buhl K, Lamothe P (2004) Selenium and other Trace Elements in Water, Sediment, Aquatic Plants, Aquatic Vertebrates, and Fish from stream in SE Idaho near Phosphate Mining. In Life Cycle of the Phosphoria Formation: From Deposition to Post-Mining Environment, Hein, James R., ed. 483–525

Hayes KF, Roe AL, Brown GE, Hodgson KO, Parks GA (1987) In-Situ X-Ray Adsorption Study of Surface Complexes: Selenium Oxyanions on Alpha-FeOOH. Science, Vol. 238, 783–786

Herring J (2004) Rock Leachate Geochemistry of the Meade Peak Phosphatic Shale Member of the Phosphoria Formation, Southeast Idaho, 367–396

Kirk LB, Childers SE, Peyton B, McDermott T, Gerlach R, Johnson TM (2009) Geochimica et CosmochimicaActa, 73(13) Supplement 661

Kirk LB, Stewart BD, Macur R, Gerlach R (2010) Geochimica et CosmochimicaActa, 74(11) Supplement 519

Maxim Technologies, Inc. (2002a) North Rasmussen Ridge Mine Expansion Final Environmental Geochemistry Study. Prepared for Agrium Conda Phosphate Operations

Maxim Technologies, Inc. (2005) Final Baseline Technical Report on Environmental Geochemistry for Manning and Deer Creek Phosphate Lease Areas (Panels F and G) at Smoky Canyon Mine. Prepared by Maxim Technologies for J.R. Simplot Company, March 2005

Pickering I, Brown G, Tokunaga T (1995) Quantitative Speciation of Selenium in Soils Using X-Ray Absorption Spectroscopy. Environmental Science and Technology, vol. 29, No. 9, 2456–2459

Potter G (1981) Design Factors for Heap Leaching Operations. Mining Engineering, v. 33, pp. 277 – 281

Presser T, Piper D, Bird K, Skorupa J Hamilton S, Detwiler S, Huebner M (2004) The Phosphoria Formation: A Model for Forecasting Global Selenium Sources to the Environment. In Life Cycle of the Phosphoria Formation: From Deposition to Post-Mining Environment, Hein, James R., ed. 299–319

Rajan S (1979) Adsorption of Selenite, Phosphate, and Sulphate on Hydrous Alumina. Journal of Soil Science, No. 30, 709–718

Seed K, Cave M, Carter J, Parker A (2000) Determination of Soil Selenium Speciation Using a New Extraction Methodology and Chemometric Data Analysis. Journal of Conference Abstracts, v. 5(2) 902–903

Whetstone (2010a) Revised Final Baseline Geochemical Study, Blackfoot Bridge Mine EIS. Prepared for U.S.Department of Interior Bureau of Land Management, Pocatello Field Office. March 2010

Whetstone (2010b) Revised Final Source Term Development Report to Support Numerical Modeling of Groundwater Flow and Solute Transport for the Proposed Blackfoot Bridge Mine. Prepared for U.S. Department of Interior Bureau of Land Management, Pocatello Field Office. November 2010

Natural acid rock drainage in the Judith Mountains, Central Montana, USA

George P. WILLIAMS, Christopher H. GAMMONS, Stephen R. PARKER

Montana Tech, 1300 West Park Street, Butte, Montana, 59701 gwilliams@mtech.edu, cgammons@mtech.edu, sparker@mtech.edu

Abstract This paper is a summary of an ongoing investigation of acid rock drainage in the Judith Mountains, Montana. Three streams draining the central peaks of the range are acidic (pH < 4) in their headwaters and become pH-neutral with distance downstream. The acidic drainage is attributed to natural weathering of pyrite-rich, hydrothermally-altered igneous rock that outcrops on the crest of the mountain range. Concentrations of copper, zinc, and thallium in the stream waters are locally well above regulatory standards. The study area provides a useful comparison to nearby watersheds that have been heavily disturbed by mining.

Keywords Geochemistry, zinc, copper, ferricrete, stream tracer, monitoring

Introduction

The Judith Mountains, one of the classic "island" mountain ranges that rise from the Great Plains of central Montana, consist of a number of late Cretaceous to early Tertiary alkaline plutons that have intruded into Paleozoic and Mesozoic sedimentary rock (Wallace 1953; Porter and Wilde 1999). Near the center of the Judith Mountains, three small streams – Collar Gulch, Chicago Gulch, and Armells Creek – form a radial drainage pattern around a zone of pyrite-rich, hydrothermally-altered porphyry termed Red Mountain (Fig. 1; described in Lindsey and Fisher 1985). Each of these streams transitions from acidic to nearneutral pH with distance downstream, is actively forming hydrous iron and aluminum oxide precipitates, and has abundant ferricrete deposits that have been incised by each active stream channel (Fig. 2). Although historic mining of precious metals has occurred elsewhere in the Judith Mountains (Robertson 1950;



Fig. 1 Location map and geology of the study area. Inset at lower right shows pH values measured at baseflow conditions and border of pyrite-rich alteration. Geology is from Goddard (1998).



Fig. 2 Photographs of Armells Creek. A) Ferricrete deposit, approximately 5 m above modern channel; B) View of Armells Creek from Red Mountain, looking NW (North Moccasin Range in background); C) Junction of east and west forks of Armells Creek, with Al-hydroxide forming in mixing zone.

Zhang and Spry 1994), the three watersheds of interest have not been heavily impacted by mining. Therefore, the study area provides an excellent opportunity to examine the geochemistry of trace metals and metalloids in acidic streams in a natural setting. In addition, the study area could be utilized as a reference site for pre-mining water quality conditions for mining-impacted streams elsewhere in the Judith Mountains, or in nearby mining districts that have similar geology, such as the closed Zortman-Landusky Au mines in the Little Rocky Mountains (Wilson and Kyser 1988; Kill Eagle et al. 2009) or the closed Kendall Au mine in the North Moccasin Mountains (Lindsey 1985).

The main objective of the current study, funded by the U.S. Bureau of Land Management, is to collect seasonal data on streamflow and water chemistry for the three drainages of interest, with a focus on documenting concentrations and loads of trace metals and metalloids. To augment routine water quality monitoring, three types of field experiments are being conducted: 1) Continuous tracer injection studies (Kimball et al. 2002) to quantify longitudinal changes in the concentrations and loads of contaminants of concern, including Al, Cu, Fe, Mn, Pb, Zn, F, sulfate, and thallium (Tl); 2) Diel (24-h) sampling to examine short-term changes in the concentrations of trace metals (Gammons et al. 2005; Parker et *al.* 2007; Nimick *et al.* 2011); and 3) Collection of a longitudinal transect of natural ferricrete samples for trace metal analysis, to compare with modern Fe- and Al-hydroxide precipitates. The latter method was recently proposed (Nimick *et al.* 2009) as an assessment technique to compare pre-mining *vs.* post mining water quality in streams where no pre-mining baseline exists. Although the above activities are being performed in all three drainages of interest, this paper will focus on the results of the synoptic tracer study in Armells Creek.

Methods

Field activities in the Judith Mountains for this project began in Sept. of 2011, and will continue through the Fall of 2013. Water quality samples are being collected approximately every two months (except winter) from selected monitoring sites (Fig. 1). Streamflow measurements are being measured at a number of these sites, with continuous water level recorders at the mouth of each stream. During June of 2012, a continuous tracer injection study was performed in Armells Creek, following the method of Kimball et al. (2002). In addition, a synoptic set of water samples, instream precipitates, and near-stream ferricrete deposits was collected from Armells Creek in July of 2012. Similar tracer tests and ferricrete samplings are scheduled for Collar Gulch and Chicago Gulch in 2013. The discussion which follows mainly deals with the results of the June 2012 tracer study in Armells Creek.

A concentrated KBr stock solution was injected into the headwaters of Armells Creek for over 24 hours at a constant rate of 11 mL/min. Tracer breakthrough and time-to-saturation were monitored at two downstream locations using automated samplers. Water samples collected from the samplers were also used to test for diel (24-h) changes in trace metal concentration. After KBr saturation was achieved, a set of filtered (0.2 um) and non-filtered water samples was collected along the main channel of Armells Creek and its tributaries at predetermined locations spaced approximately 100 m apart. At each location, field parameters (pH, temperature, conductivity, dissolved oxygen) were measured using a datasonde, and alkalinity was measured in the field by potentiometric titration. Streamflow at each main stem location was calculated based on the measured dilution of the KBr tracer (Kimball et al. 2002). All water samples were preserved with 1 % HNO3 (except samples used for ion chromatography) and later analyzed by ICP-AES for major and trace metals and by IC for anions, including bromide. The synoptic samples were later reanalyzed by ICP-MS for improved detection limits. Solute loads were calculated as the product of concentration and streamflow.

Results

Synoptic changes in the concentrations of iron (Fe), aluminum (Al), manganese (Mn), zinc (Zn), copper (Cu) and thallium (Tl) collected during the Armells Creek tracer test are shown in Fig. 3. Metal loads for the same sampling stations are shown in Fig. 4. The combined data can be used to infer hydrogeochemical processes occurring in Armells Creek. Although a significant amount of dissolved Fe and Al exists in the upper reaches of the stream, both of these elements are mainly present as suspended solids below the confluence of the east and west forks of Armells Creek (Fig. 3A, 3B). Precipitation of Fe(III)- and Al-hydrous-oxides is consistent with the ob-

served increases in pH (Fig. 1), and was confirmed visually by the presence of orange and white precipitates in the stream (Fig. 2C). Examination of the trends in Fe and Al loads (Fig. 4A, 4B) shows significant inputs of these metals from the so-called "red tributary" and the east fork of Armells. The "red tributary" is a small flow of highly acidic (pH < 3), Fe-stained water that enters Armells Creek from the east, high on the flanks of Red Mountain (Fig. 1). Upstream, this tributary has flows that emanate from the ground as a series of springs, with extensive ferricrete deposits covered with moss carpeting the forest floor. Diffuse groundwater seepage also enters Armells Creek below the "red tributary", explaining the increases in loads and concentrations of most of the metals (excepting Cu) at distances of 500 m to 750 m below the tracer injection site. These groundwater seeps may be from hillslope drainage re-mobilizing Fe from ferricrete deposits on banks above the existing stream course. The east fork is the main source of additional metal loading in lower Armells Creek (Fig. 4). The drainage areas and flows of the east and west forks are approximately similar, and although the mouth of the east fork typically has slightly higher pH than the west fork, it also contains highly acidic springs in its headwaters along the flanks of Red Mountain (Fig. 1).

Concentrations of Cu and Zn in upper Armells Creek are well above chronic regulatory standards (MDEQ 2010) for protection of aquatic life. Because these standards - shown as red lines in Fig. 3 - are dependent on hardness, they need to be computed for each individual sample based on the measured Ca and Mg concentrations. Also, it should be noted that aquatic standards in Montana are currently based on "total recoverable" metal concentrations (MDEQ 2010). Although concentrations of dissolved Zn, total Zn, and dissolved Cu dropped below aquatic standards downstream of the confluence of the east and west forks, concentrations of total Cu (acid recoverable) remained close to the standard. The de-



Fig. 3 Synoptic changes in the concentrations of total (filled symbols) and dissolved (open symbols) iron (A), aluminum (B), manganese (C), zinc (D), copper (E), and thallium (F) in Armells Creek. Also shown are regulatory standards for protection of aquatic life (chronic-Zn, -Cu) and human health (Tl). Locations of major tributary streams are shown with dashed lines. Note: top row of diagrams is in mg/L; bottom row is in µg/L.



Fig. 4 Synoptic changes in the loads of total (filled symbols) and dissolved (open symbols) iron, aluminum, manganese, zinc, copper, and thallium in Armells Creek. Locations of major tributary streams are shown with dashed lines. Note: top row (A-C) of diagrams is in mg/second; bottom row (D-F) is in µg/second.

viation between the dissolved and total lines below the east and west fork confluence (Figs. 3, 4) indicates partitioning of trace metals into freshly formed Fe and Al hydrous oxide precipitates in the approximate order Cu > Zn > Mn > Tl. Although the concentrations of thallium in Armells Creek are very low (around 1 µg/L or less), Tl is highly toxic to most living organisms (Peter and Viraraghavan 2005). Montana DEQ does not list an aquatic life standard for Tl, but the current human health standard for Tl in surface water in Montana is 0.24 µg/L (MDEQ 2010). Concentrations of Tl are well above this standard for all of Armells Creek (Fig. 3F), and the element apparently exists primarily in the dissolved phase. In this study, the hydrogeochemical behavior thallium is very similar to that of zinc, as has been reported from flooded mines in Sardinia (Cidu *et al.* 2007).

Water samples collected hourly near the mouth of Armells Gulch during the June 2012 tracer test were analyzed by ICP-AES to test for diel fluctuations in trace metal concentration. Concentrations of total Zn decreased during the day from an early morning high of 63 µg/L to a late afternoon low of 44 µg/L. This type of diel fluctuation in Zn concentration is typical of small, pH-neutral streams draining abandoned mine lands, and is thought to be caused by 24-h changes in pH and water temperature coupled with adsorption to metal oxide and biotic surfaces (Nimick et al. 2011). Among the other metals of interest, a weak diel pattern with large scatter was noted for total Al and total Fe, with higher concentrations at night and lower concentrations during the day. Nighttime increases in the concentrations of particulate metals have also been noted from many streams draining abandoned mine lands (Nimick et al. 2011). Although interesting, the diel cycles noted in Armells Creek are relatively small in magnitude, and should not be too much of a concern in the interpretation of synoptic or long term monitoring data.

Discussion

The geology of upper Armells Creek is dominated by hydrothermally-altered and pyriterich intrusive rocks that underlie Red Mountain and Judith Peak, whereas lower Armell Creek flows through outcrops of Paleozoic limestone and younger sediments (Fig. 1). This geological transition explains the overall evolution of the stream from acidic and metalrich in its headwaters, to pH-neutral and relatively metal-poor near its mouth. The abundance of ferricrete in the headwaters of Armells Creek, Collar Gulch and Chicago Gulch, all of which drain different sides of Red Mountain, suggests that the acidic drainage is natural, and has been occurring for millennia. No large mines occur in the study area, although some surface disturbances exist, including road construction and installation of radio and radar towers on the summits of Red Mountain and Judith Peak. Chemical analysis of the ferricrete deposits are in progress, following the methods of Nimick *et al.* (2009), to see if hydrogeochemical conditions present today in upper Armells Creek are similar to what was present during ferricrete formation. Findings will be reported at the 2013 IMWA meeting.

The hydrothermally-altered porphyry rocks at the headwaters of Armells Creek resemble similar rocks exposed 90 km to the north in the Little Rocky Mountains. Here, the Zortman-Landusky open pits were mined for gold at a large scale by cyanide heap-leach methods between 1979 and 1998, and left behind a legacy of serious acid rock drainage in Swift Gulch (Kill Eagle *et al.* 2009). The Judith Mountains also share geologic similarities to the closed Kendall gold mine in the North Moccasin Mountains, located just 20 km west of the study area. At Kendall, gold occurs in brecciated limestone and dolomite cut by numerous subvolcanic intrusions (Lindsey 1985; Lindsey and Fisher 1985). Due to the abundance of carbonate rock, acid mine drainage is not a problem at Kendall. However, groundwater that has contacted waste rock is elevated in dissolved thallium. and Tl removal technologies are being evaluated (e.g. Mueller 2001). The geologic source of thallium at Kendall and in the Judith Mountain drainages has not been determined

Conclusions

Three small streams located in the central Judith Mountains, Montana, are highly acidic in their headwaters and transition to near-neutral pH over a distance of several km. Judging from the abundance of ferricrete in the headwaters, this acidic drainage has been occurring for millennia. Concentrations of Cu and Zn are well above chronic standards for aquatic life in upper Armell Creek, and concentrations of thallium (Tl), although very low (around 1 µg/L), are still well above human health standards for surface water. Concentrations of total Al, Fe, and Zn in lower Armells Creek increased at night and decreased during the day, following the diel pattern shown by many pH-neutral streams draining abandoned mine lands. Overall, the study area is a good example of acid rock drainage in a natural setting, although some acceleration of pyrite-weathering rates due to road construction along the crest of the mountain range cannot be discounted.

Acknowledgements

The authors thank Chad Krause and the Lewistown, Montana office of the US Bureau of Land Management for funding this study and introducing us to the site. We also thank Heiko Langner (Univ of Montana), Thomas Prescott (Montana Tech), and Steve McGrath and Jackie Timmer (Montana Bureau of Mines and Geology) for their help with the analytical work. Heidi Reid for assistance with field work

References

- Cidu R, Biddau R, Nieddu G (2007) Rebound at Pb-Zn mines hosted in carbonate aquifers: Influence on the chemistry of ground water. Mine Water Environ 26: 88—101
- Gammons CH, Nimick DA, Parker SR, Cleasby TE, Mc-Cleskey RB (2005) Diel behavior of Fe and other heavy metals in a mountain stream with acidic to neutral pH: Fisher Creek, Montana, USA. Geochim Cosmochim Acta 69: 2505—2516
- Goddard EN (1988) Geologic map of the Judith Mountains, Fergus County, Montana. US Geol Surv, Miscellaneous Investigations Series, Map I-1729
- Kill Eagle JL, Gammons CH, Weight WD, Babcock J, Jepson W, Langner HW (2009) Results and lessons learned from a continuous tracer injection test in a small mountain stream receiving acid mine drainage. Mine Water Environ 28: 182—193
- Kimball BA, Runkel RL, Walton-Day K, Bencala KE (2002) Assessment of metal loads in watersheds affected by acid mine drainage by using tracer injection and synoptic sampling: Cement Creek, Colorado, USA. Appl Geochem 17: 1183—1207

- Lindsey DA (1985) A gold-mineralized breccia zone at Kendall, north Moccasin Mountains, Fergus County, Montana. US Geol Surv, Prof Paper 1301-C: 42—56
- Lindsey DA, Fisher FS (1985) Mineralized breccias in intrusive complexes of late Cretaceous and Paleocene age, north-central Montana. US Geol Surv Prof Paper 1301-A: 1—34
- MDEQ (2010) Montana Numeric Water Quality Standards. Montana Department of Environmental Quality, Helena, Montana, Circular DEQ-7
- Mueller RF (2001) Microbially mediated thallium immobilization in bench scale systems. Mine Water Environ 20: 17—29
- Nimick DA, Gammons CH, Parker SR (2011) Diel biogeochemical processes and their effect on the aqueous chemistry of streams: A review. Chem Geol 283: 3— 17
- Nimick DA, Gurrieri JT, Furniss G (2009) An empirical method for estimating instream pre-mining pH and dissolved Cu concentration in catchments with acidic drainage and ferricrete. Appl Geochem 24: 106—119
- Parker SR, Gammons CH, Jones CA, Nimick DA (2007) Role of hydrous iron and aluminum oxide formation in attenuation and diel cycling of dissolved trace metals in an ARD-affected stream. Water Air Soil Poll 181: 247—263
- Peter AL, Viraraghavan T (2005) Thallium: a review of public health and environmental concerns. Environment International 31: 493—501.
- Porter KW, Wilde EM (1993) Geologic map of the Lewistown 30' x 60' quadrangle, central Montana. Mont Bur Mines Geol, Open File Report 308
- Robertson F (1950) Mines and mineral deposits (except fuels), Fergus County, Montana. US Bur Mines, Information Circular 7544, 76pp
- Wallace SR (1953) The petrology of the Judith Mountains, Fergus County, Montana. US Geol Surv, Open File Rept 214
- Wilson MR, Kyser TK (1988) Geochemistry of porphyry hosted Au-Ag deposits in the Little Rocky Mountains Montana. Econ Geol 83: 1329—1346
- Zhang X, Spry PG (1994) Petrological, mineralogical, fluid inclusion, and stable isotope studies of the Gies gold-silver telluride deposit, Judith Mountains, Montana. Econ Geol. 89: 602—627

Toxicity of Metal Mixtures to *Daphnia magna* – Comparison of Laboratory and Field Data

J. WILLIAMSON¹, M. R. PASTORINHO², J. F. RANVILLE¹, J. S. MEYER³, R. C. SANTORE⁴, A. C. RYAN⁴, J. W. GORSUCH⁵, E. ROGEVICH-GARMAN⁶, C. E. SCHLEKAT⁶, R. L. DWYER⁷

¹Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO, USA; ²University of Aveiroand Centre for Environmental and Marine Studies (CESAM), Aveiro, Portugal; ³ARCADIS U.S., Inc, Lakewood, CO, USA; ⁴HDR/HydroQual, Inc., East Syracuse, NY, USA; ⁵Copper Development Association Inc., Webster, NY, USA; ⁶Nickel Producers Environmental Research Association, Durham, NC, USA; ⁷International Copper Association, Ltd., Pocasset, MA, USA

Abstract In aquatic systems impacted by mine wastes, organisms are usually exposed to metal mixtures instead of individual metals. For example, legacy acid mine drainage continues to pollute the North Fork of Clear Creek (NFCC) in central Colorado, USA. In November 2012, we collected water samples from NFCC and deployed *Daphnia magna* as in-stream biomonitoring tools. Survival and whole-body concentrations of key electrolytes in *D. magna* decreased at sites that, as a result of mine drainage inputs, had metal concentrations elevated above the upstream reference sites. In parallel laboratory toxicity tests in which *D. magna* were exposed to binary and ternary metal mixtures, approximately additive or less-than-additive toxicity occurred.

Keywords North Fork Clear Creek, acid mine drainage, aquatic geochemistry, cadmium, copper, iron, zinc

Introduction

In the mid-to-late 1800s, mining and mineral processing operations extracted valuable metals from the Colorado Mineral Belt. These processes led to unexpected environmental consequences as a result of acid mine drainage (AMD) generation. Currently an AMD-contaminated section of the North Fork of Clear Creek (NFCC) in central Colorado cannot sustain an aquatic vertebrate population and has a depauperate population of aquatic macroinvertebrates. Therefore, the United States Environmental Protection Agency (USEPA) has placed a high level of urgency for remediation of the stream. As a consequence of the AMD discharge into NFCC, pH and alkalinity are lowered, but water hardness and concentrations of dissolved metals (e.g. Cd, Cu, Ni, Zn) and suspended sediments are increased in comparison to upstream waters. The combined effects of these water quality parameters and the dissolved organic carbon(DOC) concentration control the aquatic toxicity of individual metals (Meyer et al. 2007). However, the consequences of organism exposure to metal mixtures are less wellunderstood. Laboratory toxicity testing of binary and ternary metal mixtures in standard media can provide insights into potentially non-additive effects. Field studies, while less controlled than laboratory toxicity tests, offer the opportunity to examine effects under realistic conditions and compare to results of laboratory tests. Our study goal was to gain a fuller understanding of the impact of metal mixtures on aquatic life in NFCC using both approaches. Thus, we conducted D. magna toxicity tests in the laboratory coordinated with in situ deployment of D. magna and concurrent water sampling to see if toxicity in a field setting could be predicted from laboratory toxicity tests.

Methods

Water Sampling

Six sampling sites represent changes in water chemistry as NFCC flows southeast to join Clear Creek. Two AMD point sources (Gregory Incline [GI] and National Tunnel [NT]) enter the stream in the town of

Blackhawk (Fig. 1). A relatively pristine reference site (Site 1) that has low metal concentrations is ≈1 km upstream from GI. This upstream site contains fish and numerous species of benthic macroinvertebrates that are characteristic of uncontaminated Rocky Mountain streams. Site 2 is immediately downstream of the two point sources, and the water chemistry and stream health are severely affected by the AMD inputs. Sites 3 and 4 are situated immediately above and below the city of Blackhawk's wastewater treatment plant (WWTP), ≈ 9 km downstream of Blackhawk. Site 4 is the last NFCC site before the confluence with the main stem of Clear Creek. Sites 5 and 6 on the main stem of Clear Creek are located upstream and downstream of the confluence with NFCC.

Grab samples of stream water, for analysis of major water quality parameters and metals, were collected using polypropylene containers on November 7, 15, and 17, 2012. Samples were filtered for dissolved metals in the field, and



Fig. 1 Map of the sampling sites on the North Fork and mainstem of Clear Creek in central Colorado

unfiltered samples were collected for total metals and total organic carbon (TOC) analyses. The TOC samples were collected in pre-combusted (500 °C) amber glass bottles.

In situ Biological Monitors

D. magna (a freshwater cladoceran commonly employed in standardized aquatic toxicity tests) were deployed at the six field sampling sites on November 15, 2012, for a 48-h instream exposure in polypropylene test chambers that allowed free flow of water through the chamber. Surviving Daphnia were rinsed sequentially with Milli-Q water and 10 mL of 0.1 mM EDTA for 2 min to remove particles and weakly surface–bound metals, oven dried (60 °C, 48h), weighed to the nearest 0.1 mg, extracted with 1 mL of trace-metal-grade nitric acid at 20 °C for 24h, and diluted to 10 mL with Milli-Q water before analysis for elemental content.

Laboratory Toxicity Tests

D. magna were cultured in moderately hard reconstituted (MHR) water (USEPA 2002; nominal pH of 7.4-7.8, alkalinity of 57-64 mg/L as CaCO₃, and hardness of 80-100 mg/L as CaCO₃) and were tested in MHR water to which DOC was added as Suwannee River fulvic acid at 3 mg DOC/L. Standard 48-h lethality tests using <24-h-old neonates were conducted for all single-metal (Cd, Cu, Ni, and Zn) and metalmixture tests (USEPA 2002). Negative controls and four replicate test groups consisting of five Daphnia each were employed for each tested concentration. Temperature, pH, alkalinity, and concentrations of Cd, Cu, Ni, Zn, and major inorganic anions and cations were monitored during the tests; and hardness was calculated from the measured Ca and Mg concentrations. Because the concentration-response curves for individual metals can vary from test to test, we usually conducted a Cd-only, Cu-only, Nionly, as well as Zn-only test concurrent with the binary-mixture tests. Additionally, we conducted numerous toxicity tests with each binary metal pair to determine within-day and among-week variability in results, to evaluate whether any apparently less-than-additive, additive, or more-than-additive toxicity result was due to variability alone.

Chemical Analyses

During the field study, we measured pH (VWR SP8oPC meter/VWR 14002-860 combination gel electrode), alkalinity (HACH Model AL-DT Alkalinity Test Kit), and ferrous iron (HACH DR/890 Colorimeter/1-10 phenanthrolene AccuVac ampules) in the field. Later in the laboratory, unfiltered and filtered (0.45 µm) water samples from field sites were acidified with trace-metal-grade nitric acid before being analyzed for major elements and metals using inductively coupled plasma-optical emission spectrometry (ICP-OES; Perkin Elmer Optima 5300 DV). Water hardness was calculated from the measured Ca and Mg concentrations. Unfiltered water was also analyzed for total organic carbon (TOC) concentration by persulfate oxidation/UV irradiation (Sievers531 °C TOC analyzer). Acid-digested D. magna (see above) were analyzed for elemental content using ICP-OES.

During laboratory toxicity tests, the same general analyticalprocedures (APHA 2012) and instruments were used. However, pH was determined using a ThermoScientific Orion2 Star Benchtop Meter/ThermoScientific Orion 815600 Ross Combination pH/conductivity probe.

Results

Laboratory Toxicity Tests

In Cu-Zn binary mixture tests, the toxicity always appeared to be either slightly more-thanadditive (*i.e.* the observed mortality was slightly greater than the predicted mortality) or additive (*i.e.* the observed mortality equaled the predicted mortality) when based on dissolved-metal concentrations, whether Cu was varied while Zn was held constant (Fig. 2a), or vice versa (results not shown). Similarly, the toxicity of Cu-Ni mixtures always appeared to be more-than-additive or additive (results not

shown). However, the toxicity of these Cu-Zn mixtures was less-than-additive when based on the concentrations of Cu and Zn bound to the biotic ligands, when predicted using a multi-metal biotic ligand model (results not shown). These results indicate that the dominant determinant of toxicity was Cu-Zn or Cu-Ni competitive binding to DOC, thus leaving more Cu²⁺, Ni²⁺, or Zn²⁺ available to bind to the biotic ligand than would have been available at the same dissolved-metal concentration in a Cu-only, Ni-only, or Zn-only test. Furthermore, these results demonstrate that conclusions about the additivity of metal-mixture toxicity can differ considerably when the frame of reference changes from dissolved metal to bioticligand-bound metal.

In contrast, in Cd-Cu, Cd-Ni, and Cd-Zn binary mixture tests, the toxicity appeared to be either less-than-additive (i.e. the observed mortality was less than the predicted mortality) or additive (i.e. the observed mortality equaled the predicted mortality) when based on dissolved metal concentrations (Figs. 2b, 2c, and 2d). Most notably, Ni and Zn concentrations less than 1/10 of the Ni-only or Zn-only median lethal concentration (LC50) protected against partial to 100 % Cd lethality (Figs. 2c and 2d); and Cd concentrations approximately 10x the Cd-only LC50 had to be added to the Cd-Ni and Cd-Zn mixtures before mortality began increasing above the background mortality caused by the constant Ni or Zn concentration (results not shown), again demonstrating a large protective effect of Ni and Zn against Cd toxicity. These results demonstrate a protective effect of higher-concentration metals (Cu, Ni, or Zn) against the toxicity of a more lethal metal that is present at much lower concentrations. These results also indicate that the dominant determinant of toxicity was Cd-Cu, Cd-Ni, or Cd-Zn competitive binding to the biotic ligand, whereby the relatively higher concentration of Cu²⁺, Ni²⁺, or Zn^{2+} allowed less Cd^{2+} to bind to the biotic ligand than would have been bound at the same dissolved-Cd concentration in a Cd-only test.



Fig. 2 Laboratorytoxicity of binary mixtures to D. magna. (a) Constant Zn with variable Cu. (b) Constant Cd with variable Cu. (c) Constant Cd with variable Ni (d) Constant Cd with variable Zn. The vertical gray bars indicates the range of concentrations at which the variable metal caused 50 % mortality in single metal tests.

An analogous protective effect against Cd toxicity also occurred in ternary Cd-Cu-Zn mixtures, without any apparent more-than-additive interactions between Cd and Zn (results not shown).

November 2012 Field Study

The pH and alkalinity of NFCC decreased and the water hardness increased at Site 2 after the two AMD point sources entered the stream, and the pH and alkalinity continued to decrease as the water flowed downstream to Site 3 (Table 1). These continued decreases of pH and alkalinity could have been due to slow Fe²⁺ oxidation, manifested as the continuing high concentration of dissolved Fe throughout the \approx 9-km reach between Sites 2 and 3. Influx of the WWTP effluent considerably increased the pH, and alkalinity in NFCC at Site 4, but the hardness and TOC concentration increased only slightly. Temperatures ranged from -0.5 to 3 °C at the beginning of the *D. magna* deployment.

The in-stream contributions of Cd, Cu, Fe, and Zn from the AMD point sources are manifested as large increases in dissolved and total concentrations of those metals at Site 2 (Table 1). Trends in dissolved and particulate Cu reflect several in-stream processes, most notably pH-dependent sorption to suspended particulate iron oxides. At Site 2, Cu is largely particulate where the pH is circumneutral (6.8) and suspended iron concentration is high (15 mg/L; calculated by difference between total and dissolved Fe concentrations in Table 1). At Site 3, the particulate Cu concentration is low, consistent with the lower pH (5.7) and lower susparticulate iron concentration pended (1 mg/L). Despite the higher pH (8.0) at Site 4, the particulate Cu concentration is low, likely

		Alkalinity (mg/L as	Hardness (mg/L as	TOC	Cd	(µg/L)		Cu (µg/L)	 Zn (µ	ıg/L)		Fe(j	ug/L)
Site	pН	CaCO ₃)	CaCO ₃)	(mg/L)	Total	Diss.		Total	Diss.	Total	Diss.	Т	otal	Diss.
1	8.3	25	43.4	1.59	< 0.1	< 0.1		2.6	3.2	9	27		152	15
2	6.8	12	247.3	1.54	4.7	3.5	7	0.2	3.2	1,787	1,625	38	3,373	23,437
3	5.7	3	258.0	1.41	5.8	5.4	9	4.0	90.8	2,004	1,963	3	3,580	2,520
4	8.0	53	268.5	1.75	1.9	1.7	2	1.8	14.4	740	680		629	30
5	8.2	45	101.1	2.28	< 0.1	< 0.1	1	0.7	5.6	219	180		168	15
6	8.2	44	112.6	1.50	< 0.1	< 0.1	1	1.8	6.1	267	201		290	20

^a Data are averaged from the three sampling days (November 7, 11, and 15, 2012).

Table 1 Water chemistry during 48-h field deployment of D. magna in the North Fork and main stemof Clear Creek in Central Colorado in November 2012.^a

due to the very low suspended particulate Fe concentration (<1 mg/L), which limits the amount of available sorption sites. In contrast, the large majority of zinc in the water is dissolved. Although the significant downstream decreases in the total and dissolved Cu concentrations might be explained by the concurrent loss of suspended particulate iron, the decreases of the total and dissolved Zn concentrations must be due to direct loss to the streambed. Decreases in metal concentrations due to dilution can be ignored based on the small decrease in sulfate concentration, which is a conservative tracer in this aerobic stream system in which sulfate is not reduced to sulfides (data not shown).

Because increasing alkalinity, hardness, and TOC concentrations tend to decrease metal bioavailability and thus toxicity(as does increasing pH above approximately 6.5-7; Meyer et al. 2007), the major longitudinal changes in water chemistry in NFCC can have major effects on the toxicity of Cd, Cu, and Zn to aquatic organisms. Those effects were manifested in the decreased survival of D. magna at Sites 2 and 3, where pH and alkalinity decreased considerably even though hardness increased (Table 2). Those toxicity results are consistent with the generalization that pH and alkalinity have more of a toxicity-modifying effect on cladocerans than does water hardness (e.g. Meyer et al. 2007), but the concurrent increases of the Cd, Cu, Fe, and Zn concentrations complicate that interpretation. The major decreases of whole-body Na and K concentrations and the smaller-percentage decreases of whole-body Ca and Mg concentrations are also consistent with expectation, because elevated concentrations of cationic metals can disrupt iono regulation (*e.g.* Na for Cu exposure, and Ca for Zn exposure) and thus can be lethal to aquatic organisms(Meyer *et al.* 2007).

NFCC water at Sites 2 and 3 had lower alkalinity, lower TOC concentration, and higher hardness than the MHR exposure water used in the laboratory single-metal and metal-mixture toxicity tests with Cd, Cu, and Zn (pH 7.8-8, alkalinity \approx 50-60 mg/L as CaCO₃, hardness \approx 80-90 mg/L as CaCO₃, and DOC \approx 3 mg/L in MHR water). At Sites 2 and 3, the Zn concentrations in NFCC were nearly double the midrange of the median lethal concentrations (LC50 values) determined in the Zn-only laboratory toxicity tests ($\approx 600 \ \mu g \ Zn/L$); and at Site 3, the dissolved Cu concentration in NFCC was close to the mid-range LC50determined in the Cu-only laboratory toxicity tests (≈80 µg Cu/L). Even in the relatively high hardness water, no Daphnia survived at Sites 2 and 3 due to the high Cu and Zn concentrations, low alkalinity, and relatively low TOC concentrations. The Cd concentrations at all sites were less than the mid-range LC50determined in the Cd-only laboratory toxicity tests (≈8 µg Cd/L); and because Cu and Zn have moderate to large protective effects against Cd toxicity (see above), the potential contribution of Cd to the observed Daphnia mortalities at Sites 2 and 3 was probably even less. Although the hardness at Site 4 remained approximately as high as at Sites 2 and 3, the alkalinity increased

	Daphnia 48-h	Whole-body concentration(mg/kg dry weight tissue)							
Site	survival (%)	Na	K	Ca	Mg				
1	92	137	240	5,010	198				
2	0	<11 ^a	$< 17^{a}$	3,639 ^a	148^{a}				
3	0	14^{a}	17^{a}	3,273 ^a	135 ^a				
4	100	596	444	6,508	256				
5	93	383	297	5,655	236				
6	96	392	333	6,206	232				

^a Dead *Daphnia* analyzed for whole-body electrolytes at this site because no *Daphnia* survived.

Table 2 D. magna survival and whole-body electrolyte concentrations during 48-h field deploymentin the North Fork and main stem of Clear Creek in Central Colorado in November 2012.

and the Cd, Cu, and Zn concentrations decreased. Therefore, despite the Zn concentration at Site 4 being near the LC50value determined in MHR water in the laboratory, the elevated hardness in Site 4 water (compared to MHR water) probably protected against lethality. In the main stem of Clear Creek (Sites 5 and 6), the Cd, Cu, and Zn concentrations were below the LC50 values determined for those metals in MHR water; and all the Daphnia survived, consistent with prediction for waters with those hardness and alkalinity concentrations.

Conclusions

Mine-drainage waters are complex mixtures of metals and major ions that can alter the chemistry of receiving waters in complex ways. The North Fork of Clear Creek is an example of this situation. AMD is a reactive solution; and after it enters receiving water, the speciation of metals and ions can change depending for example on temperature, pH, dissolved oxygen concentration. These reactions are kinetically limited, thus changing the concentrations of chemical constituents over time as the mixture of AMD and receiving water flows downstream. Therefore, the toxicity of the mixture can vary greatly and depends on the water chemistry at a specified point in the stream. Models of the toxicity of metal mixtures that take into account varied water chemistry (e.g. biotic ligand models) and interactions among the metals are needed to address these situations more accurately than current approaches that use water hardness as the only predictor of toxicity. Based on the laboratory study of metal-mixture toxicity that was conducted in conjunction with the field study, we conclude that metal-metal interactions among Cd, Cu, and Zn are generally either additive or less-than-additive based on the metal competition for binding to the biotic ligand. Failure to consider this competition can mistakenly lead to the conclusion that the mixtures are more-than-additive.

Acknowledgements

This project was funded by the National Institute of Environmental Health Sciences (NIEHS) on grant #1RO1ES020917-01, the Copper Development Association, the International Copper Association, Rio Tinto, and the Colorado School of Mines Department of Chemistry and Geochemistry. Will Clements and Pete Cadmus helped design the field experiment, and Ellie Traudt and Natasha Albuquerque assisted in the field. Mandee Pontash, Samantha Smith, Ellie Traudt, and Katie Dahl conducted the laboratory toxicity tests, Dan Heil performed the TOC analyses, and Thomas Gately performed the ICP-OES analyses.

References

- APHA. 2012. Standard Methods for the Examination of Water and Wastewater. 22 nded. E.W. Rice (ed.). American Public Health Association, Washington, DC.
- de March B.G.E (1988) Acute toxicity of binary mixtures of five cations (Cu²⁺, Cd²⁺, Zn²⁺, Mg²⁺, and K⁺) to thefreshwater amphipod Gammaruslacustris (Sars): alternative descriptive models. Can J Fish AquatSci 45:625–633
- Meyer, J.S., S.J. Clearwater, T.A. Doser, M.J. Rogaczewski and J.A. Hansen. 2007. Effects of Water Chemistry onthe Bioavailability and Toxicity of Waterborne Cadmium, Copper, Nickel, Lead, and Zinc to Freshwater Organisms. SETAC Press, Pensacola, Florida, USA.
- USEPA (U.S. Environmental Protection Agency). 2002. Methods for measuring the acute toxicity of effluents and receiving waters to freshwater and marine organisms. Fifth edition. EPA-821-R-02-012, U.S. Environmental Protection Agency, Washington, DC, USA.
- Warne MS, Hawker DW (1995) The number of components in a mixture determines whether synergistic and antagonistic or additive toxicity predominate: the funnel hypothesis. Ecotoxicol Environ Saf 31:23– 28
RELIABLE MINE WATER TREATMENT RELIABLE MINE WATER TREATMENT





HybridICE[™] filter design in freeze desalination of mine water

A. Adeniyi^{1,3}, J. P. Maree², R. K. K. Mbaya¹, A. P. I. Popoola¹

¹Dept. of Chemical & Metallurgical Engineering; ²Dept. of Environmental, Water and Earth Sciences, Tshwane University of Technology, Private Bag X680, Pretoria, 0001, South Africa ³corresponding author: adeniyia@tut.ac.za

Abstract The design theory of dimensional analysis combined with mathematical analysis was used on the model to establish design equations which can be used to specify critical dimensions for a HybridICE filter when the flow-rate is specified. The model is the present construction of the HybridICE filter which was found experimentally to have maximum yield at brine flow-rate of 25 L/min.

Keywords Freeze, desalination, HybridICE[™], filter, design

Introduction

The purpose of this work was to propose a method for designing an efficient HybridICE filter. This is a relatively inexpensive technology that can be used for separation of ice slurry in freeze desalination of mine wastewater. Experiments were carried out to establish the model found to have the highest yield at a flow-rate of 25 L/min. Salt removal was also found to be dependent on the refrigerant temperature. Effective desalination of mine water is required in order to reduce pollution of land and water, meet environmental regulations, provide water for reuse as potable water and even water powered hydraulic machinery. Desalination also removes scaling and corrosion potential in mine waste waters

Well established desalination methods are evaporative processes which include multistage distillation, multi-effect distillation and vapour compression distillation, and membrane processes which include reverse osmosis and electro-dialysis. Freezing is an alternative process of desalination and has also been seen as one of the more interesting methods of desalination (Cerci *et al.* 2003). One reason for this is the energy advantage of freezing processes over evaporative processes. The latent heat of fusion of ice is only 334 kJ/kg but the latent heat evaporation of water is 2 340 kJ/kg (Qin *et al.* 2008). However, one important difference between freezing processes and distillation processes is that the former require mechanical power while the latter require heat (Brian 1968). Freezing processes are also established methods in the food, pharmaceutical and dairy industries (Dickey *et al.* 1995; Petzold & Aguilera 2009).

HybridICE technology is potentially suitable for freeze desalination applied to mine water treatment. HybridICE freeze crystallization utilizes both the cooling and waste heat energy to achieve zero liquid discharge. The technology generates ice slurry in heat-exchangers which is separated into pure ice and concentrated solution in the HybridICE filter, a significant component of the technology. Most literature describes the use of wash columns for separation of ice from the slurry. Unlike wash columns, the HybridICE filter is economical, easier to operate and there is no need to wash the ice produced. Other components of the technology include a heat pump and vacuum evaporator. Design methods exist for all these components, except for the HybridICE filter. The objective of this study was to show how critical dimensions of the filter can be calculated when the required flow-rate is known.



Fig. 1 Sketch of the HybridICE filter

Theory

Fig. 1 shows a sketch of the HybridICE filter. The brine slurry is fed from the bottom of the filter (1). The slurry flows into the filter until it reaches the perforation (3) on the filtering medium (2) where the concentrated brine is removed from the filter and the ice build-up begins. The ice level grows continually until it reaches the point where it can be harvested by scraper (4) and emerges from the top orifice of the filter.

Separation is achieved through buoyancy force. Ice being less dense than water, will begin to float at the beginning of the perforation, creating an ice-brine interface. The movement of the ice bed in the filter is sustained by the pressure drive generated by the flow of the slurry into the filter. Critical dimensions that needed to be determined were the height of the filter *H*, the diameter *D* and the height of the perforation h_s .

In wash columns, ice crystal size is very important for effective separation. Larger and more uniformly sized ice crystals result in higher capacities in the wash column, thus reducing the cost of the washing step (Brian 1968). The size of the crystals formed is very important because fine crystals are difficult to wash (Lu and Xu 2010). However, in the HybridICE filter, it is also important that the ice fraction in the slurry feed into the filter is kept in a temperature region where the ice crystals do not trap impurities. The major contributors to these conditions are the temperature of the refrigerant, the brine flow-rate and the first icepoint of the process solution.

Experimental

Feedstock water

The brine used on the pilot plant was prepared by making up a 2 % by mass solution of common salt (NaCl) in water.

Apparatus

Apparatus used for the experiments included the pilot HybridICE plant situated at the Soshanguve Campus of the Tshwane University of Technology and the laboratory scale "baby" HybridICE unit. The operation of both is the same. The pilot plant handles a higher volume of process water. Fig. 2 shows the HybridICE filter in operation while Fig. 3 shows the "baby" HybridICE unit in operation.

Other instruments used were an electrical conductivity meter and a mass meter. The ice fraction was determined by filtration using a coffee-plunger machine.

Method

The flow-diagram is as shown in Fig. 4. Brine was first passed through heat exchangers where the ice slurry was generated in a continuous process. Ice slurry was then passed through the filter where the separation of the ice takes place. Brine was run on the pilot plant at flow-rates of 25, 30 and 35 L/min when the temperature of the refrigerant was at -10 °C. Samples of ice were collected and weighed. Samples of slurry were also taken from the filter bypass and the ice fraction determined using the coffee-plunger. The temperature of the refrigerant was then varied at flow-rate of 25 L/min. Electrical conductivity (EC) measurements were made on ice samples. Salt removal was calculated based on the initial EC of the



Fig. 2 HybridICE filter

Fig. 3 "Baby" HybridICE unit.



feed sample and the EC of the melted ice sample.

The behaviour of the ice bed was observed in the "baby" HybridICE unit.

Analytical

Actual yield was mass of ice produced, in kg/min.

Salt removal was calculated based on the electrical conductivity of the feed brine C_f and the electrical conductivity of the melted ice sample C_i .

Salt removal =
$$(C_f - C_i)/C_f$$
 (1)

Results and Discussion

The aim of the experiments was to establish a model for the filter design. Fig. 5 showed that maximum yield was obtained at flow-rate

25 L/min. The average ice fraction was 11 %. Fig. 6 indicated that salt removal could be improved by control of the temperature of the refrigerant. Ice behaviour was observed on the "baby" HybridICE unit to determine which other parameters to be included in the design. The observed behaviour indicated the need to provide an alternative opening for the excess concentrated brine to leave the filtration section so as to eliminate overflow in the filter.

Design Procedure

The dimensions for the filter at a flow-rate of 25 L/min, were taken as the model for the design procedure based on the results of the experiments.

Ice bed section

Fig. 7 shows the ice bed section in the filter. D is the diameter of the filter. Q is the flow-rate



Fig. 5 Yield of ice at different flow-rates

while X_i is the average ice fraction. Scraping of ice starts at residence time t and height h_i at t=0, $h_i = 0$. Ice balance on the ice section for height dh_i , time dt, gives:

$$X_i Q dt = \left(\frac{\pi D^2}{4}\right) dh_i \tag{2}$$

$$X_i Q \int_{o}^{t} dt = \left(\frac{\pi D^2}{4}\right) \int_{o}^{h} dh_i$$
(3)

$$X_i Qt = \frac{\pi D^2 h_i}{4} \tag{4}$$

$$t = \frac{\pi D^2 h_i}{4X_i Q} \tag{5}$$

At Q = 25 L/min = 25,000,000 mm³/min; $h_i = 733$ mm, D = 450 mm; substituting these into Equation (5)

 $t = \frac{(\pi \cdot 450^2 \cdot 733)}{(4 \cdot 25000000 \cdot X_i)}$

Product of Residence time *t* and ice fraction X_i , $t X_i = 4.66$

$$4.66 = \frac{\pi D^2 h_i}{4Q} \tag{6}$$

Slurry and ice section weight balance give:

$$h_s = \frac{\rho_i h_i}{\rho_s} \tag{7}$$

Assumption: Density of slurry ρ_s is 1 g/cm³, and density of ice ρ_i is 0.92 g/cm³ Equation 7 becomes:

$$h_{\rm S} = 0.92 \, h$$



Fig. 6 Salt removal at different evaporating temperatures; (flow-rate = 25 L/min)

For the height of filter H, $H = h_i + h_s$; substitution of 0.92 h_i for h_s , gives $H = h_i + 0.92 h_i$ and, clearly

$$H = 1.92 h_{\rm i}$$
 (9)

Slurry section

Flow of slurry in the slurry section (Fig. 7) was similar to the flow in pipes, when based on the Buckingham-π-Theorem. For model and prototype, the dimensionless number, h_s/D is the same (Duncan and Reimer 1998; James & Louis 2009)

At a flow-rate 25 L/min, $h_s = 675$ mm, D = 450 mm; and

$$h_{\rm S}/D = 1.5$$
 (10)



Fig. 7 Ice bed section

Wolkersdorfer, Brown & Figueroa (Editors)

(8)





But $h_{\rm s} = 0.92 h_{\rm i}$, therefore 0.92 $h_{\rm i} = 1.5 D$; and

$$h_{\rm i} = 1.63 D$$
 (11)

Substituting into equation (6), gives:

4.66 =
$$\frac{\pi D^2(1.63D)}{4Q}$$
, which implies that $D^3 = \frac{4.66 \cdot 4 \cdot Q}{1.63\pi}$

$$D = \sqrt[3]{3.64Q}$$
 (12)

Conclusions

From the results of the experimental work, the following conclusions were reached:

The present construction of the HybridICE filter affords the best yield of ice at a brine flow-rate of 25 L/min.

Salt removal can be improved by adjusting the temperature of the refrigerant.

Overflow can be eliminated by creating alternative perforations for excess brine to flow out of the ice section.



Fig. 9 Sketch of HybridICE filter at flow-rate of 10 L/min

Relationships between the flow-rate and the dimensions of the filter were established using mathematical and dimensional analysis.

Fig. 9 shows a sketch of a design of a HybridICE filter using the design equations for a flow-rate of 10 L/min. Sketch does not show scrapper.

Acknowledgements

The authors acknowledge the Tshwane University of Technology for providing research facilities and laboratory equipment and the Technology & Human Resources Program (THRIP) of the South African National Research Foundation for funding the project. Mr Frederick S. Oosthuizen is acknowledged, as the holder of the patent on the HybridICE[™] technology, for providing the plant necessary for carrying out the work.

References

Brian PLT (1968) Engineering for pure water Part 2: Freezing. Mechanical Engineering, 90, 42–50.

- Cerci Y, Cengel Y, Wood B, Kahraman N, Karakas ES (2003) Improving the thermodynamic and economic efficiencies of desalination plants: Minimum work required for desalination and case studies of four working plants. Agreement No. 99-FC-81-0183. Desalination and Water Purification Research and Development Program, Final Report No. 78, November 2003.
- Dickey LC, Craig JC, JR., Radewonuk ER, McAloon AJ, Holsinger VH (1995). Low temperature concentra-

tion of skim milk by direct freezing and vacuum evaporation. Journal of Dairy Science 78:1369–1376.

- Duncan TM, Reimer JA (1998) Chemical Engineering Design and Analysis An Introduction, Cambridge University Press 1998.
- James PA, Louis T (2009) Fluid flow for the practicing chemical engineer. John Wiley & Sons, Inc., New York, p. 14.
- Lu Z and Xu L. (2010) Freezing Desalination Process. Thermal Desalination Processes – Vol. II. Encyclope-

dia of Desalination and Water Resources (DESWARE).

- Petzold G, Aguilera JM (2009) Ice Morphology: Fundamentals and Technological Applications in Foods. Food Biophysics 4:378–396.
- Qin FGF, Chen XD, Premathilaka S, Free K (2008) Experimental study of wash columns used for separating ice from ice-slurry. Desalination 219: 223–228.

Fly ash injection into weathered mine waste

Mattias Bäckström^{1,2}, Lotta Sartz^{2,1}

¹Man-Technology-Environment Research Centre, Örebro University, 701 82 Örebro, Sweden, Mattias.Backstrom@oru.se ²Bergskraft Bergslagen AB, Harald Olsgatan 1, 714 31 Kopparberg, Sweden, Lotta.Sartz@bergskraft.se

Abstract By adding alkaline ashes through injection to weathered mine waste pH increased approximately 3 units, trace element was immobilized and flow rate decreased due to formation of hard pans. Reduction in trace element concentrations was around 96.9–99.6 % for copper, 94.7–99.7 % for zinc and 22.9–99.8 % for cadmium. For lead the best reduction was 97.3 % and the worst -393 % (increase). MSWI ashes performed worst with low buffering capacity and increase in vanadium and molybdenum concentrations.

Keywords sulfidic mining waste, MSWI ashes, trace elements

Introduction

Due to the known ferric iron driven reaction step of pyrite oxidation, oxygen exclusion alone is not a sufficient method to decrease weathering rates of historic mine waste. By adding an alkaline material, the chemical environment is changed within the deposit: pH is increased and mobilization of common ARD-related trace elements is decreased. Injection and mixing can be performed using alkaline residues such as fly ash, lime mud and green liquor dreg.

The neutralizing capacity of the alkaline material is a key parameter, determining both the neutralizing effect and the longevity of the amendment. An important factor is lowered water flow in fly ash amended systems, due to formation of hydrous Ca-Si-Al minerals (hard pan).

Expected results in larger experiments are decreased flow rates, increased pH and accord-ingly lowered trace element concentrations in the leachates.

During the last years there has been an increased interest for the use of alkaline residues in mine waste remediation. These alkaline residues include for instance lime mud, green liquor dreg and fly ash, suitable as neutralizers and in sealing layers for mine waste.

It is possible to make an impermeable layer if the alkaline additive reacts with the waste and form hardpans (Li et al. 2001). Due to the presence of quicklime (CaO) in alkaline materials pozzolanic reactions and hardpan formation are possible. A hardpan is an impermeable barrier, resulting from the formation of calcium-silicate-gel (CSH) and calcium-aluminate-gel (CAH; Bertocchi et al. 2006; Shang et al. 2006; Xenidis et al. 2002). As a hardpan makes infiltration of oxygen and water difficult, fly ash or quicklime is sometimes incorporated in sealing layers for waste rock and tailings (Hossein et al. 1999; Bulusu et al. 2007). A hardpan can however also consist of accumulation of secondary precipitates (goethite, gypsum, jarosite) near the surface of an impoundment/pile (Gilbert *et al*. 2003).

Mixing can be done using heavy machinery. One drawback, however, is that the visual appearance of the deposit can be changed. The practical mixing depth may also be insufficient in massive deposits. By injecting the material as a slurry the historical values can be preserved to a greater extent since the visual appearance is not changed.

Injection/stabilization have been used in a historic mining district in the western US, where approximately 2–3.5 Mt of tailings, initially dumped in adjacent creeks, have been *in* situ limed with calcite and $Ca(OH)_2$ or CaO. The alkaline materials were tilled into the waste and it was found that after 10 years pH had increased with two pH units (Davis *et al.* 1999).

The main objective of this study was to investigate the possibility to use fly ashes for slurry injection into oxidized historic waste rock deposits. Both chemical and physical properties of the fly ashes were considered (*e.g.* size distribution, free lime content). pH is a crucial parameter for trace element mobilization and was studied with stabilization experiments of mixtures of fly ash and historic mine waste from the Ljusnarsberg mine field, mid Sweden.

Methods

A number of ten fly ashes were collected in order to do a more detailed study on which type of fly ashes that would be most suitable for injection into weathered waste rock piles. The fly ashes used in the study are shown in table 1.

The mine waste used for the injection study was larger pieces (50–200 mm) of the

weathered Ljusnarsberg material. The hand sorted waste rock was dominated by chalcopyrite (CuFeS₂) that occurs as dissiminations, small lenses and veinlets. The chalcopyrite is more or less mixed with pyrrothite (FeS), pyrite (FeS₂) and magnetite (Fe₃O₄) and has quartz, hornblende, actinolite, biotite, chlorite and red garnet as wallrock. From the middle of the 19th century and onwards also galena (PbS) and sphalerite (ZnS) ore was mined. Remaining waste rock piles are heavily oxidized and covered with secondary precipitates.

Ten 30 L containers were filled with waste rock, together with a pipe (\emptyset 5 cm) installed in the middle of each container (which was to be used as an injection pipe). The weight of the containers filled with waste rock was approximately 50 kg (Fig. 1).

For the injection, a set of 5 criteria for injection studies stated by Wikman *et al.* (2003) concerning the properties of the alkaline material was followed: (i) It should be relatively stable in a water suspension, (ii) It must stay in the deposit after injection, (iii) It should be able to fill out the voids in the deposit, (iv) It may preferably have a sealing effect, *i.e.* allow for

Abbr.	Producer	Facility	Boiler	Fuel	Filter	Additive	D/W	CaO (%
		2						dw)
VäP5	Mälarenergi	Västerås	CFB	-	-	-	D	3
VäACV	Mälarenergi	Västerås	CFB	-	-	-	D	4.3
EonW	E.on	Örebro	CFB	Bio	Electro	Limestone,	W	4.6
						NH ₃		
EonD	E.on	Örebro	CFB	Bio	Electro	Limestone,	D	7.1
						NH ₃		
StE	Stora Enso	Fors	CFB	Bio, PC ³	Electro	NH ₃ (SNCR)	D	8.2
KorW	Korsnäs	Frövi	BFB	W, F, S ¹	Electro	$CO(NH_2)_2$	W	2.2
						(SNCR)		
KorD	Korsnäs	Frövi	BFB	W, F, S1	Electro	$CO(NH_2)_2$	D	6.4
						(SNCR)		
UppG	Vattenfall	Uppsala	Grate	Mu, In ²	El+B.F. ⁴	Ca(OH) ₂	W	2.4
UppB	Vattenfall	Uppsala	Grate	Mu, In ²	El+B.F. ⁴	Ca(OH) ₂	W	<2
Kpbg	Fortum	Kopparberg	Grate	Bio, PC ³	Cyclone	None	W	4.6

¹W, F, S: Wood, fiber- and biosludge; ²Mu, In: Municipal (60 %) and industrial waste; ³Bio, PC: Bio and pulp chips; ⁴El+B.F.: Electro and bag filter

Table 1 The ten fly ashes used in the study. All ashes came from different Swedish producers. The D/Wcolumn states if the ash had been moistened (W: wet) or not (D: dry) before the injection study. Avail-
able lime index (CaO, %) was measured according to ASTM C25.



Fig. 1 Illustration of the plastic pipe used for gravity injection of fly ash suspensions into the coarse waste rock fraction.

pozzolanic reactions and hard pan formation and (v) It should not have a particle size exceeding 1 mm.

Before starting the injection, all the moistened ashes (table 1) were sieved through a 1 mm sieve. Injection of the ashes was made by pouring an ash-slurry (a mixture of fly ash and water) through the pipe, which was successively pulled upwards. The fly ash to water ratio (in order to get suitable slurry properties) was determined using a standardized test (SS-EN 445 2007) where slurries of the materials were poured through a funnel with a diameter of 80 mm. A total of 5 kg fly ash was injected into each container.

In order to get a suitable slurry for injection according to the funnel test (SS-EN 445 2007), between 1.5 and 2 L of water was added to 5 kg of fly ash. The results from the injections are shown in table 2, focusing on criteria

Ash	Stable	Too much	Hardening	Too rapid	Comments
	suspension	separation		hardening	
VäP5	Yes	No	No	No	Easy to form slurry and to inject
VäACV	Yes	No	No	No	Easy to form slurry and to inject
EonW	No	Yes	No	No	Unable to form injectable
					suspension
EonD	Yes	No	Yes	No	Easy to form slurry and to inject
StE	Yes	No	Yes	Yes	Only 2.5 kg injected due to
					hardening
KorW	No	Yes	No	No	Unable to form injectable
					suspension
KorD	No	No	No	No	Some separation, but easy to inject
UppG	No	No	No	No	Some separation, but easy to inject
UppB	No	No	No	No	Some separation, but easy to inject
Kpbg	No	Yes	No	No	Only 2.5 kg injected due to
					separation

Table 2 Results from the injections. Columns 2 and 3 concern criteria (i) and columns 4 and 5 concern criteria (iv). Text in red color means that there were difficulties with the injection.

(i) and (iv) (Wikman *et al.* 2003). Criteria (ii) and (iii) have not yet been evaluated; they will be evaluated at the end of the experiment. The last criteria (v) was evaluated even before the start of the slurry preparations, and it was found that all the ashes that had been moistened (W in table 1) contained agglomerates larger than 1 mm and these were consequently sieved before starting the injections.

To each amended system ultrapure water (1 L) was added every week during one year (2012). After samplings electrical conductivity, redox, pH and alkalinity were measured. Electrical conductivity, redox and pH were measured with suitable calibrated electrodes. Alkalinity was measured by endpoint (pH 5.4) titration with 0.02 M HCl. Elements were analysed with ICP-MS using rhodium-103 as internal standard.

Results

Three of the ashes showed difficulties with keeping an injectable suspension, due to the fact that they were pre-moistened prior to injection. Two other pre-moistened ashes showed some difficulties with keeping the slurries in suspension, but with some gentle stirring the injection was possible. Presence of higher concentrations of carbonates is the most likely cause for this behaviour.

Two of the ashes had a free lime content high enough for hardening (StE and EonD). If the free lime content is too high rapid hardening makes the injection difficult. Hardening of the ash inside the deposit is though desired as it decreases water flow and keeps the fly ash within the deposit (less tendency to be washed out). Problems with injection mainly originated from pre-moistening of the fly ashes, which seem to increase the tendency to separate making it difficult to keep a stable suspension.

Three of the ashes showed difficulties with keeping an injectable suspension, all of these had been moistened before the injection (EonW, KorW and Kpbg). For Kpbg it was only possible to inject 2.5 kg, and for EonW and KorW no slurry at all was achieved and it was therefore not even possible to do the funnel test. The other two pre-moistened ashes: UppG and UppB showed some difficulties with keeping the fly ash slurries in suspension, but as long as the slurry was gently stirred there was no problem with the injection. This was also the case for KorD (table 2).

Two of the ashes had a free lime content high enough for hardening, these were StE and EonD (table 1 for free lime content). Hardening of the StE-ash was however a little bit too fast; it was only possible to inject 2.5 kg before the slurry had filled up and hardened in the injection pipe. Injection of EonD was easily performed with a stable suspension and some hardening, but not as rapid as for the StE-ash.

The two ashes from Västerås, VäP5 and VäACV very easily formed a stable suspension and were as well easy to inject.

	Redox (mV)	El. Cond. (µS/cm)	рН	Alkalinity (meq/L)
Mine waste	456	2 970	2.23	0
VäP5	9.2	17 800	6.22	0.24
VäACV	23	5 2 9 0	6.17	0.34
EonD	-4.2	6 840	8.96	1.43
StE	48	7 510	6.05	0.26
KorD	3.7	7 500	9.10	1.38
UppG	75	55 300	5.79	0.18
UppB	49	92 700	6.22	0.12
Kpbg	52	4 850	5.88	0.61

Table 3 Results from the general chemistry (redox, electrical conductivity, pH and alkalinity) in the injected samples of mine waste with different fly ashes (average values during 2012, n 11).

Chemical parameters were measured in the leach solutions and also to which degree the fly ash stayed in the container was evaluated. It is important that the fly ash is not washed out too fast and preferably sticks to the mine waste. It was found that in amended samples pH were at least 3 units higher than in the reference system consisting of mine waste only (table 3). Some of the amended systems also had very high electrical conductivity indicating a release of primarily soluble minerals.

Reduction in trace element concentrations was generally good with 96.9–99.6 % for copper, 94.7–99.7 % for zinc and 22.9–99.8 % for cadmium (table 4). For lead the best reduction was 97.3 % and the worst -393 % (increase). Worst performance regarding trace elements was noted for MSWI ashes with bad buffering capacity and low increase in pH. In several systems an increase in for instance vanadium and molybdenum could also be noted. These elements are not present in the mine waste and are thus most likely originating from the ashes.

Conclusions

This study has shown that it is possible to form injectable suspensions with several different ashes. It was harder or sometimes impossible to form stable suspensions with pre-moistened ashes. This is most likely due to the presence of more carbonates in the pre-moistened ashes. By adding the alkaline ashes through injection to weathered mine waste pH increased approximately 3 units, trace element leaching was in general lowered and flow rate decreased due to formation of hard pans.

Reduction in trace element concentrations was around 96.9–99.6 % for copper, 94.7– 99.7 % for zinc and 22.9–99.8 % for cadmium. For lead the best reduction was 97.3 and the worst -393 % (increase). Highest lead concentrations were noted from MSWI ashes. MSWI ashes performed worst with low buffering capacity and increase in vanadium and molybdenum concentrations.

Summarizing, slurry injection of fly ash to weathered mine waste seems to be a promising remediation method if trace element leaching can be controlled.

Acknowledgements

The authors thank the pupils of the 7th grade elementary school Kyrkbacksskolan in Kopparberg who performed most of the practical work as part of their natural science curriculum.

References

- Bertocchi AF, Ghiani M, Peretti R, Zuca A (2006) Red mud and fly ash for remediation of mine sites contaminated with As, Cd, Cu, Pb and Zn. J. Haz. Material. B134: 112–119.
- Bulusu S, Aydilek AH, Rustagi N (2007) CCB-based encapsulation of pyrite for remediation of acid mine drainage. J. Haz. Material. 143: 609–619.

	Cu (µg/L)	Zn (µg/L)	Cd (µg/L)	Pb (µg/L)	V (µg/L)	Mo (µg/L)
Mine waste	84200	479 000	1000	1590	0.5	1.2
VäP5	1280	13 900	44.3	946	9.1	107
VäACV	1370	25 400	72.5	200	47.6	74.1
EonD	1410	9 210	23.3	43.2	7.6	144
StE	760	5 960	16.3	834	0.7	0.6
KorD	730	5 720	12.7	405	5.1	7.1
UppG	1850	14 100	76.8	3990	16.6	2.3
UppB	2090	19 500	148	7820	8.6	11.5
Kpbg	2650	22 500	64.4	1600	0.2	5.9

Table 4 Selected trace element concentrations (averages during 2012, n 4–5) in the amended systems as well as in the reference system (only mine waste).

- Davis A, Eary LE, Helgen S (1999) Assessing the efficacy of lime amendment to geochemically stabilize mine tailings. Environ. Sci. Technol. 33: 2626–2632.
- Gilbert SE, Cooke DR, Hollings P (2003) The effects of hardpan layers on the water chemistry from the leaching of pyrrhotite rich tailings material. Environ. Geol. 44: 687–697.
- Hossein M, Mohamed AMO, Hassini FP, Elbadri H (1999) Ettringite formation in lime-remediated mine tailings: II. Experimental study. CIM Bulletin, 92:75–80.
- Li XD, Poon CS, Sun H, Lo IMC, Kirk DW (2001) Heavy metal speciation and leaching behaviors in cement based solidified/stabilized waste materials. J. Haz. Material. A82: 215–230.

- Shang JQ, Wang HL, Kovac V, Fyfe J (2006) Site-specific study of stabilization of acid-generating mine tailings using coal fly ash. J. Material. Civ. Eng. 18: 140– 151.
- Wikman K, Berg M, Andreas L, Lagerkvist A, Jannes S, Tham G, Sjöblom R (2003) Grouting of fly ash in sanitary landfills. Värmeforsk Rapport 830 (in Swedish).
- Xenidis A, Mylona E, Paspaliaris I (2002) Potential use of lignite fly ash for the control of acid generation from sulphidic wastes. Waste Manag. 22: 631–641.

Applications for Hydrous Ferric Oxide Mine Water Treatment Sludge – A Review

Matthew T. BAILEY^{*}; Arabella M. L. MOORHOUSE; A. James Byrom; Steven Kershaw

The Coal Authority, 200 Lichfield Lane, Mansfield, Nottinghamshire, UK. *Email: mattbailey@coal.gov.uk

Abstract Treatment of ferruginous mine waters using aerobic methods results in generation of Hydrous Ferric Oxide (HFO) precipitates, which are normally retained within treatment systems. Increases in environmental awareness upon mine abandonment over recent decades has led to programmes of treatment schemes to deal with polluting discharges. Given the large number of such schemes internationally (more than 60 in the UK at the time of writing), the management of accumulated HFO sludges is becoming an increasing problem. A perspective from a UK Government Authority is presented, considering a range of potential HFO applications and future prospects for sustainable waste management.

Keywords Hydrous Ferric Oxide, HFO, ochre

Introduction

Aerobic mine water treatment schemes, such as those operated by the UK Coal Authority, produce large volumes of ocherous sludge that predominantly comprises Hydrous Ferric Oxide (HFO). The UK Coal Authority is a statutory organisation, responsible for the legacy of abandoned coal mines and coal mining: www.coal.decc.gov.uk. It is estimated that up to 380,000 wet tonnes (at a nominal 5 % solids) of mine water treatment HFO has accumulated within the ≈ 60 UK mine water treatment systems and requires disposal (The Coal Authority 2010). A concerted effort has been made to investigate the potential 'resource' applications for HFO, which would otherwise be disposed of to landfill at substantial cost (both environmental and to the public purse). This paper provides a review of potential applications of HFO generated by mine water treatment.

Applications for HFO sludge

Dudeney *et al.* (2003) reports that the former British Coal Corporation (pre 1997) had established a market for mine water treatment HFO as a pigment within the brick and concrete industry. While this application is the only known (to the Authors) successful full scale commercial venture for the HFO in the UK, a number of alternatives have been investigated. This includes the use of HFO as a feedstock in the steel industry, conversion to a coagulant or as a sorption media in environmental applications; cited examples of which are provided in the following sections.

Pigment applications

Hedin Environmental, based in Pittsburgh PA, has developed a private enterprise marketing mine water treatment ochre generated at coal mine sites in the United States. Hedin's research, sponsored in part by a US Government Grant, identified the iron oxides (HFO) generated by coal mine water treatment were comparable to iron oxides mined for commercial pigments (Hedin 1998). In 1999, the US Patent Office granted Robert Hedin a Patent for the production of pigment grade iron oxides from polluted mine drainage (Hedin 1999). A subsequent report by Hedin (2002) identified economic issues with the production of highgrade iron oxide pigments from mine drainage HFO: primarily the requirement to

process the material (screening, drying, calcination, milling and blending) to remove organic debris (vegetation and coal fragments) and reduce water content. While the end product was of a high quality, the costs associated with processing made the material more costly to produce than mined iron oxides, although this may be offset when considering conventional HFO disposal costs. A Brazilian case study presented by Marcello (2008) investigated the use of HFO from active coal mine drainage treatment as a pigment within ceramic tile glaze. The results of the study were interpreted as broadly positive However, most favourable results occurred when the HFO was blended with an industrial standard pigment. Alternatively, the incorporation of HFO in clay bricks as a pigment and filler has been suggested, and the Coal Authority has embarked on a large scale trial in partnership with a local brick works in Co Durham, UK. At present, the process demands the entire output of HFO from the Dawdon Mine Water Treatment Plant, equating to approximately 1,500 wet tonnes/year (approx. 50 %w/w solids).

While consistency of HFO has been suggested as a major issue in pigment applications (Marcello 2008); the presence of toxic substances may be less of a problem: Domínguez and Ullman (1996) successfully demonstrates the successful incorporation of 'steel dust' (a by-product of the steel making industry) within bricks. Characterised by circa 50 % Fe₂O₃ w/w, the dust also contains high concentrations of Pb, Cr, Cd, Ni, and in particular Zn with concentrations of up to 13.8 % ZnO w/w. Incorporation of 20 % material resulted in an inert categorisation of the resultant bricks within Argentinian national regulations.

Adsorption applications

Research over recent years has suggested some novel applications for mine water treatment HFO. Specific applications within the environmental field exploit the sorption capacity of the material:

Phosphate adsorption

It has been widely suggested that HFO can be used in applications for phosphate adsorption from point sources, such as sewage effluent, septic tanks and agricultural discharges (*e.g.* Sibrell and Tucker 2012; Heal *et al.* 2005; 2003). Laboratory scale investigations using HFO generated in Coal Authority mine water treatment systems as a phosphate remover show results of up to 30.5mgP/gHFO (Heal *et al.* 2003). These results are corroborated by a later study in the USA by Wei *et al.* (2008) who achieved adsorption capacity of up to 31.97 mgP/gHFO.

Dobbie et al. (2009) goes on to propose that phosphate saturated HFO, produced during nutrient abatement operations as outlined above, could be applied to agricultural land as a soil enhancer. Results of pot and field scale trials showed that the phosphate saturated ochre functioned as a slow release fertiliser, raising pH and posing no threat from the leaching of potentially harmful metals into the soil. Further field scale trials undertaken by Dobbie et al. (2009) demonstrated the applicability of mine water treatment ochre as a phosphate removing agent during optimal flow conditions at two sites in the UK. Currently, large-scale trials of phosphate sequestration using pellitised and granular HFO are underway at two Scottish Water Ltd. waste water treatment sites (The Coal Authority 2010; Dobbie et al. 2009). Removal rates of up to 65 (±48) mgP/kgHFO/d and 195mgP/kgHFO/d were achieved at the sites, which adopted different test bed configurations, the latter suffering greater rates of clogging.

Proposing what is perhaps a less technically elaborate approach to utilising the phosphate sorption capacity, Neville (2007) undertook a series of laboratory and field investigations into the application of ochre in artificial soils. A mixture of mine water treatment HFO, digested sewage sludge and colliery spoil was investigated as a growth medium, for application in spoil tip restoration projects. Results of this investigation are similar to those obtained by Dobbie *et al.* (2009), showing the retention of bio-available phosphates, whilst mitigating the leaching of potentially harmful metals. A significant benefit of this application is that the consistency of the HFO will not impede the performance of the artificial soil; indeed the heterogeneous nature and entrainment of organic matter was found to improve the overall performance of the material. The use of HFO from passive wetland treatment systems may be particularly beneficial for use in this media where organic matter in the form of reeds, root mass and leaf litter can make up a significant proportion of the sludge.

Metal adsorption

The ion sorption capacity of HFO has been considered for use to stabilise/remove contaminant metal(loid)s from water or stabilise them within soils. In particular, the adsorption of arsenic species (As) to HFO has been well documented (*e.g.* Jang *et al.* 2008; Katsoyiannis and Zouboulis 2002; Manning *et al.* 1998; Wilkie and Hering 1995; Bowell 1994; Pierce and Moore 1982). In a 2005 paper, Doi *et al.* demonstrated at laboratory scale that HFO generated at a coal mine discharge, removed As from solution and also reduced its uptake by crop plants (radishes in this case), indicating that the HFO could be used as a remedial amendment in As contaminated soils. Indeed, research proposals have been submitted to the Coal Authority, suggesting the application of HFO from coal mine water treatment systems for the remediation of As contaminated soils (Hodson 2008). To-date, however, full scale trials for such an application have yet to be completed, although a small amount of HFO has been provided to a commercial remediation company for Pb remediation: Approximately 200 t of dried HFO was screened and blended with other iron minerals, including iron(II)sulphate (Fig. 1) before being provided for use in a pilot trial. One concern with such applications, in particular for the metalloid As, is the risk of de-sorption following a shift in environmental redox conditions that may occur as land use changes at a site (Ascar et al. 2008). Such behaviour is perhaps analogous to the problem in Bangladesh where there has been release of As into groundwater that was previously bound to hydrous ferric oxide containing sediments (Polizzotto et al. 2006).

Pelletised HFO, produced from coal mine water treatment sludge, was trialled in the field by Mayes *et al.* (2009) as a sorption media to remove Zn from hard circum-neutral mine waters. Removal efficiencies in the pilot unit were relatively high (32 %) for an influent concentration of 1.5mg/L Zn, considering the low resi-



Fig. 1. Mine water treatment HFO being blended with iron(II) sulphate at a UK location

dence time of the system of 49 minutes. Unfortunately, however, an effluent pH of up to 11.8 was observed, due to the dissolution of the portlandite cement binder that released hydroxide ions. The precipitation of calcite armour on the pellets and the inside of the tank (as a product of portlandite dissolution) combined with algae growth provided additional removal mechanisms for Zn. However, upon die-back of the algae in autumn, the system became a net-exporter of Zn: these issues need to be addressed in the design of subsequent systems.

Adsorption of anionic substances has also yielded promising results at laboratory scale: Wei and Viadero (2007) present data from adsorption trials of 'Congo Red' synthetic dye using mine water treatment HFO, yielding 389.1 mg/gHFO removal capacity.

Future prospects for HFO utilisation

Active treatment systems produce HFO on a continuous or batch basis, which often requires prompt disposal due to the lack of sludge retention capacity that is commonly seen in passive wetland systems. Whilst HFO sludge may vary chemically and mineralogically, depending upon the influent water quality, treatment process and reagents applied, it is relatively consistent at any one active treatment site. For this reason, HFO from active treatment plants is well suited as a feedstock to industrial processes, such as use as filler or as a pigment in brick manufacture, where current trials are providing encouraging results; although at present, the Environment Agency has yet to grant approval for the activity to be undertaken outside of waste management regulations (The Coal Authority 2010). The Environment Agency for England regulates waste activities, amongst other duties: www.evironment-agency.gov.uk. An additional benefit of these applications is that potentially harmful metals (such as those contained within drainage from metal mines) could be immobilised within the end products (i.e. bricks), thus offsetting a substantial disposal cost of a

material that may otherwise be classified as hazardous waste.

Adsorptive applications of HFO within the environmental sector are yet to be realised at any substantial scale, possibly due to the practical and financial obstacles of effectively managing and processing the material in the raw voluminous sludge. Trials are underway at an abandoned metal mine site in the Lake District, UK, where HFO is being applied to remove zinc from a mine water discharge. At this site, large surface area media (extruded plastic sections), coated with HFO at a nearby coal mine water treatment site, are being trialled within a pilot system by Newcastle University. Results of these trials are yet to be published.

Scottish Water Ltd. trials are yielding encouraging results for phosphate removal from waste water, although full scale trials of the design are needed with an effective backwash system or similar to increase lifecycle. If achieved, phosphate saturated ochre from this system could be used as a slow release fertiliser. A large scale field trial of utilising HFO as a component in artificial soils, analogous to the methods suggested by (Neville 2007) is planned for 2014. It is proposed that poor quality (i.e. heterogeneous) HFO from reed beds is applied to an unrestored tip, to facilitate the growth of crops that could be used as a biofuel. If successful, the principle could be applied to a multitude of otherwise low value brownfield sites. Production of a preserved horticultural mulch that incorporates the material through a patented process has also been a great commercial success (Deswarte et al. 2007).

Other less well documented avenues for HFO utilisation have been investigated by the potable water treatment industry, where a similar material is generated as part of the treatment process. It has been suggested that HFO could be incorporated within a steelworks feedstock (pers comm., L. Dennis, Northumbrian Water Ltd 2012), where the benefit of this application, despite its relatively low volume in comparison to demand, is that the high water content can assist in stockpile dust control (pers comm., R. Lord, Strathclyde University 2012). Observations by Younger *et al.* (2002) of impounded HFO note gradual changes from amorphous (low density) iron hydroxides (*e.g.* ferrihydrite) to more crystalline oxides such as haematite (Fe₂O₃) over a period of 1 - 2 decades. Haematite, the principle ore of iron, is eminently marketable if available in sufficient quantities. Such timescales may appear unrealistic for resource recovery, if not considered in the long-term context of mine water treatment site operation.

While significant potential exists for the application of mine water treatment HFO, ultimately in the UK setting, regulatory obstacles and less expensive alternatives provide the greatest obstacle in realising its resource potential.

References

- Ascar L., Ahumada I. and Richter P. (2008) 'Influence of redox potential (Eh) on the availability of arsenic species in soils and soils amended with biosolid', Chemosphere 72(10):1548-52.
- Bowell R. J. (1994) 'Sorption of arsenic by iron oxides and oxyhydroxides in soils', Applied Geochemistry 9(3):279-286.
- Deswarte F. E. I., Clark J. H., Wilson A. J., Hardy J. J. E., Marriott R., Chahal S. P., Jackson C., Heslop G., Birkett M., Bruce T. J. and Whiteley G. (2007) 'Toward an integrated straw-based biorefinery', Biofuels, Bioproducts and Biorefining, 1(4):245-254.
- Dobbie K. E., Heal K. V., Aumonier J., Smith K. A., Johnston A. and Younger P. L. (2009) 'Evaluation of iron ochre from mine drainage treatment for removal of phosphorus from wastewater', Chemosphere 75(6):795-800.
- Doi M., Warren G. and Hodson M. E. (2005) 'A preliminary investigation into the use of ochre as a remedial amendment in arsenic-contaminated soils', Applied Geochemistry 20(12):2207-2216.
- Domínguez E. A. and Ullman R. (1996) "Ecological bricks' made with clays and steel dust pollutants', Applied Clay Science 11,(2–4):237-249.
- Dudeney B., Demin O. and Tarasova I. (2003) 'Control of ochreous deposits in mine water treatment', Land

Contamination & Reclamation 11(2):259-266.

- Heal K., Younger P. L., Smith K., Glendinning S., Quinn P. and Dobbie K. (2003) 'Novel use of ochre from mine water treatment plants to reduce point and diffuse phosphorus pollution', Land Contamination & Reclamation 11(2):145-152.
- Heal K. V., Dobbie K. E., Bozika E., McHaffie H., Simpson A. E. and Smith K. A. (2005) 'Enhancing phosphorus removal in constructed wetlands with ochre from mine drainage treatment', Water Science and Technology 51(9):275 – 282.
- Hedin R. S. (1998) 'Potential recovery of iron oxides from coal mine drainage', Nineteenth Annual West Virginia Surface Mine Drainage Task Force Syposium.
- Hedin R. S. (1999) Recovery of Iron Oxides from Polluted Coal Mine Drainage. US Patent and Trademark Office, reference: 5954969.
- Hedin R. S. (2002) 'Recovery of Marketable Iron Oxide from Mine Drainage', Presented at the 2002 National Meeting of the American Society of Mining and Reclamation.
- Hodson M. E. (2008) 'Research Proposal: Remediation of arsenic contaminated soils with mine ochres'.
- Jang M., Chen W. and Cannon F. S. (2008) 'Preloading Hydrous Ferric Oxide into Granular Activated Carbon for Arsenic Removal', Environmental Science & Technology 42(9):3369-3374.
- Katsoyiannis, I. A. and Zouboulis, A. I. (2002) 'Removal of arsenic from contaminated water sources by sorption onto iron-oxide-coated polymeric materials', Water Research 36:(5141–5155).
- Manning B. A., Fendorf S. E. and Goldberg S. (1998) 'Surface Structures and Stability of Arsenic(III) on Goethite: Spectroscopic Evidence for Inner-Sphere Complexes', Environmental Science & Technology 32(16):2383-2388.
- Marcello R. G. S., Peterson M., Riella H. G. and Bernardin A. M. (2008) 'Inorganic pigments made from the recycling of coal mine drainage treatment sludge', J Environ Manage 88(4):1280-4.
- Mayes W. M., Potter H. A. B. and Jarvis A. P. (2009) 'Novel approach to zinc removal from circum-neutral mine waters using pelletised recovered hydrous ferric oxide', Journal of Hazardous Materials 162(1):512-520.

Neville K. (2007) 'The use of mine water ochre in artifi-

cial soils.' PhD thesis. Imperial College, University of London.

Pierce M. L. and Moore C. B. (1982) 'Adsorption of arsenite and arsenate on amorphous iron hydroxide', Water Research 16(7):1247-1253.

- Polizzotto M. L., Harvey C. F., Li G., Badruzzman B., Ali A., Newville M., Sutton S. and Fendorf S. (2006) 'Solid-phases and desorption processes of arsenic within Bangladesh sediments', Chemical Geology 228(1–3):97-111.
- Sibrell P. L. and Tucker T. W. (2012) Fixed Bed Sorption of Phosphorus from Wastewater Using Iron Oxide-Based Media Derived from Acid Mine Drainage. Water, Air, & Soil Pollution 223(8):5105-5117
- The Coal Authority. (2010) UK Department of Energy and Climate Change, Outine Sludge Strategy. Unpublished report

- Wei X., Viadero Jr, R. C. and Bhojappa S. (2008) 'Phosphorus removal by acid mine drainage sludge from secondary effluents of municipal wastewater treatment plants', Water Research 42 (13): 3275–3284.
- Wei X. and Viadero R. C. J. (2007) 'Adsorption and Precoat Filtration Studies of Synthetic Dye Removal by Acid Mine Drainage Sludge', Journal of Environmental Engineering 133(6):633-640.
- Wilkie J. A. and Hering J. G. (1995) 'Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes', Colloids and Surfaces 107:97–110.
- Younger P. L., Banwart S. A. and Hedin R. S. (2002) 'Mine Water: Hydrology, Pollution, Remediation', Kulwer Academic Publisher, Environmental Pollution (5):464.

Low-cost Long-term Passive Treatment of Metal-Bearing and ARD Water using Iron Rich Material

Adrian Brown

Adrian Brown Consultants, Inc., 130 W. 4th Avenue, Denver, Colorado, USA, abrown@abch2o.com

Abstract Iron-Rich Material (IRM) is the residue from processing electric arc furnace dust, and is an inexpensive passive water treatment medium for metal contaminants. IRM contains iron and akermanite (Ca₂MgSi₂O₇) which provide high amounts of the properties required for removal of metal contaminants: alkalinity, cation exchange capacity, adsorptive capacity, porosity, surface area, strength, and permeability. IRM can treat water with up to 1 g/L of metal contaminants, can remove to 10 % of its weight in metals, and can be regenerated, reprocessed, or disposed of when exhausted. This paper describes the chemistry, action, capabilities, performance, and design of IRM water treatment systems.

Keywords low cost, passive, treatment, mine water, iron-rich material, IRM, acid rock drainage, metal contaminants, lead, copper, zinc, cadmium, nickel, arsenic.

Introduction

Iron Rich Material (IRM) is a by-product of the removal of zinc from either zinc ore concentrate or zinc-containing waste material, principally generated by the steel industry as electric arc furnace dust. The process takes the zinc-containing material, adds coke and lime, and roasts the mixture in a Waelz Furnace at 1,200 °C to convert the volatile zinc into the gas phase where it is captured for sale. The zinc-depleted residue is known as "Iron Rich Material" (IRM), which has been marketed in the United States under the trade names of "HiSorb" and "Ecotite™" and in Spain under the brand name Ferrosita®.

Potential global IRM production is substantial. Approximately 10–20 kg of EAF dust is generated per tonne of EAF steel produced. Annual world production of EAF steel is currently 500 Mt (Rao 2011), creating a potential world-wide production of 5–10 Mt of IRM per year, so this material is abundantly available world-wide.

Iron Rich Material

A detailed evaluation of IRM with respect to its use as a water treatment agent has been con-

ducted by one of the US producers, Horsehead Industries (Ramesh 1992; Connors 1994; Gao 1995; Gao *et al.* 1995). The physical properties of run-of-process IRM are summarized in Table 1 and typical examples of chemical composition of IRM are shown on Table 2.

The mineralogy of IRM is complex: stoichiometric analysis, X-ray diffraction, scanning electron microscopy, and electron microprobe analysis has allowed identification and determination of the abundance of the two active components in IRM: iron compounds and akermanite (Table 3). Iron was identified in the form of α -Iron, Wustite (FeO), Hematite (Fe₂O₃), and Magnetite (Fe₃O₄).

As can be seen from Table 2 and Table 3, the composition of IRM is variable; this is the result of the diverse sources of the raw mate-

Parameter	Value	Unit
Surface Area	9.7	m²/g
Pore Volume	25	%
Void Volume	41.2	%
Bulk Density	1.5	g/mL
True Density	3.5	g/mL

Source: Gao, 1995, Table 3-1

Table 1 Physical characteristics of IRM

Element	Palmerton, PA ¹	Calumet, IL ²
Fe	28.20 %	41.70 %
Ca	10.70 %	7.44 %
Si	8.40 %	n.a.
Zn	4.10 %	1.36 %
Mn	3.60 %	3.47 %
Al	3.60 %	0.30 %
Mg	1.60 %	3.75 %
Cu	0.62 %	0.31 %
Na	0.55 %	0.28 %
Cr	0.31 %	n.a.
Κ	0.31 %	0.07 %
Pb	0.18 %	0.03 %
Ti	0.17 %	n.a.
Ni	0.12 %	0.06 %
0	36.44 %	n.a.
S	1.10 %	0.18 %

¹Source: Gao, 1995, Table 3.2; ²Source: This study; "n.a." indicates not analyzed

 Table 2 Chemical composition of US-produced

 IRM

Phase	Formula	Palmerton, PA	Calumet, IL			
Iron Oxides	$FeO_x (x = 0-1.5)$	36 %	54 %			
Akermanite	Ca ₂ MgSi ₂ O ₇	18 %	25 %			
Source: Calculated from Table 2						

Table 3 Mineral composition of IRM

rials that are used in its production, and the differing configurations and operations of Waelz furnaces.

Mode of operation of IRM as a treatment medium

The mode of operation of IRM when acting as a treatment medium for metals in wastewater is described by Gao (1995) as follows:

(*Cevery single IRM particle essentially contains ferrihydrite along with a crys-talline silicate phase, akermanite, in close proximity (in the order of 100 Å) to one another. Akermanite (calcium magnesium silicate) has a unique ability to produce hydroxyl ions through incongruent hydrolysis reaction without being washed out from the fixed bed. The si-*

multaneous presence of akermanite and ferrihydrite in a single particle has a synergistic effect on the sorption process: while akermanite helps neutralize aqueous-phase hydrogen ions (thus enhancing sorption capacity of ferrihydrite), neighboring sorption sites in ferrihydrite quickly remove dissolved heavy metals" (Gao 1995, 8–1).

Metal removal by IRM

The ability of IRM to remove metal constituents from wastewater has been investigated by passing water containing metals through test columns containing IRM (Gao 1995; Gao *et al.* 1995), and by observation of wastewater treatment during testing and use of IRM (this study). The experience of the effectiveness of metal removal by IRM is summarized in Table 4.

The removal capacity has been found to be dependent on the contact time between the wastewater and the IRM for both zinc and lead removal: the longer the contact time the greater the uptake capacity of IRM for metals (Table 5). The uptake capacity of IRM is also a weak function of the concentration of the metal in the wastewater (Table 6).

The metal uptake capacity of IRM in the research is supported by testing performed for this study by applying high concentration zinc (chloride) to IRM. Loading of zinc on coarse IRM of 5.2 % by weight was achieved, and additional uptake was available. It is estimated that for high wastewater metal concentrations (>1.5 meq/L) metal loading of up to 10 % by weight of IRM is achievable.

Quality of discharge from IRM treatment

The effluent quality resulting from properly designed treatment of wastewater by IRM is in general as follows prior to exhaustion of the treatment capacity of the IRM:

• Divalent metals lead, copper, zinc, nickel, and cadmium are essentially removed.

"Reliable Mine Water Technology"

(semi)- Metal	Removal Effectiveness	Effluent (mg/L)	Capacity (% wt of IRM)	Comment	Reference
Pb	v. Effective	0.001	> 5	Primary target	Gao (1995)
Cu	v. Effective	0.01	> 5	Primary target	Gao (1995)
Zn	Effective	0.02	> 5	Primary target	Gao (1995)
Ni	Effective	0.005	Unknown	Primary target	Gao (1995)
Cd	Effective	0.001	> 5	Primary target	Gao (1995)
Fe	Effective	0.1	> 5	Capacity estimated ¹	This study
Mn	Effective	0.01	> 5	Capacity estimated ¹	This study
As	Effective	0.01	Unknown	Capacity not reached	This study
Se	Limited	0.02	Likely limited	High solubility	This study
Ag	Unknown			Untested ²	
Al	Unknown			Untested ²	
Ba	Unknown			Insoluble sulfate	
Hg	Unknown			Low solubility	
Mo	Unknown	0.05	Released by IRM	-	Gao (1995)

¹Estimate assuming divalent form capacity similar to zinc; ²Ag, Al concentrations in test liquors too low to allow evaluation of removal effectiveness or capacity; v.: very

|--|

Contact Time Metal Removal (wt % of IRM)	1 min 1.2	10 min 2.7	1	h 3.9	1	ı d 5.9	1 week 7.2	Table 5 Metal removal ca- pacity of IRM vs. contact
Source: Data from Gao (1995), for lead at 0.145 meq/L in influent.						time		
Influent Zinc Concen IRM Zinc removal car	tration	mg/L % by wt	3	6	15 1.1	30 1.3		<i>Table 6</i> Metal removal ca-
Source: Data from Gao (1995), for zinc with contact time = 1 min								metal concentration

- Multivalent iron, manganese and selenium are partially or totally removed.
- Arsenic is partially removed
- Mineral acidity is removed.
- Calcium and magnesium are generally unchanged or are increased by dissolution or ion exchange, but can also be partially removed by precipitation as gypsum, calcite, or dolomite.
- pH is elevated, to between 8 and 12 depending on age of the IRM and contact time
- Sulfate and other non-metallic influent constituents essentially unchanged.

The quality of discharge from typical IRM treatment of an ARD-sourced wastewater is illustrated in Table 7, using data from a large scale vat test of IRM conducted for this study.

Ecotoxicity of effluent from IRM treatment

Samples of effluent from treatment of ARDsourced water have been evaluated for ecotoxicity for two standard indicator species (Table 8). The tests indicate that the two standard indicator species can survive in essentially undiluted IRM, showing that the effluent is generally benign to aquatic life.

Hydraulics of IRM during wastewater treatment

The hydraulic conductivity of intact IRM was measured in this study, and was found to range from 5×10^{-6} to 5×10^{-8} m/s. These values are sufficient to allow flow through the

Field Parameters	Influent	Effluent
рН	5.9	10.6
Conductivity (µS/cm)	3070	2830
Temperature (°C)	14.1	14.6
Major lons (mg/L) and parameters		
TDS	5230	4300
SO ₄	3190	2780
Cl	31	36
Ca	300	670
Mg	410	170
(semi)-Metals (mg/L)		
As	0.150	0.009
Cd	0.006	0.001
Cr	0.005	0.005
Fe	290.000	0.090
Mn	150.000	0.008
Мо	0.003	0.044
Ni	0.068	0.003
Se	0.086	0.013
Zn	41.000	0.022

 Table 7 Typical treatment of ARD-sourced water

 by IRM

particles of IRM, and the high porosity of the particles (Table 1) also allows ready access for diffusion within the particles.

Granular IRM has a high inherent permeability, in the order of 5×10^{-4} to 5×10^{-2} m/s, varying considerably between different production locations and batches of IRM. This hydraulic conductivity is typical of a coarse sand and gravel, which is consistent with the appearance and measured grainsize distribution of the IRM.

Hydraulic conductivity can be affected by the physical and chemical effects of the water treatment process:

- **1.** Capture of iron hydroxide particulates formed by oxidation of the influent water by filtration (can cause plugging of pore volume).
- 2. Precipitation of metal hydroxides formed within the IRM during treatment onto the IRM matrix (reduces pore volume).
- **3.** Changes in volume of the IRM caused by ion exchange between the wastewater and

	Water Flea Daphnia magna	Fathead Minnow Pimephales promelas
48-hour LC ₅₀ , % of IRM effluent	> 100	94

Table 8 Ecotoxicity testing of effluent from IRMtreatment of ARD-sourced water

the IRM (can result in an increase or a decrease in pore volume).

- **4.** Changes in volume of the pore space in the IRM by adsorption of metals from the influent (can cause a decrease in the pore volume).
- **5.** Precipitation of over-saturated compounds due to treatment; particularly precipitation of gypsum due to increase in calcium concentration by ion exchange.

Testing of the treatment process indicates that the cumulative effect of all these processes has the effect of reducing hydraulic conductivity of the IRM as shown in Table 9.

These changes in hydraulic conductivity resulted in each case in an increase in head loss through the IRM treatment medium of less than 0.1 m; the reduction in permeability had no significant impact on the effectiveness of the testing system.

Performance of an actual passive IRM treatment facility

The first major application of IRM for water treatment at a metal processing facility in the United States occurred at the Palmerton Zinc Cinder Bank Superfund Site. A total of 90,000 t of IRM was placed in a constructed trench to bedrock at the downhill toe of portion of a large zinc cinder bank. Since 1979 the IRM has been treating an average of 500 m³/d of metalcontaminated mine water. This wastewater stream has been cleaned up as illustrated in Fig. 1, with in excess of 98 % reduction in lead, cadmium, and zinc for more than 30 years. The facility is almost entirely passive, requiring only monthly effluent monitoring since its in-

Tost	Hydraulic	Conductivi	ty (m/s)	Coursel	
lest	Before	After	Change	Cause	
Column Test [Connors 1994]	1.5×10^{-2}	9.0 × 10 ⁻³	-40 %	Iron oxide within column	
Column Test [this study]	2.8×10^{-4}	1.4×10^{-4}	-50 %	Iron oxide precipitate on inlet	
Vat Test [this study]	1.1×10^{-3}	5.3×10^{-4}	-51 %	Iron oxide precipitate on inlet	

¹Reference to "iron oxide" is to ochre-colored precipitate, believed to be hydrated ferrous oxide but not tested.

Table 9 Permeability changes in IRM treatment beds

stallation. To date a total of 768 t of zinc, 1.6 t of lead, and 1.8 t of cadmium have been captured by the IRM in the trench, representing 0.76 % of the IRM mass in the trench.

Design methodology

The design of an IRM treatment system for a specific site comprises four elements, as follows:

- 1. Check that IRM can remove the metal contaminants in the wastewater stream. The ability of IRM to remove the metal contaminants in the wastewater can be preliminarily checked by reference to Table 4. For substantial applications of the technology, proof of applicability by direct testing using the actual wastewater is recommended.
- **2.** Check that the concentration of metal contaminants is suitable for IRM treatment. The applicability of IRM as a treatment medium is limited to wastewaters

where the concentration of metals is sufficiently low to avoid plugging of the medium by (particularly) gypsum precipitation. During treatment, calcium is released from akermanite by dissolution and ion exchange, which can lead to supersaturation and precipitation of gypsum. A working rule of thumb is that if the total metal contaminant concentration exceeds 1 g/L and the total sulfate concentration exceeds 1.5 g/L in the wastewater, a geochemical as well as bench test check of the possibility of plugging of the IRM treatment medium by precipitation should be conducted before proceeding.

3. Determine the required quantity of IRM for treatment of the wastewater stream. The total mass of metal contaminant that is required to be removed is computed from the known flow rate, the metal concentration(s), and the desired treatment period. The required IRM mass to achieve that removal is computed by assuming



Fig. 1 Effluent from long-term performance of an IRM mine water treatment system

that it will take up a minimum of 5 % of its weight in total metal contaminants. Bench scale testing of the uptake should be conducted using the actual wastewater stream and the actual IRM which will be used, to verify this computation.

4. Determine the required quantity of IRM to obtain the design contact time. The default retention or contact time is 1 day, which corresponds to the 5 % uptake performance (Table 5). The quantity of IRM that is required to provide sufficient porosity to achieve that retention or contact time can be computed using the measured porosity and density of the IRM, or the values presented in Table 1 above.

A balanced design may be achieved by adjusting the contact time so that quantity of IRM just provides the required uptake capacity and the required retention volume.

IRM treatment systems

IRM wastewater treatment systems have the following components:

- 1. Gathering System. Wastewater to be treated is collected and piped to the IRM treatment facility. Where possible, this should be conducted anaerobically to avoid the need to pre-filter the input stream to remove oxidized iron and manganese precipitates.
- 2. Input. An input zone is generally required for introduction of the treatment water to the system. This is usually a permeable, inert material, such as gravel, separated from the downstream IRM by a geotextile or other permeable medium. If the influent wastewater contains particulates, the input system should be designed to remove them prior to the water entering the IRM. As the methodology is intended to be passive, the filtration should also be passive where possible.
- **3.** Treatment. The wastewater should pass through a relatively long and narrow IRM

pathway, enclosed within a concrete- or synthetic membrane-lined cell from which oxygen is excluded. This approach creates serial treatment, so that the IRM close to the entry point is subject to the highest concentration of metal contaminants in the influent stream, and thus achieves the maximal uptake amount (approaching 10 % of metal by weight in the IRM). The downstream portion of the IRM serves as a polishing area, ensuring that the metal contaminant concentrations in the effluent water meet relevant and applicable discharge standards.

- 4. Discharge. Treated water should be discharged to contact the atmosphere, preferably in a cascade and/or a wetland. This will result in aeration which will satisfy any oxygen demand prior to release to a surface stream. Incomplete iron and manganese removal may result in some precipitation in this area. In some jurisdictions, it may be necessary to adjust the pH of the effluent water to meet discharge standards, which often require an upper bound pH of 9. This is most easily and sustainably achieved by blending the effluent with equal parts of stream water.
- 5. Waste disposal. One of the key benefits of IRM treatment systems is that they do not require waste disposal. Properly designed, the wastewater source will in general be depleted before the IRM uptake capacity is exhausted. In the event that this is not achieved, the spent IRM may be either removed for non-hazardous disposal, regenerated using ammonia (Gao 1995), or reprocessed in a Waelz furnace and the metal content recovered.

Conclusion

Iron Rich Material is an abundant, low cost recycled material which is ideal for passive removal of metal contaminants from mine water and other wastewater streams. IRM comprises an alkaline source in conjunction with an ion exchange medium and adsorptive iron substrate, in a structurally sound, high permeability, high surface area material. It has the ability to uptake as much as 10 % by weight of metal contaminants. In application, the treatment medium is generally enclosed to maintain anaerobic conditions, and serial treatessentially ment removes all metal contaminants from the wastewater stream. It provides a reliable treatment system, which requires only remote monitoring for most operational applications, and does not in general require filtration or waste disposal.

References

Connors TM (1994) Hydraulic behaviors of an iron-rich heavy metal sorbent in a packed bed column. Master of Science in Civil Engineering Thesis, Lehigh University, May 1994.

- Gao YM, Sengupta AK, Simpson D (1995) A new hybrid inorganic sorbent for heavy metals removal. Water Resources, 29(9), 2095–2205.
- Gao YM (1995) Sorption enhancement of heavy metals onto a modified iron-rich material. Doctor of Philosophy in Civil (Environmental) Engineering Thesis, Lehigh University, Bethlehem PA, August 1995.
- Ramesh A (1992) Selective sorption of heavy metals using an iron-rich waste byproduct, Master of Science in Civil Engineering Thesis, Lehigh University, Bethlehem, PA, 1992.
- Rao SR (2011) Resource recovery and recycling from metallurgical wastes. Elsevier 2011.

Development of Treatment Solutions for the Central City/Clear Creek Superfund Site in Colorado

Kevin W. Conroy, Brian D. Huff, Neal T. Gallagher

Golder Associates Inc., Lakewood, Colorado, USA, kconroy@golder.com, bhuff@golder.com, ngallagher@golder.com

Abstract The Central City/Clear Creek Superfund Site was added to the CERCLA National Priorities List in 1983, and is being remediated under the management of the Colorado Department of Public Health and Environment with major funding from the USEPA. Historic mining and milling activities resulted in watershed contamination of cadmium, copper, iron, manganese and zinc. The objectives of the project were to ultimately design and build a full-scale automated lime high density sludge (HDS) precipitation water treatment plant (WTP) to treat mining influenced water (MIW) at a design flow ranging from 680 to 2,270 L/min.

Keywords Acid mine drainage active treatment, high density sludge (HDS), lime precipitation, mining influenced water (MIW)

Introduction

The Central City/Clear Creek Superfund Site (Site) was added to the CERCLA National Priorities List in 1983, and is being remediated under the management of the Colorado Department of Public Health and Environment (CDPHE) with major funding from the USEPA. The Site encompasses more than 1,030 km² of the Clear Creek watershed, situated in the Rocky Mountains approximately 50 km west of Denver, Colorado. Multiple waste piles, tailings impoundments, draining mine adits and impacted groundwater resources exist within the watershed. Historic mining and milling activities resulted in the watershed becoming contaminated with cadmium, copper, manganese and zinc all of which can exceed water quality standards, impact aquatic life and pose a threat to human health. A key aspect of the overall remediation effort is the design and eventual construction of an active treatment facility to treat mining influenced water (MIW) including collected underground mine seepage and impacted groundwater.

The objectives of the project are to ultimately design and build a full-scale and fully functioning lime high density sludge (HDS) precipitation water treatment plant (WTP), which will treat a design flow anticipated to range from 680 to 2,270 L/min. A unique aspect of this project is its proximity to the historic mining towns of Black Hawk and Central City, Colorado. Both towns are now low-stakes gambling centers with significant historic mining influence. Their geographic locations also posed special challenges for siting and access to water collection areas. The OU4 WTP will be located within a tight canyon bounded by Colorado Highway 119 to the east and the North Fork of Clear Creek (North Fork) to the west. Part of the solution to find a suitable site for the WTP was a partnership with the Colorado Department of Transportation (CDOT) to combine a highway construction project with site development. Blasting of rock and rerouting of Highway 119 provided approximately 0.45 ha for construction of the WTP. The project also demanded innovative solutions to facility siting challenges and attention to detail to blend the facility with local the historic ambience.

Influent to the OU4 WTP will consist of four acid rock drainage sources on the Site including the Gregory Incline tunnel (GI), National Tunnel (NT), and surface (SW) and groundwater (GW) from the Gregory Gulch drainage, which currently contribute to metal contamination in the North Fork. In order to dampen some of the flow variability equalization of influent will occur in a 1,120 m³ below grade influent equalization vault. Treated water from the WTP will be discharged to Clear Creek Section 13b. Colorado Water Quality Control Division Stream Standards (stream standards) for Clear Creek Section 13b (CWQCD 2010; CWQCD 2011) are used for comparison purposes, as effluent limits have not yet been established for the site.

In the treatment process addition of hydrated lime to acidic wastewaters causes dissolution of lime, which in turn elevates pH by increasing the presence of hydroxide ions. Ferric iron (Fe³⁺) is less soluble at typical lime treatment and effluent pH ranges of 8–10 (USEPA 1983). In addition, ferric iron type sludges typically settle and dewater better than ferrous iron (Fe²⁺) type sludges. Therefore, Fe³⁺ is preferable to Fe²⁺. Since Fe²⁺ is known to be present in the incoming wastewater a pretreatment step using oxidation was tested in bench and pilot studies to oxidize Fe²⁺ and to promote treatment of manganese (Mn), which will produce denser solids.

HDS is an improvement on conventional lime treatment which can produce thickener underflow solids (underflow) concentrations upwards of 20 % (w/w) or more, thereby reducing the cost of solids handling and disposal. HDS is an established and widely implemented technology used commonly in industry for active abiotic treatment of MIW dominated by iron chemistry (Coulton et al. 2004). HDS treatment involves recycle of thickener underflow to an intermediate densification tank prior to the reaction tank where solid particles are contacted with lime slurry, encouraging lime to coat the solids. Coating of solid particles with lime provides greater surface area for contact with raw influent when solids are introduced into the reaction tank. The larger lime coated surface area of particles as well as higher pH of particles in contrast to surrounding solution promotes precipitation reactions to occur on the surface of existing particles and therefore, the size and density of formed particles is increased. (MEND 1994). HDS treatment is typically applied to MIW with substantially higher metal concentrations than those found in the OU4 influent source waters (Coulton *et al.* 2004). Bench and pilot studies were therefore able to prove process effectiveness and define design parameters for full-scale design.

Methods

An influent design basis report was compiled (Golder 2011) from available data including previously performed characterizations (Tetra Tech RMC 2002; Tetra Tech RMC 2004) and stream gauge data (USGS 2011) for the four individual MIW source areas. Golder also implemented a sampling campaign to collect further water quality and water flow data to help resolve data gaps. Based on the characterization effort expected source blend ratios were developed for use in bench testing, pilot testing, and full-scale design. Throughout testing an average blend and worst case blend were used, representing the expected average blend of the four sources and worst case blend of the four sources with respect to metal load (solids production). The worst case metal load is expected to happen during low flow to the WTP (Golder 2011).

HDS bench test objectives included definition of treatment pH, reaction time, and dosing of lime, polymer, and oxidant. Jar testing was used for the majority of the bench tests. Tests performed include titration testing, oxidation testing, visual polymer screening, and benchscale HDS testing. Titration and oxidant testing was performed at pH 8.8, 9.2, and 9.7. Oxidation was performed via hydrogen peroxide (H₂O₂) dosed at 0.0008 mol O_2/L and 0.0014 mol O_2/L , or one and one and a half times the theoretical dose required to oxidize Fe and Mn in the average blend. Visual polymer screening was performed using three types of anionic polymer dosed between 1 and 7 mg/L on average blend water titrated to a pH of approximately 10. Bench HDS testing was performed by mimicking the effect of solids recycles on average blend water titrated to approximately pH 10. This testing was performed to 26 recycles with varying polymer dose between 2.5 and 5.5 mg/L as observed settling characteristics changed.

HDS pilot testing objectives built on bench results to further define process parameters for full-scale design of the OU4 WTP. Pilot testing was performed at 1.9 L/min. Data collected was intended to pinpoint the range of treatment pH, define oxidation requirements and verify oxidation benefits, determine minimum reaction time, size the thickener, determine influent solids generation rate, define the ideal solids recycle ratio (SRR), determine solids dewaterability and toxicity, and define effluent toxicity assessed using Whole Effluent Toxicity (WET) testing.

Water used during pilot testing included the average and worst case (low flow) water blends. Low flow water blend was used in the final stages of pilot testing as an indicator that selected process parameters were capable of treating the highest influent metal load expected at the WTP. The equipment used for pilot testing consisted of a 19 liter densification tank, 190 liter reaction tank with adjustable hydraulic retention time (HRT) of 30, 20, and 10 min, and a 380 liter thickener and rake. Polymer mixing was initially achieved by static mixer and after clogging in the static mixer proved an obstacle, in a 10 liter flocculation tank. Hydrated lime (Ca(OH)₂), polymer (BASF 4105), and oxidant (H₂O₂) were metered as 10 %, 0.01 %, and 0.7 % (w/w) solutions respectively.

Dosing of lime slurry was automated using feedback from the reaction tank pH probe. Results from visual settling tests run on thickener feed samples dictated polymer dosing which ranged between 0.2 and 0.5 mg/L. Oxidant was dosed as H₂O₂ somewhat below theoretical requirement for Fe and Mn oxidation at a steady 0.009 mol O₂/L due to operational difficulties with the metering equipment. SRR was optimized during commissioning of the pilot resulting in a SRR of 20:1 being used for the remainder of pilot testing. Four stages of pilot testing were performed. Startup of the pilot, optimization of SRR, and build-up of solids inventory was accomplished during commissioning. During Cycle A, the pilot unit was operated at three distinct pH set points of 8.5, 9.0, and 9.5 with oxidation. In Cycle B, the pilot was operated at three distinct pH set points of 9.0, 9.5, and 10.0 without oxidation. During Cycle C, optimal conditions determined during Cycles A and B were tested, and reaction tank HRT was optimized.

Analytical samples of unfiltered decant from settled thickener feed were taken at each pH set point. During Cycle C, one sample was taken during the 30 min HRT test from settled thickener feed decant and filtered through a Whatman 40 filter, neutralized to a pH of 6.9, and sampled for WET testing as well as analytical testing. Cycle C at 30 min HRT thickener solids were sampled for Toxicity Characteristic Leaching Procedure (TCLP). Off-site filter press analysis was performed on thickener solids to verify dewaterability.

Full-scale design of the OU4 WTP was completed using bench and pilot test results as a foundation for unit processes and equipment, including lime delivery, reaction tank HRT, optimal range of treatment pH, thickener sizing, underflow recycle pump sizing, solids storage requirements, polymer dosing, oxidation requirements, and filter press sizing. Innovative technologies were incorporated into design of the WTP including continuous backwash sand filters and a high density lime makeup and delivery system. Proximity of the WTP to the town of Black Hawk influenced the characteristics of the building and outer portions of the site. It also influenced the decision to place the clarifier inside of the WTP building. The relatively small footprint of the site also influenced WTP design and configuration.

Results and Discussion

The influent design basis provided ratios for the average and low flow influent blends. These generally consisted of approximately 45 % GI, 15 % NT, 30 % SW, and 10 % GW (v/v) and 83 % GI and 17 % NT (v/v) respectively, with some variation throughout testing. GI contributed the majority of Fe, Mn, and zinc (Zn) load to the average blend. Copper (Cu) in the average blend was sourced somewhat evenly between GI, SW, and GW. The bulk of the cadmium (Cd) load came from the SW, followed closely by GW and GI. The majority of Fe in the average and low flow blends was Fe²⁺, 108.1 mg/L and 183.8 mg/L respectively, indicating

oxidation should benefit effluent quality and settling characteristics of solids.

Average blend water was used throughout bench testing. Results of bench testing indicated that without oxidation effective treatment below chronic stream standards could be achieved at pH 9.7 and with oxidation at pH 9.2. During bench HDS testing, underflow solids gradually increased in percentage as recycles increased. A maximum underflow percent solids of 5.5 % was achieved after 26 recycles. Bench HDS test polymer demand gradually increased with recycle, reaching a peak of 5.5 mg/L. Bench HDS test lime demand varied 0.35 to 0.50 g Ca(OH)₂/L to reach pH 9.7 to pH 10.3. From results of visual polymer screening conducted at the bench-scale, it was found that 3-5 mg/L of BASF 4105 was most effective in formation of flocculated particles and removal of 'pin floc' in decanted jar test water after three minutes.

Pilot HDS treatment of average blend influent treated metals below stream standards (Table 1). Average blend pilot effluent was below stream standards in all tests, with the exception of parameters for which laboratory detection limits were above stream standards and Cu (d) in Cycle B at pH 9.0. Treatment performance generally improved with oxidation at comparable pH. Results indicate a pH of 8.5 with oxidation and pH 9.5 without oxidation would be effective in treating average influent to the OU4 WTP. An inherent advantage exists in operating at a pH of 8.5, as neutralization of treated effluent would not be required prior to discharge. Low flow blend water was used during Cycle C of pilot testing. Tests were run at a pH of 8.5 with oxidation, identified in Cycles A and B as optimal, and HRT varied between 30, 20, and 10 min. As HRT lowered, a noticeable decrease in performance was observed (Table 2). Treated pilot low flow blend was below stream standards in all tests, with exception of parameters for which the laboratory detection limits were above stream standards, Mn at 10 min HRT, and Cu in the neutralized test at 30 min HRT (likely an outlier).

Pilot testing effluent measured during Cycle C passed WET testing – no significant toxicity was found in the treated effluent. TCLP tests run on pilot thickener solids demonstrate that pilot generated solids are well below the TCLP D-List maximum contaminant levels (MCLs); see Table 3. These results indicate pilot generated solids are not a hazardous waste per RCRA guidelines and can therefore be disposed of in a municipal landfill.

During pilot testing underflow percent solids was consistently near 20 %, with a maximum value of 23.1 %. Settling tests indicated design would be performed based on solids load for thickening in place of rise rate for clarification. Sizing calculations demonstrate a 15 meter diameter thickener would provide effective clarification and thickening. Offsite filter press performance testing of pilot thickener underflow indicated solids were compressible to 53 % solids at 690 kPa pressure.

Based on the results of the influent characterization, bench and pilot studies, full-scale

	Oxidant	Cd (d)	Cu (d)	Fe (d)	Mn (d)	Zn (d)	SO_4
	$mol O_2/L$	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Average blend	-	0.0265	0.54	57.5	16.5	6.8	1,350
Acute standard ^{1/}	-	0.00051	0.0036	-	1.9	-	-
Chronic standard ¹		0.00015	0.064	-	1	0.74	-
Cycle A pH 8.5	0.0009	< 0.00045	0.002	< 0.022	0.0068	< 0.0045	1,000
Cycle B pH 9.0	-	< 0.00045	0.005 ^{2/}	0.16	0.058	0.03	970
Cycle A pH 9.0	0.0009	< 0.00045	0.0015	0.027	0.0088	0.0068	980
Cycle B pH 9.5	-	< 0.00045	0.0015	< 0.022	0.0012	0.0045	970
Cycle A pH 9.5	0.0009	< 0.00045	0.0024	< 0.022	0.00064	< 0.0045	990
Cycle B pH 10.0	-	< 0.00045	0.0029	0.03	0.012	0.013	960

< indicates analytical results was below laboratory MDL

1/ Colorado Clear Creek Segment 13b stream standards

2/ Exceeds acute stream standard

Table 1 Average blend influentent pilot results

	Oxidant	Cd (d)	Cu (d)	Fe (d)	Mn (d)	Zn (d)	SO 4
	mol O ₂ /L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Pilot low flow blend		0.011	0.32	120	30	6.8	1,700
Acute standard 1/	-	0.00051	0.0036	-	1.9	-	-
Chronic standard 1/	-	0.00015	0.064	-	1	0.74	-
Cycle C pH 8.5 HRT 10 min	0.0009	< 0.00045	< 0.0014	0.038	1.4 3/	0.0067	1,800
Cycle C pH 8.5 HRT 20 min	0.0009	< 0.00045	< 0.0014	< 0.022	0.63	< 0.0045	1,800
Cycle C pH 8.5 HRT 30 min	0.0009	< 0.00045	< 0.0014	< 0.022	0.435	< 0.0045	1,800
Cycle C pH 8.5 HRT 30 min ^{2/}	0.0009	0.00085 4/	0.0022	< 0.022	0.66	0.11	1,900

< indicates analytical results was below laboratory MDL

1/ Colorado Clear Creek Segment 13b stream standards

2/Whatman 40 filtered and HCL neutralized to pH 6.9 prior to analytical sampling

3 / Exceeds chronic standard

4/ Exceeds acute standard

design was completed. Design parameters defined during bench and pilot testing were incorporated in the design and sizing of fullscale OU4 WTP process equipment. For full-scale design, aeration was incorporated for oxidation in place of chemical oxidation due to human and environmental safety concerns. Using aeration, Fe²⁺ and Mn oxidation is expected to be more pH dependent than with chemical oxidation. To address this effect, contingency was built into the design to operate to pH 10 when periods of elevated Fe²⁺ and Mn may require enhanced oxidation and higher operating pH to meet discharge standards. To neutralize and meet discharge pH requirements, a CO₂ neutralization unit process was incorporated.

Lime system capacity was designed meet lime demands of influent water ranging between 680 to 2,270 L/min at pH 8.5 to 10.0. Calculated lime demand was 1,817 kg/d at maximum flow conditions. Under 1,225 kg/d, hydrated lime is generally more cost effective than quicklime (NLA 1995). This encouraged design of a high density lime (HDL) system, which can deliver 35 % Ca(OH)₂ slurry to the process. Benefits of HDL include no dewatering of slurry over extended periods of time without mixing, no scale of delivery piping and elimination of the recirculation typically Table 2 Low flow blend influent pilot results

required in lime delivery to keep slurry mixed.

Underflow produced during pilot study exhibited increased settling rate compared to bench study underflow. Pilot underflow became darker as testing continued, suggesting the presence of higher oxidation states of Mn. Pilot underflow percent solids was upwards of 20 % at a SRR of 20:1, which was used for fullscale solids storage and underflow recycle design basis. Capacity was also built in to accept underflow to 10 %. A unique aspect of the OU4 plant is that solids storage was designed in the thickener due to site space limitations. In addition, a cylindrical bottom in the thickener was included in the design to discourage short circuiting of decant through thickener solids during filter press draws and solids recycle pumping.

Dewatered pilot underflow achieved 53 % solids at 690 kPa pressure. Contingency was designed into the OU4 WTP filter presses to dewater solids to 35 % solids under continual operation of one press throughout an 8 hour shift during high flow periods. The filter presses are redundant, providing increased contingency during high flow and high solids load periods. The OU4 WTP is designed to operate automated twenty four hours per day, seven days per week, with personnel onsite daily for an eight to ten hour shift.

	As	Ba	Cd	Cr	Pb	Hg	Se	Ag
	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Underflow TCLP	0.022	0.053	0.028	0.009	0.013	0.00003	0.025	0.004
TCLP D-List MCL ^{1/}	5.0	100	1.0	5.0	5.0	0.2	1.0	5.0
Motale are total fracti	on							

Metals are total fraction

1/ United States Resource Conservation and Recovery Act (RCRA)

Table 3 Pilot solids TCLP results

Conclusions

Use of bench and pilot testing to prove HDS technology effective in treatment of expected OU4 influent water allowed effective definition of design parameters and understanding of necessary contingencies to be designed into the fullscale 680-2,270 L/min WTP. Full-scale design parameters including lime demand, polymer dosing, oxidation, underflow and filter cake percent solids, settling and thickening characteristics of solids, and reaction time were tested and defined during bench and pilot testing. Flexibility was designed into the full-scale WTP for operation under varying metal loads and influent flow anticipated throughout the year to effectively treat influent Mn considering the use of air for oxidation. The design SRR of 20:1 was determined to be most effective for thickening of underflow solids. Reaction time in the full-scale WTP was designed to be thirty minutes at 2,270 L/min. A maximum underflow percent solids of 23.1 % was measured and bench and pilot influent was effectively treated below stream standards. The multiple OU4 WTP influent sources will experience extreme seasonal variations in flow and metal load. It was necessary to design the OU4 WTP with sufficient contingencies to effectively meet treatment performance goals when unpredictable changes in seasonal flow rate and metal load from influent sources were expected. The OU4 project required a thorough and extensive characterization and process development effort to ensure that water quality objectives in Clear Creek, including restoration of sustainable fish populations, could be achieved. Innovative solutions to facility siting challenges and attention to detail to blend the facility with local the historic ambience were also paramount. The OU4 WTP will improve the overall quality of Clear Creek, a source of drinking water for multiple municipalities downstream, mitigating impacts of nearly a century of mining activity in the region around Central City.

References

Colorado Water Quality Control Division (CWQCD) (2010) Regulation No. 38: Classifications and Numeric Standards for South Platte River Basin, Laramie River Basin, Republican River Basin, Smoky Hill River Basin (5 CCR 1002–38). Denver, Colorado: CWQCD

- Colorado Water Quality Control Division (CWQCD) (2011) Regulation No. 31: The Basic Standards and Methodologies for Surface Water (5 CCR 1002–31). Denver, Colorado: CWQCD
- Coulton R, Bullen C, Williams C, Williams K (2004) The formation of high density sludge from mine-water with low iron concentrations. 2004 International Mine Water Association Symposium 24–30 Newcastle upon Tyne, United Kingdom: International Mine Water Association.
- Golder Associates Inc. (Golder) (2011) Revised Influent Design Basis for Clear Creek/Central City Superfund Site Operable Unit 4 Water Treatment Plant Design. Denver Colorado: Adam Hobson
- Mine Environment Neutral Drainage (MEND) (1994) Report 3.32.1: Acid mine drainage-Status of chemical treatment and sludge management practices. MEND, Canada
- National Lime Association (NLA) (1995) Lime: Handling, Application and Storage. Arlington, Virginia: National Lime Association
- Tetra Tech RMC (2002) Data Review and Evaluation Report, Remedial Investigation/Feasibility Study, Clear Creek/Central City Superfund Site, Operable Unit 4. Longmont, Colorado: Tetra Tech RMC
- Tetra Tech RMC (2004) Clear Creek/Central City Superfund Site – Operable Unit 4: Final Remedial Investigation Report. Longmont, Colorado: Tetra Tech RMC, USEPA Region VIII, and CDPHE
- United States Environmental Protection Agency (USEPA) (1983) Design Manual: Neutralization of Acid Mine Drainage (Publication No. EPA-600/2-83-001). Cincinnati, Ohio: Office of Research and Development Industrial Environmental Research Laboratory
- United States Geological Survey (USGS) (2011) Peak Streamflow for the Nation, USGS 06718550 North Clear Creek Above Mouth near Black Hawk, CO. Retrieved from:
 - http://nwis.waterdata.usgs.gov/nwis/peak?site_no= o6718550&agency_cd=USGS&format=html

Water Management and Treatment for the Copperwood Mine Project

Kevin W. Conroy¹, Anna M. Moderski²

¹ Golder Associates, Inc., 44 Union Boulevard, Suite 300, Lakewood, Colorado, USA, Kevin_Conroy@golder.com; ²Anna_Moderski@golder.com

Abstract This paper will discuss the water treatment planning and engineering for a mining project in the Upper Peninsula of Michigan. This has included completion of a detailed probabilistic simulation of the water management system coupled with a geochemical model to predict the final water quality to be treated in the water treatment facility. One of the stated goals for the project is to minimize discharge from the site and reuse water to the extent practical. However, if discharges from the site are required, they must comply with NPDES permit requirements as outlined in the Part 57 rules in Michigan.

Keywords tailings water treatment, mercury, water reuse

Introduction

Mining in the Upper Peninsula has experienced a resurgence in interest the past five years with multiple projects in the process of being permitted and constructed. Orvana Resources signed mineral leases in the fall of 2008 and 2010 for a proposed silver-copper mine for property near the Michigan-Wisconsin boarder on the shores of Lake Superior. Positive Prefeasibility and Feasibility Studies have been completed and a Part 632 Mining Permit has been received from the State of Michigan for the Copperwood project.

The process water balance governs the management, storage, and to a minor degree the treatment of water in the tailings slurry (TS) and the tailings disposal facility (TDF), underground mine dewatering, and water in the process circuit. Three objectives of the water balance were to identify the fluctuations of water volumes in the process circuit on a daily basis over the operating life of the facility; to provide an estimate of the range of potential water deficits and water surpluses that may occur during operations so that appropriate sources of make-up water as well as provisions for storage or disposition of surplus water can be provided for; and to provide a basis for sizing the TDF, the treatment plant, and other facilities.

Of particular concern throughout the planning process has been the management and treatment of mining impacted water from the project given its location near Lake Superior and the water quality requirements as developed in the Great Lakes Initiative. If discharges from the site are required, they must also comply with NPDES permit requirements as outlined in the Part 57 rules for the State of Michigan. Application of these two sets of criteria as end-of-pipe treatment goals allowed for contaminants of potential concern and resulting contaminant removal efficiencies to be identified.

The treatment facility must be capable of treating a range of contaminants requiring a robust and flexible treatment process that is quite different from conventional mine water treatment applications. Specific contaminants of potential concern include mercury at a very low level, 1.3 ng/L. Additional contaminants of potential concern were established as constituents estimated to be at higher concentrations than the end-of-pipe treatment goals, as well as those parameters that might negatively impact the treatment units and their ability to remove other contaminants. The final contaminants of potential concern include ammonia, barium, beryllium, boron, copper, lead, mercury, selenium, silver, vanadium, and zinc.

Conceptual Water Balance

The first step in developing the process water balance was to prepare a conceptual model of the proposed water management system. The conceptual model consists of the system components and description of the interactions between the components.

Fig. 1 presents a schematic of the process water balance design basis. In summary, prior to operation of the process mill the TDF will have been constructed in parallel with the other site activities and begin to receive underground mine water, precipitation, and experience evaporation. Operation of the process mill results in a net water demand. The process mill water demand is supplied by three sources, in order of preference: Water in ore; TDF decant water; and make-up water.

The conceptual model evaluates water sources in the in ore; TDF decant water and required make-up water based on main model inputs such as the production schedule, climatic data, underground mine flow, TDF feasibility and water treatment feasibility. The boundary conditions for the model include the climatic data in the area of the site and the process mill water demand.

Climate

The climate can have a significant impact on the operation of the water management system. The tailings disposal facility has a substantial catchment area that generates significant runoff volumes during precipitation events. Therefore, a detailed record of climatic factors, precipitation, evaporation, and temperature were assembled that included data from 1977 to 2010. The record was sufficiently long to capture the long-term climatic variability in the area.

This region has a humid continental climate which is strongly influenced by the presence of Lake Superior. This indicates that the area generally experiences cool summers and weather patterns driven by the phenomenon commonly known as "lake effect". Lake effect influences a variety of factors including temperature, amount and timing of precipitation (including snowfall), and cloud cover.

The proximity of Lake Superior also results in increased cloudiness and precipitation because of the large amount of moisture available for air masses to acquire as they travel across the lake. This is a common occurrence since the predominant wind direction is from the west. This effect is exacerbated in the winter as cold air blows across the warmer lake acquiring moisture which it then releases as it comes in contacted with the colder land mass; thus resulting in frequent heavy snowfall.



Wolkersdorfer, Brown & Figueroa (Editors)
Growth and depletion of the snowfall on the TDF occurs as a function of temperature.

Dynamic, Probabilistic Water Balance

The conceptual model was the basis for developing a mathematical model of the water management system. A dynamic, probabilistic simulation program (GoldSim) was used. Sizing of the three stages of the TDF included the operational storage required for the supernatant pond as it increases and decreases over the operating seasons and years, as well as storage of the design storm, which was selected as the 72-h/half-PMP storm event. The general operating strategy avoids the accumulation of an excessive amount of water in the TDF that will require treatment at closure. The water balance model was developed to reclaim and re-use as much water as possible from the TDF.

The water in ore is calculated as a function of the ore production and moisture content, 3 %. The TDF has been designed to store the solids and manage the liquids from the Copperwood tailings, both during the period of operations and after closure. The solids will be retained in the impoundment together with some of the liquid. Liquids not retained will be collected via underdrains or decanted from the tailings surface. The TDF decant sump water will be recycled to the process mill for re-use in the process or treated and released in compliance with applicable water quality standards. Some water from a make-up source will be required when the water in the ore and TDF water is unable to fulfill the process mill water demand.

The conceptual model included an assessment of the variability and uncertainty in the data and system operations. The interactions between the system components were represented by empirical relationships or rules derived from the planned operating practices and analysis of the projected site data. For example, the operational rules for deciding whether to send water from the TDF to the process mill or treat and release.

Chapter 40, Code of Federal Regulations (40 CFR) Part 440 Regulation, for new source copper mines specifies allowable water discharge quantities. The allowable amount of discharge is the calculated difference between annual precipitation falling on the treatment facility and annual evaporation over the same area. A provision identified in 40 CFR Part 440 states that additional discharge is allowable if the mine can demonstrate that a build-up of contaminants would interfere with the milling process, which is the case for the project. The water treatment plant starts treating and either reclaiming water to the process mill or discharging water as soon as there is excess water in the TDF. Closure of the TDF can occur when the supernatant in the TDF allows for exposed tailings to be present. The projected water treatment rate allows for all TDF water to be treated within 4 years of cessation of operations and discharged to the receiving environment

The results of the water balance modelling effort indicate that an 80 m³/h treatment facility will be required to achieve project goals.

Water Quality Characterization

The water quality is dependent on the quality and quantity of the Tailings Slurry (TS) and Underground Mine (UM) geochemical characterization and precipitation sampling data. Predicted contaminants in the TS water are total organic carbon (TOC), total dissolved solids (TDS), total suspended solids (TSS), ammonia, and metals including barium, beryllium, boron, cadmium, chloride, copper, lead, mercury, selenium, silver, vanadium, and zinc. Predicted contaminants in the UM water include TDS, TSS and metals including barium, boron, cadmium, chloride, copper, lead, mercury, selenium, silver, and zinc. The TDF contaminant concentration is variable throughout active mining operations. Specific contaminants of potential concern in the TDF include ammonia, barium, boron, copper, lead, mercury, selenium, silver, vanadium, and zinc. It is assumed that selenium is present in the selenate form and mercury is present in the mercurous form. Selenate and mercurous are the most common forms of selenium and mercury found in mining and other industrial wastewaters.

Treatment Design Basis

Treatment goals were established for discharge to the receiving environment (tab. 1). It was assumed that the discharges to the receiving environment are sufficient for reuse in the process mill.

Based on the projected TDF contaminant concentrations data processes including membrane microfiltration, reverse osmosis (RO), and mercury post-treatment by ion exchange have been selected as most appropriate for the project as shown in Fig. 2. The system also includes mechanical evaporation to reduce the volume of brine from the reverse osmosis system and produce a dry solid for disposal. This combination of water treatment technologies will allow for effective reuse of treated water as well as fully compliant discharge to the receiving environment.

Treatment System

The microfiltration system includes a twostage reaction system followed by microfiltration. The first-stage reaction system allows for the softening of the water, removing a portion of the calcium and silica. The second-stage allows for polishing the pH to the target range of 10.5 to 11.1 and for additional mixing and precipitation of metals, calcium, and silica. Most metals are precipitated in the form of insoluble metal hydroxides. Other precipitates include barium sulfate, calcium carbonate and the magnesium-silica complex. The microfiltration system provides an absolute barrier to the passage of solids at a particle size cutoff of about 0.1 µm. This results in the removal of most colloids; and therefore, provides a filtrate that exhibits a very low silt density index, making the filtrate an appropriate feed for a RO unit. Sludge will be dewatered by a filter press and disposed of onsite.

Prior to the RO unit, the filtrate is adjusted to a pH of 6 and preconditioned with an antiscalant and an oxidant chemical to protect the RO membrane units. The preconditioned water is treated through adsorption using granular activated carbon (GAC) for removal of

Parameter	Units	End of Pipe Treatment Targets	% Removal Required	% Removal Projected
Total Dissolved Solids (TDS)	mg/L	500	85.8%	99.9%
Barium, Dissolved	mg/L	0.12	65.4%	100.0%
Boron, Dissolved	mg/L	5	10.3%	69.7%
Cadmium, Dissolved	mg/L	0.000918	7.4%	100.0%
Chloride	mg/L	50	89.7%	100.0%
Copper, Dissolved	mg/L	0.003	99.0%	99.9%
Lead, Dissolved	mg/L	0.003	44.2%	95.5%
Mercury, Low Level, Total	ng/L	1.3	98.6%	99.7%
Mercury, Dissolved	ng/L	1.3	98.6%	99.2%
Nitrogen, ammonia	mg/L	0.029	75.3%	97.7%
Selenium, Dissolved	mg/L	0.005	84.7%	98.9%
Silver, Dissolved	mg/L	0.00006	97.3%	13.3%
Vanadium, Dissolved	mg/L	0.012	59.2%	13.3%
Zinc, Dissolved	mg/L	0.043	43.7%	13.3%

Table 1 Treatment Targets and Required Removal Efficiencies

TOC. When the media is saturated (all adsorption sites exhausted) the media must be removed and disposed of. The GAC effluent will be fed to the RO unit.

RO treatment is a high-pressure membrane filtration process that utilizes a series of semi-permeable membranes. Prior to RO unit, the treatment stream is fed from through a 5 µm cartridge filter. Water and low levels of some ionic constituents pass through the membranes while the majority of the dissolved salts are retained on the brine side of the membranes. The RO System includes three RO units, two in series (primary and secondary RO units) and one to treat the brine from the first two RO units (brine recover RO unit). This configuration maximizes overall water recovery and minimizes the brine quantity.

The water is fed by a high pressure system to the primary stage RO unit. The permeate from the primary stage RO Unit and from the brine recovery RO unit is recombined and treated in the secondary stage RO unit. The permeate from the secondary stage RO unit is transferred to the permeate system. Brine from the primary and secondary stage RO units is stored to allow for an adequate reservoir prior to the brine recovery RO unit. Approximately 11.5 % of the forward feed is fed back to microfiltration system reaction tank and the remaining brine is transferred to the RO brine tank where hydrochloric acid is added to decrease the pH prior to evaporation. By recycling a portion of the brine, the overall water recovery is increased; and therefore, the volume of brine requiring further treatment is decreased by approximately 11.5 %. The brine will be fed to the evaporator/crystallizer system from the RO brine tank.

An overall water recovery rate of approximately 87 % is projected by modeling for the RO system. An increase to the overall water recovery rate above 90 % is anticipated during detailed design.

The combined permeate from the RO units will be fed to the ion exchange system. The ion exchange system consists of two pressure vessels in a lead/lag configuration containing proprietary mercury-specific media. The ion exchange system is used to reduce the mercury concentration remaining in the permeate from the RO system in order to meet the stringent Great Lakes Initiative mercury limit of 1.3 ng/L. The treated water is gravity fed to the receiving environment. When the active sites on the resin are exhausted, the media is replaced and the spent media is disposed of. The two-column system is operated in to allow complete exhaustion of the first column before the media is replaced.

The evaporator/crystallizer system is a vapor recompression evaporator system sized to handle up to 11.3 m³/h of brine. It is an energy efficient system that can provide up to



Fig. 2 Water Treatment Plant Selected Unit Processes

99 % volume reduction for waste streams. Steam is required for this system at start-up; therefore, a boiler will be rented or steam will be taken from another process on the site. The pH of the brine stream is adjusted by the addition of hydrochloric acid prior to entering the heat exchanger to prevent scaling. The heat exchanger serves to preheat the feed and recover heat from the evaporator distillate. After the heat exchanger the feed then passes through the deaerator where carbon dioxide and other strippable (volatile organics not expected to be present) constituents are removed prior to the evaporation step. It should be noted that if mercury is present and volatilizes it will be condensed with the distillate and require further treatment possibly by an additional ion exchange unit.

From the deaerator the feed is transferred to the evaporator where caustic may be required to adjust pH to an optimal value. The brine slurry from the evaporator sump is continuously recirculated to the top of the vertical heat-transfer tubes where it falls as a thin film and a portion of it is vaporized. The vapor is then compressed and introduced into the shell side of the vertical tube bundle to provide the energy for evaporation of incoming brine. The heat of compression from the compressor significantly increases the temperature of the compressed vapor and provides that energy. The temperature difference between the vapor and the brine film causes the vapor to release its heat of condensation to the falling brine and to condense on the outside of the tubes as distilled water. This distillate is collected at the bottom of the condenser and flows to the distillate tank. A small vent stream from the distillate tank maintains the evaporator vessel at a slightly positive pressure. The hot distillate is the heat exchange fluid described above that preheats incoming feed to the evaporator system.

The concentrated brine is removed as a slip stream from the evaporator sump and then further processed in a crystallizer. Antifoam is fed to the crystallizer to preventing foaming in the process. The brine becomes supersaturated in the crystallizer and salts form and precipitate out of solution. The waste stream from the crystallizer is a solid. Solids will be further dewatered by a filter press prior to disposal. The average estimated generation rate for waste solids is three tons per day.

Water Management and Treatment

The simulation duration was set equal to the mine life for the specified production schedule and a one-day time-step was evaluated. The simulation projections indicate that the selected design configuration of the water infrastructure will support the project objectives.

The selected water treatment technology is expected to meet or exceed all applicable regulatory requirements, including meeting water quality standards and concentration thresholds of measured constituents in any water released to the environment from the facility. Natural resource conservation protection and mitigation measures remain key components in the project design and ongoing environmental analysis.

References

- AECOM Technologies (2009) Copperwood Project, Ironwood Township, Gogebic County, MI – Environmental Impact Assessment, Draft Summary Report, November 25.
- Golder Associates, Inc. (2012) Copperwood Project, Ironwood Township, MI – Water Treatment Feasibility Design and Cost Estimates Report. April 12.
- Puhlmann T, Voss C, Esper J, Amaral RD (2006) Development and Operation of a Water Balance at Rio Paracatu Mineração, Brazil. ICARD 2006, vol. 7. Proceedings, 7th International Conference on Acid Rock Drainage (ICARD), St. Louis, 1632-1641 [CD-ROM]

Constructed Wetland Treatment Systems for Mine Drainage– Can They Really Provide Green and Sustainable Solutions?

Paul Eger¹; Candace L. KAIRIES BEATTY²

¹Global Minerals Engineering, Hibbing, MN, United States. paul.eger@globalmineralseng.com ²Winona State University, Winona, MN, United States. ckairiesbeatty@winona.edu

Abstract Constructed wetlands offer green and sustainable treatment, but how long will they really work? A wetland in northeastern Minnesota has been successfully treating mine drainage for almost 20 years. The primary removal processes include adsorption, ion exchange and complexation. These reactions have a finite lifetime since they depend on the existence of suitable removal sites. Removal will eventually cease unless new removal sites are generated or added. New sites are generated each year as vegetation dies and decomposes. For this wetland, the annual increase in metal removal capacity is about equal to the annual metal input; theoretically providing sustainable treatment.

Keywords Copper, nickel, peat, adsorption, complexation

Introduction

Wetlands have been used to treat a variety of water quality problems, including agricultural, municipal and industrial discharges (Hammer 1989, Moshiri 1993, Kadlec and Knight 1996, ITRC 2003). Wetlands have also been successful in treating coal and metal mine drainage and can be an attractive alternative to more conventional treatment methods (Hedin et al. 1994, Eger et al. 1996, Sobolewski 1997). Wetlands can be less costly to build, use processes that naturally occur to remove metals from the water (e.g. adsorption, filtration), and offer a system that ideally should operate with little to no maintenance for extended periods of time. Because mine drainage problems can persist for hundreds of years, the longevity of any system is a critical issue.

Surface flow wetlands were constructed to treat neutral mine drainage at the Dunka Mine in northeastern Minnesota (Eger and Eger 2005). A model was developed to evaluate treatment lifetime and the results suggest that one of the wetlands can provide a long term treatment alternative.

Wetland

The wetland treatment system was designed by STS Consultants, Ltd., and built by LTV Steel Mining Company in an existing wetland in 1992 (Frostman 1992). The wetland was originally a combination of emergent (wet meadow) and scrub-shrub type wetlands. The majority of the woody vegetation, which consisted primarily of alder (alnus sp.), was removed from the site. The basic design for the system included the construction of a series of soil berms, which were built to control water levels and to maximize contact between the drainage and the substrate (Fig. 1). Soil berms were built with glacial till (sandy silt) available from a surface overburden stockpile on the property. After the berms were constructed, a 30 cm layer of a mixture of local peat and peat screenings was applied to the entire area except the top of the berm. The screenings were a waste material generated during the processing of horticultural peat and consisted mostly of wood fragments and long peat fibers. This material was selected to increase the permeability of the peat to at least 10⁻³ cm/s and to provide available or-



Fig. 1 Schematic of the wetland treatment system examined in this study

ganic carbon. In the spring of 1992, the berms were hand-seeded with Japanese Millet, while the open water areas were seeded with cattails. To obtain the cattail seeds, cattail heads were placed in a container of water with a small amount of liquid soap and several large metal bolts. The mixture was agitated until the heads broke and the seeds were dispersed. The slurry was then broadcast by hand over the wetland. The majority of the flow to this system originated from the base of a waste rock stockpile. The wetland was originally about 7000 m² but was expanded in 1995 by an additional 10,000 m².

Methods

Water samples of the inflow and outflow of the original wetland treatment system were initially collected twice a month by LTV personnel. Sample frequency from the original part of the wetland decreased to quarterly in 2004. During the initial phase of the study metals were analyzed by atomic absorption spectroscopy (AAS) but the analytical technique switched to inductively coupled plasma-mass spectrometry (ICP-MS) in about 2005. Samples were analyzed by Northeast Technical Services in Virginia, MN.

Continuous measurements of inflow and outflow water levels were made with a Steven's Model F recorder, and the flow was calculated from the standard equation for a 60 degree Vnotch weir. Due to potential problems with the recording equipment under freezing conditions, continuous flow estimates were generally only available from May through October.

Results *Flow*

Since continuous flow measurements were only available for May through October, the average daily flow calculated over this period has been used to compare the change in flow over time.

Average input flows ranged from 110– 136 L/min for 1992 to 1994. In 1995 the top of the stockpile that provided the majority of the flow to the wetland was capped with a 40 mil LDPE liner. Flows decreased in 1995 and average flows after capping generally ranged from 22–52 L/min. Flow in 2007 was the highest of the post-closure flows (106 L/min), the result of 43.6 cm rainfall in September and October. Annual precipitation for 2007 was 100.7 cm, substantially above the long-term average precipitation of 72.4 cm.

Output flow was generally greater than input flow except during hot dry periods when evapotranspiration losses were large. During the summer of 1998 the output flow was 19– 23 L/min less than the input. In July, when the input flow decreased to 15–19 L/min, there was no flow at the outlet.

Water Quality

There was little variation in pH in the wetland. Both input and output pH generally ranged from 6.7 to 7.6. From 1992 to 1994, the input nickel concentration to the wetland treatment system was typically on the order of 1 mg/L in the spring, and then increased to approximately 6 mg/L in early summer. Concentrations then remained relatively constant until the seep froze in late fall (Fig. 2).

In 1995, input nickel concentrations decreased substantially. The nickel concentrations in the input to the wetland remained low in the spring, but only increased to 2–3 mg/L in the summer. Maximum concentrations gradually decreased to less than 1 mg/L by 1999. Concentrations remained in this range until high rainfall occurred in the fall of 2007 when concentrations increased to over 3 mg/L.



Fig. 2 Nickel concentration, input and outflow, over time

Outflow nickel concentrations were about 90 % lower than the input values (Fig. 2). Prior to capping the stockpile, outflow concentrations exceeded the initial chronic toxicity limit of 0.213 mg/L more than about 50 % of the time. As flow decreased, the frequency of compliance increased and outflow concentrations were generally below the initial limit.

Mass Removal

Overall mass into and out of the wetland was calculated by multiplying the average concentration for the month by the average daily flow for that month. Daily flow data were generally available from May through October, but for April, November and December, there were only a few individual flow readings. Since both flow and precipitation in November and December tended to be low, the average of the limited individual measurements was assumed to be a reasonable estimate of flow. An average value may not provide a reasonable estimate of spring melt flow, since the volume and timing of flow depends on the amount of moisture in the snow pack, temperature and rainfall. However, metal concentrations during April were about one-half the summer values, so the total mass input during April, even with higher flows, would tend to be lower than summer months. From 1992 through 1995, when input load was the highest, the May to October

input mass accounted for 86 % of the annual load (Eger *et al.* 2000).

After 2000, data collection from the original portion of the wetland was reduced. As a result, the overall mass removed in this portion of the wetland was estimated from the total removal for the entire wetland based on area. The estimated mass removal ranged from about 1 - 27 kg/a with an average of about 5 kg/a.

Discussion

The lifetime of a wetland treatment system is a function of the metal removal processes, the size of the wetland and the input load. For surface flow wetlands, the primary metal removal processes are a combination of adsorption, ion exchange and complexation with the organic substrate (Eger et al. 1994). Removal occurs as water contacts the substrate with most of the removal occurring in the top 20 cm of the wetland (Eger et al. 1994). The removal capacity has been estimated from laboratory and field measurements to be on the order of 10,000 mg Ni/kg dry peat (Eger and Lapakko 1988, Eger et al. 1996). When the wetland was first built, the design was based on average input values for 1990–1991. For this time period, average daily flow was 78 L/min and the average nickel concentration was 5.4 mg/L (Eger et al. 1996). Based on a wetland area of 7000 m², an effective removal depth of 20 cm, a peat bulk density of 0.1 gm/cm³, a maximum removal capacity of 10,000 mg nickel/kg dry peat, and flow from April through November (245 days), the design lifetime *t* was calculated from:

$$t = \frac{R_R}{M} \tag{1}$$

with

Lifetime [a] t

 $R_{\rm R}$ total removal capacity of the wetland [kg Ni]

M load [kg Ni/a]

This calculation assumed that all the input nickel is removed and provided an initial lifetime estimate of about 10 years (Eger and Wagner 2002).

In 1995 the entire top of the stockpile was covered with a 40 mil low density polyethylene liner (LDPE). The cover prevented water from contacting most of the reactive material in the stockpile. Flow dropped about 62 %, from an average May to October flow of 125 L/min during 1992–1994, to 47 L/min for the post-closure period (1996–2011).

By preventing precipitation from infiltrating the stockpile and contacting the reactive material, the transport of reactive products was significantly reduced. Nickel concentrations decreased from an average of 3.98 mg/L for 1992–1994 to 0.92 mg/L for 1996–2011. Since both flow and nickel concentrations decreased, the overall load to the wetland decreased by about 90 %. By reducing the load, the estimated lifetime was increased by about a factor of 10, from the initial design lifetime of 10 years to around 100 years.

The "ideal" passive treatment system will provide permanent treatment with little to no maintenance. However, in this system over 90 % of the nickel removal occurs within the substrate, through a series of reactions (adsorption, ion exchange, chelation) associated with the organic fraction of the peat. These types of removal mechanisms have a finite capacity and the wetland will have a fixed life unless new removal sites can be generated at a

rate greater than or equal to the incoming metal load.

New sites are generated as vegetation dies and new organic substrate accumulates. The average rate of peat accumulation in northern wetlands is about 1 mm/year (Craft and Richardson 1993). If the removal capacity of the newly accumulated material is assumed to be 10,000 mg nickel/kg, the wetland would add 7 kg of nickel removal capacity each year as calculated from (2):

$$\Delta R_{R} = f_{PA} \times R_{Ni} \times A \tag{2}$$

where

 $\Delta R_{\rm R}$ Increase in removal [kg/a] rate of peat accumulation [-]

fрд

*R*_{Ni} nickel removal capacity

wetland area Α

Since the average rate of mass removal was 5 kg/a and the estimated increase in capacity is 7 kg/a, the wetland is generating excess removal capacity and therefore in theory should be able to provide sustainable treatment (Fig. 3).

If the treatment is to be sustainable and effective, not only must there be new metal removal capacity generated, but the metal must be retained within the wetland. Mass balances calculated on wetland test cells demonstrated that over 99 % of the removed metals were associated with the substrate and less than 1 % of the total removal occurred in the vegetation (Eger et al. 1994). These results were consistent with earlier studies on metal removal in a white cedar wetland (Eger and Lapakko 1988) and with data reported by others (Skousen et al. 1992, Wildeman et al. 1993). Sequential extraction tests, conducted on a series of substrate samples collected from test cells constructed at the Dunka Mine, demonstrated that only 1-2 % of the nickel was water soluble and could, therefore, be easily removed from the substrate (Eger et al. 1994, Eger et al. 1996).

Additional evidence for the permanent nature of the removal in the wetland is that nickel removal continued despite a decrease in



Fig. 3 Nickel mass removal in the wetland system and projected nickel removal capacity.

the input concentration of about a factor of five. If the nickel was weakly bound to the substrate, nickel would be released from the substrate as nickel concentrations in the water decreased, and no removal would occur. Although continuous flow data is only collected from May through October, water quality samples are collected whenever there is water flowing into or out of the wetland. Over the twenty years of operation, output concentrations have rarely exceeded input values, and there has always been nickel removal in the wetland (Fig. 2).

Conclusions

Since 1995, when the Dunka mine was closed and the stockpiles capped, nickel loads into the W1D wetland have dropped by an order of magnitude. Nickel has been removed every year and there has been no evidence of nickel release from the wetland. The annual nickel removal in the wetland is now about the same as the estimated annual production of new removal sites. If conditions remain unchanged, treatment could continue indefinitely.

References

Craft, CB and Richardson, C. (1993) Peat accretion and N, P, and organic C accumulation in nutrient-en-

riched and unenriched Everglades peatlands. Ecological Applications 3:446-458.

- Eger, P and Eger, P (2005) Controlling mine drainage problems in Minnesota – Are all the wetland treatment systems really above average? In: Proc. 22st Annual Meeting ASMR, Breckenridge, CO, June 19–23, 2005.
- Eger, P and Lapakko, KA (1988.)Nickel and copper removal from mine drainage by a natural wetland. In: Proc. 1988 Mine Drainage and Surface Mine Reclamation Conference, Pittsburgh, PA April 19-21, V. 1. Mine Water and Mine Waste, 301–309. U.S.D.I. Bureau of Mines IC9183.
- Eger, P and Wagner, J (2002) The use of wetlands to remove nickel from mine drainage – is perpetual treatment really possible? In: Proc. 19th Annual Meeting ASMR, Lexington, KY, June 9–13, 2002.
- Eger, P, Wagner, J, Kassa, Z, and Melchert, G (1994) Metal removal in wetland treatment systems. In: Proc. International Land Reclamation and Mine Drainage Conference/3rd International Conference on the Abatement of Acid Drainage. Pittsburgh, PA, April 25-29, 1994.
- Eger, P, Wagner, J and Melchert, G (1996) The use of overland flow wetlands to remove metals from neutral mine drainage at LTV Steel Mining Co.'s Dunka mine. Minnesota Department of Natural Resources, Division of Minerals, St. Paul, MN. 90 p. plus appendices.

- Frostman, T (1992) Constructed peat/wetland treatment system for heavy metal removal. Achieving land use potential through reclamation, Proc. 9th Annual Meeting, Duluth, MN, June 14-18, 1992. p. 255-259.
- Hammer, DA, Ed. (1989) Constructed peat/wetland treatment system for wastewater treatment. Municipal, Industrial, and Agricultural. Lewis Publishers, Chelsea, MI.
- Hedin, RS, Nairn, RW, and Kleinmann, RLP (1994) Passive treatment of coal mine drainage. Bureau of Mines IC9389, Washington, D.C.
- Kadlec, R and Knight, R (1996) Treatment Wetlands. CRC Press, Boca Raton, Fl.

- Moshiri, GA, Ed. (1993) Constructed wetlands for water quality improvement. Lewis Publishers, Boca Raton, FL.
- Skousen, J, Sexton, A, Garbutt, K, and Sencindiver, J (1992) Wetlands for treatment acid drainage. Green Lands 22 (4): 31-39.
- Sobolewski, A (1997) The capacity of natural wetlands to ameliorate water quality: a review of case studies. In: Proc. Vol. IV 4th International Conference on Acid Rock Drainage, Vancouver, B.C., Canada. p. 1551-1563

Removal of uranium from a neutral mine water using uncoated and iron oxyhydroxide coated iron tailings.

Linnéa Fahlqvist^{1.2}, Mattias Bäckström^{1.2}, Lotta Sartz^{2.1}, Bert Allard¹

¹Man-Technology-Environment Research Centre, Örebro University, 701 82 Örebro, Sweden, linnea.fahlqvist@oru.se ²Bergskraft Bergslagen, Harald Olsgatan 1, 714 31 Kopparberg, Sweden

Abstract Mine water (pH 8) from the Lovisagruvan mine contains 25 µg/L of uranium. Magnetite tailings, uncoated or coated with iron oxyhydroxide, was tested in column experiments as filter material for removal of uranium. The uncoated filter systems did not retain uranium or change the pH. Coated filters, however, led to a significant pH increase, particularly in the down-flow columns and 97–99 % uranium was removed, as long as pH was ≥ 10.5 . A formation of a Ca-UO₂-CO₃-species as well as co-precipitation with and adsorption to an assumed Ca-OH-CO₃-phase (and adsorption to the iron oxyhydroxid at pH >8.5-9) may explain the observations.

Keywords Uranium, mine water treatment, neutral mine water, iron oxyhydroxide filter

Introduction

Lovisagruvan is a small mine in the Bergslagen province, mid Sweden, with a yearly production of some 40 000 metric tons of rock containing 50 % of sulfide ore (lead-zinc-silver). Water is continuously pumped from the mine at a rate of ca $5 \text{ m}^3/\text{h}$ into a sedimentation pond above ground, after passing through three sedimentation ponds underground (at depths of 145, 105 and 55 m, respectively). The mine water is eventually released into a recipient, after a residence time of around three days in the final sedimentation pond above ground. The concentration of zinc and lead in the water, after sedimentation, is of the order 700 and 400 µg/L, respectively, but there is also a residual concentration of uranium at the level 25 µg/L, mainly as dissolved species (>80 %). The water is near neutral (pH around 8) with an alkalinity around 2 meq/L (Fahlqvist et al. 2012).

Various geological barriers or filters, serving as metal scavengers and adsorbents, can be designed and used for treatment of mine water. Geologic materials coated with iron oxyhydroxides have been shown to be efficient as metal adsorbents and filters for treatment of mine water (Benjamin *et al.* 1996, Chang *et al.* 1997). Both cationic metal species as well as anionic metal complexes can be adsorbed and retained by such filters. Barriers and filters can, in general, be designed for down-flow or up-flow, *i.e.* the direction of the water flow is down-words from top to bottom or up-words, from bottom to top. Both types have their advantages. The down-flow filter has an easier construction, but the water distributes more evenly in an up-flow filter, and the risk for clogging (or channeling) is less because fine material is less prone to accumulate in the bottom of the filter (Forsvarsbygg 2009).

The efficiency of a magnetite based filter, with or without iron oxyhydroxide coating and down-flow or up-flow design, to reduce the uranium concentration in the Lovisa mine water is studied in the present project. The efficiency to reduce the concentrations of zinc and lead has previously been reported (Fahlqvist *et al.* 2012).

Material and methods Filter material

Iron tailings with magnetite residues from Stråssa, a closed iron mine located near Lovis-

agruvan, were used as filter material. Both uncoated tailings (UT) and iron oxyhydroxide coated tailings (ICT) were tested. The iron oxyhydroxide coating was prepared from a slurry of iron sulfate (FeSO₄, Nitor; 82 g), water (1.5 L) and lime kiln dust (SMA, Spectra A; 1 L) that was mixed with the magnetite tailings in two steps: (1) Proportion 0.2 L slurry to 1 L tailings, exposure for 24 hrs; (2) Sieving and drying and new exposure, proportions 0.15 L slurry to 1 L tailings from step (1).

Column tests

Columns were made of plastic drainage pipes (diameter 160 mm and length 650 mm) with plastic tubings attached to both ends. The columns were packed with 75 mm coarse gravel which distributes the incoming water over the entire filter surface. A geotextile was placed on top of the gravel to prevent the filter material from mixing with the gravel, followed by 500 mm of tailings, another geotextile and 75 mm of gravel on top. Four columns were prepared; two with untreated tailings (UT) and two with iron oxyhydroxide coated tailings (ICT). One down-flow and one up-flow column was designed for each type, UT and ICT (Fig. 1).

Water from the mine was pumped from the sedimentation pond above ground into a 1 m³ container and transported to the laboratory. A pump (Fontänpump FP 1000, Gardena) was placed in the container to keep any particles from settling. Water was pumped from the



Fig. 1 left (a) Model of down-flow filter.; right (b) Model of up-flow filter.

container to the columns at a rate of approximately 10 L/d. Total volumes through the filters were 1 600–3 100 L. Sampling was performed daily (except for the first days when samples were taken more frequently) five days a week during thirteen months. Samples of non-filtered water were taken every time more water was added to the container.

Precipitation tests

Removal of uranium from solution by precipitation/co-precipitation was studied in batchwise tests. (1) Saturated $Ca(OH)_2$ -solution (between 0–25 mL) was added to 25 mL of filtered (0.45 µm nylon filters) mine water; totally 33 batches.

(2) Saturated Ca(OH)₂ -solution (between O-25 mL) was added to 25 mL of filtered (0.45 μ m nylon filters) mine water, followed by FeSO₄ that was added to give a total concentration of 0.8 g Fe/L; totally 26 batches.

Water analysis

Water samples from the tests were filtered through polycarbonate filters with different pore sizes (0.1 μ m, 0.4 μ m, 0.2 μ m and 0.05 μ m for column test samples; 0.45 μ m for the precipitation test samples) and analyzed with respect to pH (electrode Lab 850, Schott Instruments), electrical conductivity (electrode Conductivity meter FE30/FG3, Mettler Toledo), alkalinity (titrator Titroline easy, Metrohm), sulfate (IC, Metrohm) and metals (ICP-MS, Agilent 7500 cx). Samples for metal analysis (filtered as described above, but also non-filtered from column tests) were acidified to 1 % HNO₃ (distilled acid), and rhodium solution (Merck) was added as an internal standard.

Results and discussion Characterization of the mine water

Results from analyses of the mine water are given in table 1. The high pH and the significant alkalinity indicate the presence of carbonates in the bed-rock. The water is saturated with respect to $CaCO_3$ but below saturation with respect to $CaSO_4$ (Ca-concentration

	El. cond. (µS/cm)	Redox potential (pe)	рН	Alkalinity (meq/L)	Sulfate (mg/L)	Uranium (µg/L)
Mean value	390	2.5	8.06	2.3	52	25
Std. dev.	32	0.49	0.30	0.44	4.0	3.9
Ν	22	22	22	22	8	9

Table 1 Electrical conductivity, redox potential, pH, alkalinity, sulfate and uranium concentrations inthe water from Lovisagruvan (mean and standard deviation).

around 40 mg/L). The redox potential (pe) corresponds to an apparent standard potential E° of 0.60-0.65 V, which is slightly below 0.70-0.75 V that is the expected range for environmental waters in contact with air (Allard 1982).

Column tests

Initially the UT filtration led to a pH-increase to 8.5, but as more water passed through the columns the values decreased to the initial level, *i.e.* around 8 or slightly below (Fig. 2a). The ICT filtration led to an initial pH-increase to 12.6, due to the presence of lime kiln dust from the coating process. After some 1500 L had passed the column a pH-level of around 8 was obtained in the up-flow system and around 10, or slightly below, in the down-flow system (Fig. 2b). Thus, there is no significant pH-effect from the UT-system at steady-state. In the ICT-system, with the added lime kiln dust, there is no remaining pH-effect after some 1500 L in the up-flow systems, but still an enhanced pH in the down-flow systems. Possibly also this effect will level out with time (after a larger volume has passed through the column).

The redox potential in the UT filters started at higher levels than for the incoming water (pe 3.1 compared to 2.5) but the redox potential decreased during the test period, ending at pe 1.1. In the ICT filters the redox potential started at pe around -0.1, increasing to 1.1 in the up-flow filter and 0.1 in the down-flow filter. The corresponding apparent standard potentials E° would, however, be around 0.68-0.70 V initially in both the UT and ICT systems, *i.e.* slightly higher than for the incoming mine water. The measured potentials after more than 1500 L through the columns correspond to apparent E°-values around 0.54-0.58 in both systems, *i.e.* a slight reduction of the potential but still representing aerated solutions. Uranium would be entirely in the hexavalent state at these potentials.



Fig. 2 left (a) pH in water filtered through UT (pH in incoming water: 8.06); right (b) pH in water filtered through ICT (pH in incoming water: 8.06).



Fig. 3 left (a) U in water filtered through UT (U concentration in incoming water: 25 μg/L); right (b) U in water filtered through ICT (U concentration in incoming water: 25 μg/L).

Alkalinity increased from 2.3 meq/L to 2.5 meq/L through the UT filters. ICT filters initially raised the alkalinity to about 40 meq/L, but after 400 L the alkalinity was 1.8 meq/L in the up-flow filter and 2.0 meq/L in the downflow filter. An increase in alkalinity (in UT) may reflect uptake of carbon dioxide from the atmosphere and at the same time a pH-buffering effect that kept pH constant at the level 8-8.5. The initially high alkalinity from the ICT filters would be caused by residual alkalinity from the added lime kiln dust that was flushed from the filters. The alkalinity decrease in the ICT after long time indicates the loss of carbonate by flushing out from the filter, or the precipitation of Ca-carbonate.

The UT filters did not change the electrical conductivity, but in the ICT filters the conductivity increased from 390 μ S/cm to 8 500 μ S/cm. After 500 L the electrical conductivity had decreased to the same level as in the incoming water. The initially high electrical conductivity from the ICT filters would be caused by residual alkalinity from the added lime kiln dust.

Sulfate concentrations were unaffected after the UT columns but were initially much higher in water filtered through the ICT (about 500 mg/L compared to 52 mg/L in incoming water). However, after 200 L the concentrations were only a few mg/L above the level in the incoming water. Possibly there was some sulfate remaining from the coating process (using FeSO₄).

Uranium concentrations increased slightly in the UT filters, from 25 µg/L in incoming water to around 28 µg/L in the up-flow filter and 29 µg/L in the down-flow filter and remained stable throughout the test period (Fig. 3a). Leaching tests of the material used in the filter showed, that the magnetite tailings contained leachable uranium in the range 0.023-0.065 mg U/kg dw. Thus, the tailings had a uranium content at the 0.1 ppm-level or higher, which is not unexpected since the granitic host-rock would have a uranium content at least at the ppm-level. Evidently, the reduction of the uranium concentration by adsorption in the UT filters was minor, or negligible.

In ICT filters the initial removal of uranium was 97 % in the up-flow filter and 99 % in the down-flow filter. The down-flow filter continued to be effective throughout the test period, when pH was above 9.8-10, while the uranium concentrations started to increase in the up-flow filter after about 400 L (Fig. 3b), and reaching around 20 μ g/L after around 1000 L, corresponding to a pH of 10–10.5. At the end of the test period the values were almost as high as in the incoming water (22 μ g/L compared to 25 μ g/L).

Thus, when comparing uranium concentrations with pH values for the water passing



Fig. 4 Reduction of the uranium concentration in solution as a function of pH in the ICT up-flow and down-flow filter columns; also precipitation tests (lab scale test) with addition of Ca(OH)₂, as well as with Fe(II) plus Ca(OH)₂.

through the ICT filters (Fig. 2b and 3b) there is an obvious correlation. Uranium concentrations are increasing with decreasing pH in the up-flow filter systems, starting at pH around 11. In the down-flow filter systems the concentration did not increase even though pH dropped below 10.

Precipitation tests

Initial pH (before $Ca(OH)_2$ -addition) was 8.06. Addition of 1 to 3 mL of saturated Ca(OH)₂-solution led to an increase in pH to around 11.2. The concentration of uranium in solution decreased from 26 μ g/L to about 0.1 μ g/L (>99 % reduction, Fig. 4). Subsequent additions of saturated Ca(OH)₂-solution led to further pH-increase to a maximum of 12.3 after 25 mL, close to the equilibrium pH of the Ca(OH)₂-solution around 12.5-12.6. The uranium concentrations in solution remained constant at the 0.1 µg/Llevel. The addition of Ca(OH)₂ also led to the formation of a white precipitate, notably CaCO₃, since the original mine water is in equilibrium with calcite. Kaplan et al. (1998) also noted a significant decrease in uranium(VI) concentrations above pH 10.3 in the presence of carbonate solids. In the experiment with iron addition the decrease in uranium concentrations starts already at pH 5 and above. The lowest uranium concentrations were obtained at pH >10.

The co-precipitation with iron (as Fe(III)hydroxide) in the whole pH-range 5–12 and with CaCO₃-Ca(OH)₂ at pH>10 is the logical explanation to the almost quantitative removal of uranium from solution. The results from the up-flow ICT filter is similar to the precipitation experiment with addition of saturated $Ca(OH)_2$ -solution, and the results from the down-flow ICT filter reflect the precipitation with both iron and $Ca(OH)_2$. Possibly there is also a formation of UO_2 - CO_3 surface complexes that contributes to the transfer of uranium from solution to the solid phase. Also the iron oxyhydroxide coating contributes to the adsorption on the solid filter phase at pH 8.5-9 and above.

There was no significant difference in the uranium retention between the up-flow and down-flow systems (ICT) during the first 500 L, but from 500 to 1500 L, the retention was gradually reduced in the up-flow system but constant in the down-flow system. This was a reflection of the change in pH, decreasing from around 10.5 to 8 in the up-flow system but only down to around 10 in the down-flow system. The differences between up-flow and downflow may be the result of different flow-rates and hold-up times (lower flow-rate in the down-flow systems). Eventually, the two flow directions will establish the same steady-state conditions. It seems evident, that the assumed Ca-OH-CO₃-phase is largely responsible for the uranium retention and that this phase is gradually washed-out from the filter matrix. The iron oxyhydroxide is an active adsorbent at pH of 8.5-9 and above.

Uranium speciation

Uranium is hexavalent (as uranyl, UO_2^{2+}) in all the systems, and none of the systems are sat-

urated with respect to any well-defined solid uranium mineral phase. Hydroxide complexes would dominate in a carbonate free system (Allard 1982; Missana et al. 2002). However, the mine water has an alkalinity at the level 2-3 meq/L. The dominating uranium species in incoming mine water, as well as in the water passing through the UT filter, can be assessed as $UO_2(CO_3)_2^{2-}$, with contributions of other anionic species, $UO_2(CO_3)_3^{4-}$, and possibly also $(UO_2)_3(CO_3)_6^{6-}$ (Allard *et al.* 1984). Other species present would be UO₂(OH)₂ and UO₂CO₃, both neutrally charged and present at much lower concentrations (%-level or less). According to Zheng et al. (2003) the uncharged complex Ca₂UO₂(CO₃)₃ may form in near neutral Ca-CO₃-solutions. The formation of a Ca-UO₂-CO₃ complex was also suggested by Gustafsson et al. (2009). Calcium concentrations are around 40 mg/L in the mine water, and additional calcium may be released from the coating.

Conclusions

Uranium is not retained by the uncoated filter matrix (UT) at pH 8. Adsorption is minor, since the mineral surfaces would be negatively charged (pH_{zpc} <8), as well as the dominating uranium species (carbonate complexes) in solution.

Uranium is almost quantitatively retained by the iron oxyhydroxide coated filter matrix (ICT) at pH around 10 or above. The retention process may be co-precipitation with an assumed (ill-defined) Ca-OH-CO₃-phase, as well as adsorption on the solid iron oxyhydroxide coating as long as pH is around 8.5-9 or higher. Retention is minor in the coated (ICT) system at pH around 8, *i.e.* pH of the original mine water. Thus, the assumed Ca-OH-CO₃-phase seems to be largely responsible for the uranium retention and this phase is gradually washed-out from the filter. The iron oxyhydroxide is an important adsorbent, but only at pH of 8.5-9 and above.

Further studies are in progress of the nature and detailed composition of the coating (elements and phases), its uranium-holding capacity and its stability, as well as of the uranium speciation.

Acknowledgement

Technical assistance from Erik Larsson and Jan Nilsson (Bergskraft Bergslagen) and metal analyses performed by Viktor Sjöberg (Örebro University) are greatly acknowledged.

References

- Allard B (1982) Solubilities of actinides in neutral or basic solution. In Edelstein NM (Ed), Actinides in Perspective, Pergamon Press, New York, p 553–580
- Allard B, Olofsson U, Torstenfelt B (1984) Environmental actinide chemistry. Inorg. Chem. Acta 94: 205– 221
- Benjamin MM, Sletten R S, Bailey R P, Bennett T (1996) Sorption and filtration of metals using iron-oxidecoated sand. Water Res. 30 (11): 2609–2620
- Chang Y, Li C, Benjamin MM (1997) Iron oxide-coated media for NOM sorption and particulate filtration. Am. Water Works Assoc. 89 (5): 100–113
- Fahlqvist L, Sartz L, Bäckstrom M (2012) Removal of zinc and lead from a neutral mine water using iron tailings and iron oxyhyroxide coated iron tailings. In McCullough CD, Lund MA, Wyse L (Eds), Proc. Internat. Mine Water Association Ann. Conf. 2012, IMWA 2012, Bunbury, p 584A-584G
- Forsvarsbygg (2009) Forsøk med Blueguard olivingranulat som rensemedium for tungmetallholdig avrenning fra Tverrfjellet gruver. Rena desember 2009. (in Norwegian)
- Gustafsson J P, Dässman E, Bäckström M (2009) Towards a consistent geochemical model for prediction of uranium(VI) removal from groundwater by ferrihydrite. Appl. Geochem. 24: 454–462
- Kaplan DI, Gervais TL, Krupka KM (1998) Uranium(VI) sorption to sediments under high pH and ionic strength conditions. Radiochim. Acta 80(4): 201–211
- Missana T, García-Gutiérrez M, Mafiotte C (2002) Experimental and modeling study of the uranium (VI) sorption on goethite. J Coll. Interf. Sci. 260: 291–301
- Zheng Z, Tokunaga T K, Wan J (2003) Influence of calcium carbonate on U(VI) sorption to soils. Environ. Sci. Technol. 37 (24): 5603–5608

A Novel Electrochemical Process for Aqueous Oxidation of Acid Mine Drainage using Advanced Power Electronics and Real time Control

Kay M. Florence., Philip G. Morgan

Hydro Strata Ltd., Stradey Business Park, Llangennech, Carmarthenshire, SA14 8YP, UK; kflorence@hydro-industries.co.uk

Abstract An electrochemical treatment process using an external power supply connected to an electrical circuit consisting of oxidising electrodes immersed in an acid mine drainage (AMD) source water offers a simple, efficient, effective, chemical-free active treatment for removal of iron. In trials, electrochemical oxidation measured by an ORP meter produced clear water and recoverable iron sludge without the need for pH adjusting chemicals for some AMD source waters. This paper presents an overview of the electrochemical oxidation process, their reactions steps and scale-up for a commercial electrochemical reactor incorporating advanced power electronics and real time control.

Keywords Acid Mine Drainage, electrochemical treatment, advanced oxidation.

Introduction

Acid mine drainage (AMD) can contain high concentrations of dissolved (semi)-metals and sulphate, often with very low pH values. Unless treated, such waters may not be discharged into the natural environment. The acid water is formed as a result of bacterial oxidation when pyrites are exposed to oxygen and water after or during mining processes (Maree et al. 2004). Currently, the favoured industrial methods of treating acid water are pH neutralisation using lime, biological neutralisation-adsorption in natural or man-made wetland systems, oxidation using aeration, ozone, or hydrogen peroxide and more recently reverse osmosis (RO). However, many of these processes have limitations, for example, lime neutralisation requires the quarrying, production of un-slaked or slaked lime which produces large quantities of unstable iron rich sludge, wetlands require specially constructed sites occupying large areas of land while iron precipitates irreversibly on RO membrane filters, thus requiring complex chemical backwashing and frequent replacement.

Oxidation of untreated pyrite by bacteria (Silverman 1967; *e.g. Ferrovum myxofaciens sp*;

Hendrick and Johnson 2012) is achieved by two mechanisms: direct oxidation (electron transfer) between the pyrite particles and bacterial cells, and indirectly by further oxidation of ferrous ions to the ferric state, thereby regenerating the ferric ions required for chemical oxidation of pyrite. Such reactions can be regarded as electrochemical. An electrochemical oxidation process can similarly be achieved by oxidising AMD using oxygen over potential electrodes, to become electron deficient to favour the higher oxidation state of the ferric ion.

Electrochemical water treatment is achieved by passing AMD water between two or more oxidising electrodes. Excitation of the electrodes is controlled by an advanced programmable power electronic system, which can provide a variable AC/DC power source. In addition, real time monitoring of key physicochemical-electrical parameters such as ORP and electrical impedance important to both water treatment process and stability of power electronics process, provides the knowledge base for automatic feed-back control, adjustment to fluctuating changes in feed water quality to maintain optimum treatment performance and electrical energy usage. Such systems have already been applied successfully to large scale remediation of aluminium rich contaminated groundwater, drinking water treatment (removal of humic/fulvic acids and contaminant metals), wastewater treatment (phosphate) and general industrial effluent as whole (Khanniche *et al.* 2001).

Electrochemical Approach

The electrochemical treatment of AMD water has been reviewed with reference to the aqueous oxidation of pyrite by molecular oxygen produced by the electrolysis of water employing oxidising electrodes.

$$2 H_2 O \rightarrow O_2 + 4 H^+ + 4 e^-$$
 (1)

The electro-oxidation path is considered a consequence of two steps:

- **1.** The oxidation of pyrite by molecular oxygen to sulphate and ferrous iron;
- **2.** The oxidation of pyrite by hydrogen peroxide as result of the corresponding cathodic reduction of molecular oxygen.

$$O_2 + 2 H^+ + 2e^- \rightarrow H_2O_2$$
 (2)

Step (i)

$$FeS_2 + \frac{7}{2}O_2 \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$
 (3)

 $Fe^{2+} + \frac{1}{4}O_2 + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O$ (4)

 $Fe^{3+} + 3 H_2O \rightarrow Fe(OH)_{3(s)} + 3 H^+$ (5)

This is a heterogeneous in-direct reaction with respect to oxygen produced from an oxidising electrode, acting as the anode. The rate of reaction is a function of current density (Am^{-2}) applied to the electrode and production of oxygen. Other oxidising derivatives and radicals *e.g.* ozone, hydroxyl radical [•OH], superoxide anion radical [•O₂] and hydro-peroxyl radical [•OH₂] have not been considered in this paper. The reactions were carried out at the natural pH of the AMD source waters. Step (ii)

$$FeS_2 + \frac{15}{2}H_2O_2 \rightarrow$$

$$Fe(OH)_{3(s)} + 2H_2SO_4 + 4H_2O$$
(6)

This is a heterogeneous in-direct reaction with respect to the reduction of oxygen produced from an oxidising electrode by the corresponding cathode. Likewise the reactions were carried out at the natural pH of the AMD source waters.

The limiting rate in Step (i) is the formation of molecular oxygen sufficient to oxidise the pyrite. An intermediate $Fe_3O_4 \cdot xH_2O$ green/black hydrated magnetite was observed during the oxidation of pyrite to $Fe(OH)_3$ ferric hydroxide during start-up.

Power Electronics, Controls and treatment process

The power electronics system comprises an AC to DC converter and a universal programmable matrix converter which feeds power to the oxidising electrodes housed in a reactor cell (Fig. 1):

Modern closed-loop control techniques are used to deliver the required voltage, current and frequency to initiate electrochemical oxidation from the surfaces of the oxidising electrodes housed in an insulated reactor. The reactor is described as an 'open cell' whereby the anodes and corresponding cathodes have no cell or membrane partitioning allowing oxidation-reduction reactions to occur simultaneously within the reactor housing.

An industrial example of the above treatment process is shown Fig. 2.



Fig. 1 Treatment process schematic



Fig. 2 Example of an industrial electro-oxidation treatment unit (10,000 Lh⁻¹)

Results

Fig. 3 below shows photographs taken before, during and after the treatment of an AMD sample using electro-oxidation process. Samples and trials were conducted on 4 source AMD discharges (coal mine sites) in the UK and included:

- Open cast coal field site, Merthyr Tydfil, S.Wales, UK;
- Disused mine discharge, Ynysarwed, S.Wales, UK;
- Disused mine pumping schemes, Blenkinsopp, UK
- Disused mine pumping scheme, Dawdon, UK.

The electro-oxidation reaction time for all samples was 4 minutes.

Fig. 3A shows untreated samples of high clarity with pyrite in soluble form. Fig. 3B shows formation of ferrous iron leading to the formation of insoluble ferric floc (Fig. 3C) under slow stirring conditions (10 minutes). Fig. 3D shows dense settled ferric sludge following 30 minutes of unhindered settlement. Samples taken from Ynysarwed, Blenkinsopp were pH neutral and fresh water sources. The sample from Merthyr was a fresh water source but pH 4.0 whereas the Dawdon sample was high salinity and low pH 4.2. All samples precipitated ferric sludge; however the saline sample produced a very fine floc with hindered settlement. pH of this sample showed a decrease in pH to 3.5 units. Samples from Ynysarwed and Blenkinsopp showed no variation in pH after treatment whereas the more acidic sample from Merthyr showed an increase of pH to 6.4 after treatment.

A further laboratory based experiment was conducted using Ynysarwed mine water to determine the current density most effective for Fe (II) removal by electrochemical oxidation. Fig. 4 below shows that with a set two minute treatment time. Fe concentration decreases with an increase in current density. Five amps were sufficient to decrease Fe (II) concentrations from 73.4 mg/L to 0.2 mg/L (European drinking water quality standard).

Table 1 shows the changes in measurable parameters at increasing current densities.



Fig. 3 Treatment reaction stages of AMD water

Wolkersdorfer, Brown & Figueroa (Editors)



Discussion

The results from the 4 trials at Ynysarwed, Blenkinsopp, Merthyr and Dawdon show that electrochemical oxidation offers a potential treatment process to precipitate ferric sludge for AMD discharges over a range of pH values and source waters without the need for pH correction.

The more detailed study at Ynysarwed shows a positive correlation between the conversion of Fe²⁺ to Fe³⁺ and its subsequent precipitation and removal with an increase in current densities applied to the oxidising electrodes ($r^2 = 0.99$). An increase in current density *i.e.* production of molecular oxygen and hydrogen peroxide increased the ORP (mV) potential of the AMD source water ($r^2 =$ 0.95). The increase in ORP with increasing current density and reduction in pH supports the hydrolysis of water to molecular oxygen and Steps (i) and (ii) for oxidation of pyrite by oxygen and hydrogen peroxide. ORP would appear to offer a simple and effective control to monitor and control the treatment process via feed-back loop to the AC-DC and universal matrix controllers to optimise both treatment performance and energy efficiency.

In common with the water and wastewater sector, other examples of electrochemical water treatment are relatively scant. In part this has been due to over-simplification of what is a complex treatment reaction and scale-up from laboratory based reactors to industrial based electrochemical reactors leading to the conclusion that electrochemical treatment processes as being uneconomical at the laboratory stage.

Current	Untreated	1 A	2 A	3 A	4 A	5 A
pН	6.69	6.81	6.17	5.9	5.64	4.62
Temperature (°C)	16.81	18.36	17.69	18.41	17.46	17.89
Dissolved Oxygen (%)	31.2	50.3	54.4	54.4	56.5	57.8
Conductivity (µs/cm)	1813	1736	1651	1726	1280	1341
ORP (mV)	-15.7	-10.5	26.1	42.7	70.7	151.6
Fe II (mg/L)	73.4	42.9	32.9	20.3	10.1	0.2
Fe III (mg/L)	0.3	0.1	0.2	0.1	0.2	0.2

Table 1 Measured parameters for the Ynysarwed electrochemical oxidation experiment

Recent advances in industrial electrochemical reactor design and operation (Dunne 2009) have demonstrated typical operating costs for iron and aluminium removal from upland groundwater supplies at 0.2 kWhm⁻³. Benefits over conventional treatment processes included small footprint, low sludge volume, reduced chemical requirement, wide ranging and effective treatment compared to chemical precipitation, membrane filtration and RO treatment processes.

Conclusions

Electro-chemical oxidation to precipitate iron sludge from pyrites employing advanced power electronics and instrumentation offers an economically viable alternative process to lime neutralisation, ozone and hydrogen peroxide dosing, biological wetland treatment and RO treatment systems. Precipitation of ferrous hydroxide is via oxygen formed by oxidation of water at the anode and hydrogen peroxide via reduction of oxygen at the cathode. Iron sludge precipitated from AMD samples appeared independent of source and pH.

Acknowledgements

We thank the Coal Authority for samples and testing at Ynysarwed, S.Wales, UK, Blenkinsopp

and Dawdon UK mine water sites. Miller Argent Ltd., for iron rich water samples and photograph at Merthyr Tydfil, S.Wales, UK.

References

- Dunne L (2009) Corrib gas Terminal Sets Environmental Management Standard in Construction. Engineers Journal. 63(4): 198–201.
- Hedrick S, Johnson BD (2012) A Modular Continuous Flow Reactor System for the Selective Bio-oxidation of Iron and Precipitation of Schwertmannite from Mine – impacted Waters. Bioscience Technology. 106: 44–49.
- Khanniche MS, Morgan PG, Khanniche KN, Jobling CP, Khanniche N (2001) A Novel Electro-Chemical Process for Water Treatment. Rev. Energ. Ren: Power Engineering: 63–67.
- Maree JP, Strydom WF, Adlem CJL, de Beer M, Tonder GL, Dijk van BJ, (2004) Neutralisation of Acid Mine Water and Sludge Disposal. Division of Water, Environment and Forestry Technology. 1057/1/104; Nov 2004. South African Water Research Commission.
- Silverman MP (1967) Mechanism of Bacterial Pyrite Oxidation; J Bacteriol. 94(4): 1046–1051.

Factors influencing nanofiltration of acid mine drainage

Roberta Fornarelli¹, Mark Mullett², David Ralph³

¹ Hatch Associates, 144 Stirling St, Perth, 6000, Western Australia, Australia, RFornarelli@hatch.com.au
 ² Hatch Associates, 144 Stirling St, Perth, 6000, Western Australia, Australia, MMullett@hatch.com.au
 ³ Murdoch University, 90 South St, Murdoch,6150, Western Australia, Australia, D.Ralph@murdoch.edu.au

Abstract Membrane technology is an established strategy to treat acid mine drainage (AMD). Nanofiltration offers economical advantages over reverse osmosis, and allows for concentrating and recovering valuable metals from AMD waters. Understanding the relationship between AMD pH and membrane charge is required to ensure compliance with stringent discharge criteria, and to maximize metal recovery for profit. The membrane iso-electric point (IEP) is a significant parameter in the rejection of ions. Maximum metal recovery was observed when the pH was lower than IEP. Ongoing research is exploring the opportunity to customize the position of the IEP by membrane surface modification.

Keywords Acid Mine Drainage, Nanofiltration, Feed pH, Iso-electric point, Ion rejection

Introduction

Acid mine drainage (AMD) is a typical by-product of the mining industry and it is well known for its impact on environmental sustainability and water security (Evangelou 1998). Johnson and Hallberg (2005) highlight two key points in the choice of suitable technologies to treat AMD: i) it is fundamental to consider AMD remediation as a resource, thus encouraging recovery and recycle of the products of AMD treatment (Nodwell and Kratochvil 2012); ii) legislation defines discharge criteria that may determine the choice of a system to effectively remove sulfate as well as metals and acidity from mine waters.

Membrane treatment by reverse osmosis (RO) and nanofiltration (NF) is an established strategy for heavy metal removal as it is capable of achieving strict discharge criteria while providing high efficiency, easy operation and space saving (Fu and Wang 2011). Recent studies successfully applied membrane separation to treat AMD (Zhong *et al.* 2007; Rieger *et al.* 2009; Al-Zoubi *et al.* 2010; Mortazavi and Chaulk 2012). RO and NF provided similar rejection performance for polluting metals, however NF was suggested as the preferable treat-

ment due to lower operating costs, *e.g.* higher fluxes at lower pressure, and its ability to selectively concentrate and recover metals and sulfuric acid.

The separation mechanism of NF membranes involves membrane surface charge, i.e. electrorepulsion, and sieving effects (Qin et al. 2004). Feed pH determines both the membrane charge density and charge polarity by establishing the zeta-potential of the membrane surface. Many studies focusing on the relationship between feed pH, membrane charge, and ion rejection, agree on the significant effect of feed pH, and minimum rejections are usually obtained at the isoelectric point (IEP) (Artug 2007; Qin et al. 2004). Since the IEP of commercially available NF membranes ranges between pH 3 to 5 (Childress and Elimelech 1996; Tanninen et al. 2004; Artug 2007), thus bracketing the pH range of most AMD streams, understanding the rejection behavior for a particular membrane-AMD problem is critical for evaluation of a NF treatment strategy.

The objective of this study was to test a commercially available NF membrane on an AMD solution to further understand the relationship between rejection performance and feed pH. The pH of the original solution was modified to create feeds ranging between 1.5 and 4.5. The IEP of the membrane was first empirically estimated by a NaCl-Na₂SO₄ synthetic solution characterized by sulfate concentrations in the range of typical AMD solutions (Al-Zoubi *et al.* 2010).

Methods

AMD solution was provided by Aditya Birla Nifty Copper mine (Western Australia). The AMD composition at the original pH of 4.5 is shown in Table 1. AMD discharge criteria are site-specific and have to comply with increasingly stringent environmental targets. The criteria for sulfate and metals range between drinking and general purposes water guidelines (Table 1).

A synthetic solution of about 600 mg L⁻¹ sodium chloride and 18 g L⁻¹ sulfate (NaCl and Na₂SO₄) was produced to empirically determine the position of the IEP as the rejection minima is observed at the IEP. The sulfate concentration used was representative of sulfate levels of typical AMD solutions (Al-Zoubi *et al.* 2010). Artug (2007) acknowledged that filtration using NaCl-Na₂SO₄ ion system is important to characterize the membrane in terms of the position of IEP and surface charge polarity.

The schematic diagram of the cross-flow flat sheet membrane test unit is shown in Fig.

Parameter	Unit	Concentration	Discharge Criteria
pH	-	4.5	6-8.5
Ca ²⁺	mg L-1	480	50
Cu2+	mg L-1	410	1-50
K+	mg L-1	310	-
Mg ²⁺	mg L-1	770	50
Mn ³⁺	mg L-1	440	0.005-0.5
Na+	mg L-1	2000	-
Cl-	mg L-1	2300	-
SO42-	mg L-1	6900	250-1000

Table 1 Composition of AMD solution provided by Aditya Birla Nifty Copper mine. Discharge criteria as defined in Rieger et al. (2009) and ANZECC (2000).

1. A Dow NF270 polyamide nanofiltration membrane (0.0138 m²) was used because of the availability of published work describing its zeta potential and IEP. Filtration experiments were carried out at operating pressures of 5 to 8 bar and permeate flux of 25 to $35 \text{ Lm}^{-2} \text{ h}^{-1}$. The feed flow rate and temperature were constant at 200 L h⁻¹ and 24 ± 1 °C, respectively. The experiments were carried out in full re-circulation mode (both permeate and retentate were re-circulated to the feed tank).

The experiments with NaCl-Na₂SO₄ solution were carried out with feeds ranging from pH 4 to pH 2.6 at 0.2 pH decrements using HCl. The aim of these experiments was to estimate the position of the IEP by observing rejection



Fig. 1 Schematic diagram of lab-scale NF unit test.

minima (Artug 2007). The published NF270 IEP range is between pH 2.5 and 4 (Tanninen *et al.* 2004; Artug 2007; Al-Rashdi *et al.* 2012).

The experiments with the AMD solution (Table 1) were carried out similar to the NaCl-Na₂SO₄ tests with the pH ranging from 4.5 to 1.5 in 0.2 unit decrements by adding HNO₃. A total of 5 L of AMD solution was available and a 2 L feed tank was used in each test. The collection of permeate and feed samples started after 15 min of filtration at each pH value (120 mL per sample). Samples were sent to an external laboratory for analysis. Membrane rejection performance was calculated for each ion as the concentration ratio between the permeate and the feed sample. At each sampling point a total volume of 240 mL was removed for sampling purposes, and an equivalent volume of replacement feed was added to the 2 L feed tank. These additions caused a 2 to 5 % increase in ion concentration relative to the original feed (Table 1).

Na⁺ and SO_4^{2-} were obtained at pH equal to 3.04 (Fig. 2a and b), suggesting the IEP being at the vicinity of pH 3. This is consistent with previous studies (Tanninen et al. 2004; Artug 2007; Al-Rashdi et al. 2012). Minimum rejection at IEP is explained by the fact that sieving effect is the only active separation mechanism, as membrane charge is zero at the IEP (Qin et al. 2004). The membrane is positively charged for pH values lower than 3 and negatively charged at pH values higher than 3. Rejections of Na⁺ and SO_4^{2-} followed the same trend (Fig. 2a), as the retention of Na⁺ ions depended on the rejection of SO_4^{2-} due to electroneutrality condition (Artug et al. 2007). Decreasing rejection of Na⁺ at pH < 2.8 (Fig. 2a) was also observed by Tanninen and Nystrom (2002) and was attributed to a decreased positive surface charge due to an increased concentration of H⁺ ions. Negative Cl⁻ rejections (Fig. 2b) indicated Donnan effects (Tanninen et al. 2004): the concentration of Cl⁻ increased in the permeate while SO_4^{2-} was rejected in order to maintain electroneutrality (Artug et al. 2007).

Results and Discussion

Fig. 2 shows ion rejection vs. pH for the NaCl-Na₂SO₄ solution. Minimum rejections of Cl⁻,

Results of the experiments on the AMD solution are shown in Fig. 3 and 4. Rejections



Fig. 2 Ion rejection at varying pH for the NaCl-Na₂SO₄ solution. a) Rejection of sulfate and sodium ions. b) Rejection of chloride ions.

Fig. 3 Ion rejection at varying pH for the AMD solution provided by Aditya Birla Nifty Copper mine. a) Rejection of sulfate. b) Rejection of calcium, copper, magnesium, and manganese ions. Significant decreasing trends of cations rejections are observed for pH higher than 3 (p-value < 0.05). above 95 % were achieved for all cations at feed pH lower than 3, however significant decreasing rejections were observed at increasing pH (Fig. 3b, p-value < 0.05) (as also found by Zhong *et al.* 2007 and Al-Rashdi *et al.* 2012). Cations were highly rejected when membrane was positively charged (pH < 3), but the rejection decreased as the membrane became increasingly negative (at pH > 3).

A different trend was observed for sulfur whose rejection increased at feed pH > 3 (Fig. 3a), in accordance with an increasingly negatively charged membrane (Szoke *et al.* 2002; Al-Zoubi *et al.* 2010). Note that at pH values lower than 2, sulfur ion was mostly present as bisulfate ion (Tanninen *et al.* 2004), which readily transmitted. Lower rejections were also due to the positively charged membrane at pH < 3.

The concentration of sulfate and metals in the permeate was compared with discharge criteria as defined in Table 1 (Fig. 4). At pH values higher than the IEP, sulfate concentrations were well below the upper guideline of 1000 mg L⁻¹ and reached the sulfate limit as required by drinking water criteria (Fig. 4d). On the contrary, metal concentrations, and particularly calcium, copper and magnesium, approached the upper bound of the discharge criteria at feed pH higher than the IEP (Fig. 4a) and b). The concentration of manganese in the permeate did not meet the discharge criteria at all pH values (Fig. 4c).

Our results confirmed the findings of previous studies on the importance of membrane charge to determine ion rejections in NF-AMD problems (Zhong *et al.* 2007; Al-Zoubi *et al.* 2010; Al-Rashdi *et al.* 2012). NF is a suitable technique to treat mine water as it allows concentrating and recovering valuable metals, while meeting discharge criteria. However, understanding the interaction between membrane IEP and AMD pH is important to maximize the rejection and recovery of metals. For this particular system, at a 50 % volume recovery, the Cu²⁺ concentration in the permeate could approach 180 mg L⁻¹ at pH > IEP, while 100 mg L⁻¹ can be approached at

pH < IEP (we acknowledge other membranes are available that would provide superior rejections). Due to this phenomenon the discharge criteria may be exceeded if the membrane charge is not well understood. In addition, higher concentrations of Cu^{2+} in the permeate at pH > IEP may represent a significant loss of metal that could otherwise be recovered.

To achieve the highest recovery of metals, the membrane IEP needs to be higher than the AMD pH. Test work conducted on different



Fig. 4 Ion concentrations in permeate samples at varying pH for the AMD solution provided by Aditya Birla Nifty Copper mine. Concentration of a) copper, b) calcium and magnesium, c) manganese, d) sulfate with relative discharge criteria as defined in Table 1.

Wolkersdorfer, Brown & Figueroa (Editors)

membranes will ensure membranes characterized by a suitable IEP relative to the AMD pH are selected. Alternatively, surface membrane modification to customize the position of the IEP relative to the AMD pH can be considered (Kim *et al.* 2002; Mukherjee *et al.* 2005). This represents a potentially novel technology application to maximize metal recovery.

Contrary to our expectations, minimum rejections of sulfate ion at the IEP were not detected when testing the AMD solution. On the other hand, minimum sulfate rejection was obtained in the tests conducted on the NaCl-Na₂SO₄ solution, which is in accordance with the literature (Artug 2007). To the best of our knowledge, there is no published work showing minimum rejections at the IEP for AMD solutions as most of the studies focus on simple single or binary ion systems (Artug 2007; Qin *et al.* 2004). This aspect is currently the objective of further investigations.

An indicative cost analysis comparing NF to RO was performed using an economic model. The model was based on known fabrication costs for similar scale projects conducted by the authors. The key variables were the product flow rate, volume recovery and number of membrane stages. The model also takes into consideration the material of construction, level of control and automation, and the potential complexity of CIP/cleaning arrangements. The operating parameters input to the model were as described in Al-Zoubi et al. (2010) and listed in Table 2. Capital investment was calculated on the basis of feed and permeate flow rates, and volumetric recovery. At a constant pressure of 15 bar the permeate flow rate for the two NF membranes was about double that for RO (Table 2). The capital cost for NF was about 10 % less than for RO. In term of operational costs, to obtain a permeate flux of 20 L m⁻² h⁻¹, an operational pressure of 10 and 14 bar was needed for NF and RO, respectively (Table 2). This pressure difference translated in about 30 % savings of operational costs associated with energy requirements.

Conclusions

The importance of pH of an AMD solution and IEP of the NF membrane in determining ion rejection was demonstrated in this study. Optimum metal rejection occurred when the solution pH was below the IEP and diminished significantly as the solution pH deviated above the IEP. Anion rejection followed the opposite trend. Understanding these phenomena is important to comply with discharge criteria and maximize metal recovery. Novel approaches are needed to ensure that appropriate membranes and operating parameters are chosen

Parameter	Unit	Nanofiltration GE-Osmonics DK	Nanofiltration NF99	Reverse Osmosis RO HR98PP		
	Capital	l Cost Estimate				
Feed Pressure	bar	15	15	15		
Permeate Flux	L m ⁻² h ⁻¹	38	43	22		
Estimated Cost	AUD \$m	2.75	2.7	3.02		
Cost Difference relative to RO	%	-9	-11	-		
	Operational Cost Estimate					
Permeate Flux	L m ⁻² h ⁻¹	20	20	20		
Feed Pressure	bar	10	10	14		
Estimated Cost	AUD \$ pa	750.9	750.9	1051.2		
Cost Difference relative to RO	%	-29	-29	-		

Table 2 Capital and operational cost comparison between two nanofiltration and one reverse osmo-sis applications to AMD treatment. Data are taken from Al-Zoubi et al. (2010), where tests were con-ducted at: feed flow rate = 600 L h^{-1} ; volumetric recovery = 75 %; temperature = 20 °C; pH = 2.4.

to suit the specific AMD problem. Ongoing research aims at exploring the opportunity of customizing the position of the IEP by surface membrane modification.

Acknowledgements

The authors are grateful to Hatch Technologies for funding this study and to Aditya Birla Nifty Copper mine for providing the AMD water sample.

References

- Al-Rashdi BAM, Johnson DJ, Hilal N (2012) Removal of heavy metal ions by nanofiltration. Desalination 315: 2–17.
- Al-Zoubi H, Rieger A, Steinberger P, Pelz W, Haseneder R, Hartel G (2010) Optimization study for treatment of acid mine drainage using membrane technology. Separation Science and Technology 45:2004—2016
- ANZECC (2000) National water quality management strategy. Australian and New Zealand Guideline for Fresh and Marine Water Quality (2000)
- Artug G (2007) Modelling and simulation of nanofiltration membranes. Doctoral thesis dissertation. Cuvillier Verlag, Gottingen
- Childress AE, Elimelech M (1996) Effect of solution chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes. Journal of Membrane Science 119:253–268
- Evangelou VP (1998) Pyrite chemistry: the key for abatement of acid mine drainage. In: Geller A, Klapper H, Salomons W, editors. Acidic Mining Lakes: Acid Mine Drainage, Limnology and Reclamation. Berlin7 Springer; 1998. p. 197–222.
- Fu F, Wang Q (2011) Removal of heavy metals ions from wastewaters: a review. Journal of Environmental Management 92:407–418.
- Johnson DB, Hallberg KB (2005) Acid mine drainage remediation options: a review. Science of the Total Environment 338:3–14.
- Kim KS, Lee KH, Cho K, Park CE (2002) Surface modification of polysulfone ultrafiltration membrane by

oxygen plasma treatment. Journal of Membrane Science 199: 135–145.

- Mortazavi S, Chaulk J (2012) Treatment of acid mine drainage streams using membrane separation. In: Proceedings of the 9th International Conference on Acid Rock Drainage, edited by WA Price, C Hogan and G Tremblay, May 20–26, 2012, Ottawa, Ontario, Canada.
- Mukherjee P, Jones KL, Abitoye JO (2005) Surface modification of nanofiltration membranes by ion implantation. Journal of Membrane Science 254: 303– 310.
- Nodwell M, Kratochvil D (2012) Sulphide precipitation and ion exchange technologies to treat acid mine water. In: Proceedings of the 9th International Conference on Acid Rock Drainage. Edited by W. A. Price, C. Hogan, and G. Tremblay, May 20–26 2012, Ottawa, Ontario, Canada.
- Qin JJ, Oo MH, Lee H, Coniglio B (2004) Effect of feed pH on permeate pH and ion rejection under acidic conditions in NF process. Journal of Membrane Science 232:153–159
- Rieger A, Steinberger P, Pelz W, Haseneder R, Hartel G (2009) Mine water treatment by membrane filtration processes- Experimental investigations on applicability. Desalination and Water Treatment 6(1– 3):54-60
- Szoke S, Patzay G, Weiser L (2002) Characteristics of thin-film nanofiltration membranes at various pH-values. Desalination 151:123–129.
- Tanninen J, Nystrom M (2002) Separation of ions in acidic conditions using NF. Desalination 147: 295– 299.
- Tanninen J, Platt S, Weis A, Nystrom M (2004) Longterm acid resistance and selectivity of NF membranes in very acidic conditions. Journal of Membrane Science 240:11–18.
- Zhong CM, Xu ZL, Fang XH, Cheng L (2007) Treatment of acid mine drainage (AMD) by ultra-low-pressure reverse osmosis and nanofiltration. Environmental Engineering Science 24(9):1297-1306.

Chromium (VI) removal from effluents using zeolite

Yageshni GOVENDER-RAGUBEER¹, Mariekie GERICKE²

Biotechnology Division, Mintek, Private Bag X3015, Randburg, South Africa ¹yageshnig@mintek.co.za, ²mariekieg@mintek.co.za

Abstract This study focused on evaluating the removal of Cr (VI) from effluents using natural zeolite. The results indicated that zeolite can adsorb Cr (III) cations, but not Cr (VI) anions ($HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$). To increase the adsorption of Cr (VI), different surface modification methods were evaluated. The best results were obtained using zeolite modified with 100 mmol Fe (III) for 24 hours. Treatment of solutions containing 20 mg/L Cr (VI) in columns packed with modified zeolite resulted in solutions containing <0.02 mg/L Cr (VI), which meets the WHO and South African effluent discharge limits of 0.05ppm.

Keywords zeolite, adsorption, Cr(VI)

Introduction

The impact of chromium pollution originating from the ferrochrome industry in South Africa is very poorly understood with limited information available. It has been reported that beneficiated South African chromite ores contain between 0.38 to 0.76 mg/L of Cr (VI), which is known to be toxic, carcinogenic and extremely soluble in water (Glastonbury *et al.* 2010). Over the past decades, various different Cr (VI) treatment options such as ion exchange on polymeric resin (Mohan *et al.* 2005), reduction of Cr (VI) to Cr (III), reverse osmosis and adsorption on activated carbon (Leyva-Ramos *et al.* 1994) have been investigated.

Natural zeolites have shown high sorption capacities for inorganic cations including metals (Barros *et al.* 2006). Natural zeolites are crystalline micro-porous alumina-silicates with a very well defined structure that consists of a framework formed by tetrahedral of SiO₄ and AlO₄ (Diale *et al.* 2011). The isomorphous substitution of Al³⁺ for Si⁴⁺ in the tetrahedral results in a negative charge on the zeolitic framework, which can be balanced by exchangeable cations (Leyva-Ramos *et al.* 2008). Therefore natural zeolites can exchange cations but not anions, necessitating the surface modification of natural zeolite in order to remove anions from solution. In this study the ability of modified South African zeolite to remove Cr (VI) from effluents was evaluated. The objective was to meet the South African Department of Water Affairs effluent discharge limit and the WHO limit for drinking water of 0.05 mg/L.

Methods

Materials

Natural zeolite, derived from Clinoptilolite mined in South Africa, was obtained from Pratley Perlite Mining Co. (PTY) Ltd. A particle size of 2–4 mm was used for all tests.

Surface modification of zeolite

Three surface modification methods, using NaOH, NaCl and Fe (III), were investigated in this study.

Surface modification using NaOH

The zeolite was treated with 4 M NaOH at 60 °C for 24 hours, using a 1:5 zeolite to NaOH ratio. Following the 24 hour modification period, the sample was rinsed six times with dH_2O to remove any excess NaOH and the modified zeolite was dried at 25 °C for 24 hour (Foldesova *et al.* 2000).

Surface modification using NaCl

The zeolite was contacted four times, 6 hours each, with 1 M NaCl at 60 °C using a 1:10 zeolite to NaCl solution ratio. Following the 24 hour modification period, the zeolite was washed with 2 L dH₂O at 40 °C and dried at 60 °C for 24 hours (Barros *et al.* 2006).

Surface modification using Fe (III)

Zeolite (60 g) was added to 180 mL of 20 mmol Fe (III) solution. The mixture was shaken at 150 rpm at 25 °C for 24 hours. After 24 hours, the pH level of the mixture was adjusted to 9 using 2 M NaOH. The mixture was allowed to settle and the supernatant removed. The modified zeolite was washed six times with dH_2O to remove excess Fe (III) and dried at 25 °C for 24 hours (Du *et al.* 2012).

Cr (VI) and Cr (III) adsorption tests

Tests were conducted using 2.5 g each of the unmodified and modified zeolite, added to 20 mL of 20 mg/L Cr solution to determine the Cr (VI) and Cr (III) adsorption capability of the zeolite. All tests were conducted in shake flasks at 25 °C, 100 rpm for 24 hours. The filtrate from each test was analysed using Inductively Coupled Plasma (ICP) analysis.

Optimisation of the Fe (III) modification process

The tests were performed in shake flasks at 25 °C, 100 rpm for 24 hours, with a ratio of zeolite to Cr solution (20 mg/L) of 1:5. The filtrate from each test was analysed for Cr using ICP analysis.

Effect of Fe (III) concentration on zeolite surface modification

The method described by Du *et al.* (2012) was adapted to determine the effect of Fe (III) concentration on the zeolite surface modification. During the preparation of the Fe (III)-modified zeolite, 20 g of zeolite was added to 60 mL of the Fe (III) solution at concentrations ranging between O-1 M.

Effect of contact time during surface modification on Cr (VI) adsorption

Zeolite was modified with 100 mmol Fe (III) at contact times varying from 4–96 hours using the method described previously.

Effect of Cr (VI) concentration on the Cr (VI) adsorption efficacy of zeolite modified with Fe (III)

The effect of Cr (VI) concentration on the adsorption efficacy of the zeolite modified with 100 mmol Fe (III) for 24 hours was investigated by varying the initial C (VI) concentration between 10–1000 mg/L.

Column studies

The test work was performed in 500 and 1000 mm glass columns. A 1 L synthetic solution containing 20 mg/L Cr (VI), at a pH level of 5, was passed through the columns containing zeolite coated with 100 mmol Fe (III) at a flow rate of 1.5 mL/min. The eluted solution was analysed for Cr using ICP analysis. Two approaches as indicated in Fig. 1 were used:

- In the first approach, the Cr (VI) solution was passed through the same column twice and the eluent from each cycle was analysed.
- In the second approach, a two stage column set-up was used with the eluent from column one producing the feed for column two.

Results and Discussion Zeolite surface modification

The results obtained from the Cr (VI) and Cr (III) adsorption tests using the modified and unmodified zeolite are summarised in Table 1.

The results obtained indicated that unmodified zeolite and zeolite modified with NaCl and Fe (III) were capable of removing >98 % Cr (III) from solution, whereas the NaOH modified zeolite could only remove 59 % of the Cr (III). These results demonstrated that surface modification of zeolite is not required for the adsorption of Cr (III).



Zeolite in its unmodified state could only remove 16 % of the Cr (VI). However modification of zeolite with NaOH and NaCl resulted in an increase in Cr (VI) removal of 39 % and 20 % respectively. The highest Cr (VI) removal of 52 % was obtained when using the zeolite modified with Fe (III). These results are similar to the results obtained by Du et al. (2012) who showed that enhanced adsorption of Cr (VI) occurs in soils derived from volcanic ash and tuff which contained significant amounts of Fe(III) coated zeolite. In order to improve the 52 % Cr (VI) removal by Fe (III) modified zeolite, further optimisation of various process parameters such as the Fe (III) concentration, contact time and Cr (VI) concentration during the chemical surface modification process were optimised.

Optimisation of the zeolite modification process

Effect of Fe (III) concentration on zeolite surface modification

Six shake flask tests were conducted to determine the optimum Fe (III) concentration required for surface modification of the zeolite

Test	Adsorbent	Initial [Cr],	Final [Cr],	Cr Adsorbed,
		20 mg/L	mg/L	%
1	NaOH zeolite	Cr(VI)	12.20	39
2	NaOH zeolite	Cr(III)	8.20	59
3	NaCl zeolite	Cr(VI)	16.10	20
4	NaCl zeolite	Cr(III)	0.50	98
5	Fe(III) zeolite	Cr(VI)	9.54	52
6	Fe(III) zeolite	Cr(III)	0.06	99
7	Unmodified	Cr(VI)	16.80	16
8	Unmodified	Cr(III)	0.48	98

Table 1 Summary of the results obtained duringsurface modification

to ensure maximum Cr (VI) removal. The results of this test are summarised in Table 2.

The results indicated that unmodified zeolite could only remove 20.5 % of the Cr (VI). The method described by Du *et al.* (2012) specified that 20 mmol of Fe (III) should be loaded onto natural zeolite for efficient Cr (VI) removal. However results from this study indicated that zeolite modified with 20 mmol Fe (III), resulted in only 47.5 % Cr (VI) removal. However when the Fe (III) concentration was further increased, there was a subsequent increase in the amount of Cr (VI) removed, with

Test	[Fe (III)] mmol	Final [Cr(VI)] mg/L	Cr(VI) removed, %	Fe in solution, mg/L
1	0	15.9	20.5	< 0.02
2	20	10.5	47.5	< 0.02
3	50	0.7	96.5	< 0.02
4	100	< 0.02	99.9	< 0.02
5	500	< 0.02	99.9	1.53
6	1000	< 0.02	99.9	36.46

Table 2 Results obtained during determination ofthe effect of [Fe (III)] on zeolite surface modifica-tion and Cr (VI) removal. An initial [Cr (VI] of 20mg/L was used for all tests.

99.9 % removal obtained at Fe (III) concentrations of 100, 500 and 1000 mmol. However at Fe (III) concentrations of 500 mmol and 1000 mmol, Fe concentrations of 1.5 and 36.8 mg/L respectively were detected in the test solutions, which could indicate leaching of the zeolite Fe (III) coating.

Effect of contact time during surface modification on Cr (VI) adsorption

In this test, zeolite was modified with 100 mmol Fe (III) at contact times varying between 4-96h. The results indicated that zeolite modified with Fe (III) for 4 and 8 hours, could only adsorbed 93 % and 95 % of the 20 mg/L Cr (VI) present in solution (Fig. 2A). However as the modification period was increased from 8 to 24 hours, the adsorption capacity of the zeolite increased, resulting in a 99 % adsorption of Cr (VI). Thus for all future studies, zeolite coated for 24 hours with 100 mmol Fe (III) was used.

Effect of Cr (VI) concentration on the Cr (VI) adsorption efficacy of zeolite modified with Fe (III)

The effect of Cr (VI) concentration on the adsorption efficacy of the modified zeolite was investigated by varying the initial Cr (VI) concentrations between 10 and 1000 mg/L. The results obtained (Fig. 2B) indicated that:

- At initial Cr (VI) concentrations between 10–20 mg/L, 99.9 % of the Cr (VI) could be adsorbed by the zeolite.
- At Cr (VI) concentrations between 30–100 mg/L, only 52–72 % of the Cr (VI) could be adsorbed.
- It was also noted that at Cr (VI) concentrations > 100 mg/L, the absorbance efficiency of the zeolite was significantly decreased to between 1and 30 %.

Column tests

Approach 1: Effect of contact time on Cr (VI) adsorption

The results obtained are summarised in Table 3. After passing the Cr (VI) solution once through the 500 mm column, only 37 % (7.4 mg/L) of the Cr (VI) was adsorbed by the zeo-lite. When the solution was passed through the column a second time (Cycle 2), the Cr (VI) in



Fig. 2 (A) Effect of the surface modification time on the removal of Cr (VI) using Fe (III) modified zeolite. (B) Effect of initial Cr (VI) concentration on adsorption efficiency of Fe (III) modified zeolite

"Reliable Mine Water Technology"

Column length, mm		Feed [Cr], mg/L	Product [Cr], mg/L	Cr adsorbed, %
500*	Cycle 1	20.0	12.6	37.0
	Cycle 2	12.6	10.3	18.2
	Total adsorption	20.0	10.3	48.5
1000**	Cycle 1	20.0	3.5	82.6
	Cycle 2	3.5	1.8	52.1
	Total adsorption	20.0	1.8	90.8

Table 3 Adsorption resultsusing glass columns packedwith modified zeolite

*0.9 kg zeolite used per column ** 1.8 kg zeolite used per column

Column length, mm		Feed [Cr], mg/L	Product [Cr], mg/L	Cr adsorbed, %
500	Cycle 1	20.0	11.8	41.0
	Cycle 2	11.8	8.5	27.9
	Total adsorption	20.0	8.5	57.5
1000	Cycle 1	20.0	3.6	81.9
	Cycle 2	3.6	< 0.02	99.9
	Total adsorption	20.0	< 0.02	99.9

Table 4 Adsorption results using a 2-stage glass column system packed with modified zeolite

solution decreased from 12.6 to 10.3 mg/L, which was still significantly higher than the permitted discharge limit of 0.05 mg/L.

The results obtained using the 1000 mm column indicated that after Cycle 1, 82.6 % of the Cr (VI) was adsorbed. However a significant Cr (VI) concentration of 3.5 mg/L remained in solution. During Cycle 2 only an additional 1.6 mg/L of C (VI) was removed, resulting in a final product containing 1.8 mg/L of Cr (VI), which is above the discharge limit of 0.05 mg/L. It should be noted that <0.02 mg/L Fe was detected in the feed and product solutions in any of the tests, indicating that the washing step during the Fe (III)-zeolite surface modification procedure was adequate.

Approach 2: Effect of adsorbent concentration on Cr (VI) removal

In order to improve Cr (VI) removal, the use of two stage column systems was evaluated. The results obtained from the 2-stage tests are summarised in Table 4. The results indicated that (using the 500 mm column) only 41 % of Cr (VI) was removed during Stage 1. However, a final eluent containing 8.5 mg/L Cr (VI) was obtained after the second stage. When using the 1000 mm columns, 81.9 % of Cr (VI) was removed during Stage 1. However when a second column was added, the Cr (VI) removal increased to 99.9 %, with the eluent containing <0.02 mg/L Cr (VI), indicating that this solution can be discharged as it falls below the discharge guideline value of 0.05 mg/L. These results showed that the extent of Cr removal was affected more by the ratio of zeolite-to-solution rather than longer contact time, suggesting that the extent of metal removal is more restrained by the approach towards equilibrium than by kinetics.

Conclusions

During the process optimisation test work in shake flasks, it was found that optimum Cr (VI) adsorption of 99.9 % could be achieved when using zeolite modified with 100 mmol Fe (III). Two approaches were evaluated using 500 and 1000 mm glass columns. In the first approach the Cr (VI) solution was passed through the same column twice, providing longer contacttime. In the second approach a two stage column set-up was used with the eluent from column one producing the feed for column two (using double the amount of adsorbent, *i.e.* providing equilibrium conditions favouring greater adsorption). The results obtained indicated that the second approach was a better option compared to the first approach, suggesting that during these experiments the extent of metal removal is more restrained by the approach towards equilibrium than by kinetics. The preliminary results obtained during this study indicated that the use of natural South African zeolite is a potential treatment option for Cr (VI) removal from solutions. However further test work will focus on the adsorption capacity, kinetics and scale up of the process.

Acknowledgements

This paper is published with the permission of Mintek of South Africa.

References

- Barros MASD, Zola AS, Arroyo PA, Tavares CRG, Sousa-Aguiar EF (2006) Chromium uptake from tri-component solution in zeolite fixed bed. Adsorption 12: 239–248.
- Du G, Li Z, Liao L, Hanson R, Leick S, Hoeppner N (2012) Cr(VI) retention and transport through Fe(III)coated natural zeolite. J Hazardous Materials 221-222:118-123

- Foldesova M, Dillinger P, Lukae P (2000) Adsorption and desorption of Cr(III) on natural andc hemically modified Slovak zeolites. J Radioanalytical and Nuclear Chemistry 245: 435–439
- Glastonbury RI, van der Merwe W, Beukes JP, van Zyl PG, Lachmann G, Steenkamp CJH, Dawson
- NF, Stewart HM (2010) Cr(VI) generation during sample preparation of solid samples- A chromite ore case study. Water SA 36: 105–110
- Leyva-Ramos R, Juarez-Martinez A, Guerrero-Coronado RM, (2012) Adsorption of chromium (VI) from aqueous solutions on activated carbon. Water Science Technology 30: 191–197.
- Leyva-Ramos R, Jacobo-Azuara A, Diaz-Flores PE, Guerrero-Coronado RM, Mendoza-Barron J, Berber-Mendoza MS (2012) Adsorption of chromium (VI) from an aqueous solution on a surfactant-modified zeolite. Colloids and Surfaces A: Physicochemical Engineering Aspects 330: 35–41.
- Mohan D, Singh KP, Singh VK (2005) Removal of hexavalent chromium from aqueous solution using low cost activated carbon fabric cloth. Indian J Engineering and Chemical Research 44: 1027-1042.

A Periodic Table of Passive Treatment for Mining Influenced Water – Revisited

James J. GUSEK

Sovereign Consulting Inc., 5902 McIntyre Street, Golden, CO 80403 USA, jgusek@sovcon.com

Abstract The technical community of regulators and engineers that specializes in passive water treatment design understands that each source of mining influenced water (MIW) has its unique signature, either imposed by the natural geochemical conditions of the ore body and surrounding mine waste, or by resource recovery processes. A passive treatment "decision tree" approach to generic design has been generally accepted in various forms. However, the complexity of MIW lead to the introduction of a "Periodic Table of Passive Treatment" (Gusek 2009) as a useful design tool to satisfy the need to embrace a larger range of MIW chemistries. This paper revisits the concept to include the effects of adsorption and other passive treatment mechanisms.

Keywords MIW, Adsorption, (semi)-Metals

Introduction

The Periodic Table of Elements (PTE) was first introduced by the Russian chemist Dmitri Ivanovich Mendeleev in 1869. Fifty-seven of the elements had been discovered prior to that date, and the rest discovered since then. The scientific and industrial revolution of the 18th and early 19th centuries yielded most of the rest of the elements that Mendeleev categorized. Mendeleev's contribution to science was monumental; he organized the elements into similar groups which we now know are governed by how their atomic structures are arranged. For a more in-depth approach to the PTE from different perspective, the reader is referred to "An Earth Scientist's Periodic Table of the Elements" (Railsback 2004).

The term "mining influenced water" covers the breadth of solutions ranging from what might be termed traditional acid rock drainage (ARD), neutral mine drainage and mining process solutions. The multiplicity of MIW sources compounds the problems facing engineers charged with designing MIW treatment systems. Consequently, every treatment system, whether active or passive, seems to require some site-specific customization. Before passive treatment approaches to various groups in the PTE can be discussed, it is appropriate to consider the accepted definition of the term "passive treatment". In the past, "constructed wetlands" was in common usage but this term carries much regulatory baggage and does not properly characterize many passive treatment unit processes.

To paraphrase Gusek (2002):

(*P*assive treatment is a process of sequentially removing contaminants and/or acidity in a natural-looking, man-made bio-system that capitalizes on ecological, and/or geochemical reactions coupled with physical sequestration. The process does not require power or chemicals after construction, and lasts for decades with minimal human help.

Passive treatment systems are typically configured as a series of sequential process units because no single treatment cell type works in every situation or with every MIW geochemistry. It is an ecological/geochemical process because most of the reactions (with the exception of limestone dissolution) that occur in passive treatment systems are biologically assisted. Lastly, it is a removal process because the system typically provides filtration or immobilization of the metal precipitates that are formed. Without this mechanism, precipitates would be flushed out of the system, and the degree of water quality improvement could be compromised.

Certainly, treating some MIW parameters is considered "easy", such as iron and hydrogen ion (the basic unit of acidity). These parameters have been the focus of typical coal geology derived MIW treatment since the early 1980's. In comparison, "difficult" parameters such as common anions (e.q. sodium, chloride, and magnesium and other components of total dissolved solids [(TDS]) are conserved in traditional passive treatment systems; passive treatment is not considered an appropriate technology. Next are the elements associated with traditional metal mining: iron (again), copper, lead, zinc, cadmium, mercury, and arsenic. These elements are typically found in metal mine ores and wastes as sulfides and passive treatment designers typically focus on creating conditions favorable to sulfide precipitation such as those found in biochemical reactors (BCRs). That paradigm, however, now has several process alternatives that were not considered in depth in previous work (Gusek 2009).

For the sake of simplicity, the focus of the discussion will be elements and compounds that are problematic or "interesting" ones associated with MIW as summarized in Table 1.

Predominant Treatment Mechanisms in Passive Systems

The following treatment mechanisms are thought to prevail in passive systems addressing "traditional" acidic and alkaline MIW. Carbonate alteration (italicized below) is a passive mechanism that has not been specifically addressed by PTS designers.

- Biological sulfate reduction w/alkalinity improvement
- Metal sulfide formation
- Oxidation

DTE		Common Aquaque Spaciae/Accepieted
	Elements	Common Aqueous Species/Associated
Group		Parameters
1	Hydrogen (H), Sodium (Na), and Potassium (K)	TDS, Acidity
2	Magnesium (Mg), Calcium (Ca), Barium (Ba),	TDS, Ra-226
	Radium (Ra)	
3	No traditional MIW elements or compounds	N/A
4	No traditional MIW elements or compounds	N/A
5*	Vanadium (V) and Uranium (U) [*Actinide Series]	V_2O_6, U_3O_8
6	Chromium (Cr), Molybdenum (Mo)	Cr ⁺⁶ , Cr ⁺³ , Mo ⁺⁵ , Mo ⁺⁶
7	Manganese (Mn)	Mn ⁺² , Mn ⁺⁴ , Acidity
8	Iron (Fe)	Fe ⁺² , Fe ⁺³ , Acidity
9	Cobalt (Co)	Co ⁺² , Acidity
10	Nickel (Ni)	Ni ⁺² , Acidity
11	Copper (Cu), Silver (Ag), Gold (Au)	Cu ⁺² , Ag ⁺² , AgCN complex, Au-Chloride?
		AuCN complex, Acidity
12	Zinc (Zn), Cadmium (Cd), Mercury (Hg)	Zn^{+2} , Cd^{+2} , Hg^{+2} , Hg^{+1} (organic), Acidity
13	Aluminum (Al), Thallium (Tl)	Al^{+3} , SO_4^{-2} Tl^{+1} , Tl^{+3} , Acidity
14	Carbon (C), Lead (Pb)	HCO_3 , TOC, BOD ₅ , Pb ⁺² , Pb carbonate
		complex
15	Nitrogen (N), Phosphorous (P), Arsenic (As),	NH_3 , N_2 , NO_2 , NO_3 , PO_4 , As^{+3} , As^{+5} ,
	Antimony (Sb)	multiple As-complexes/ionic species
16	Oxygen (O), Sulfur (S), Selenium (Se)	O_2 , SO_4 , HS ⁻ , Selenite, Selenate
17	Fluorine (F), Chlorine (Cl)	TDS
18	Noble Gases, No traditional MIW elements	N/A

Table 1 PTE Groups, Elements and Species of Interest in Passive Treatment Systems
- Carbonate dissolution
- Carbonate alteration
- Organic adsorption & complexation
- Plant uptake
- Abiotic adsorption

Conventional wisdom and much research has shown that micro-biologically facilitated reduction and oxidation reactions and carbonate dissolution were the most important removal mechanisms and organic complexation, plant uptake and adsorption play minor as well as temporary roles. This paper not only challenges this misconception but introduces another mechanism: carbonate alteration; *e.g.* conversion of CaCO₃ to metal carbonates like ZnCO₃ or FeCO₃.

Passive Treatment System Design Components

From a passive treatment system designer's perspective, there are eight basic components available "off-the-shelf":

- Sulfate reducing bioreactors [AKA compost wetlands, SRBRs, vertical flow ponds, and biochemical reactors (BCRs)]
- Aerobic wetlands,
- Anoxic limestone drains,
- Limestone up-flow ponds,
- Limestone diversion wells,
- Aeration & Settling ponds,
- Successive alkalinity producing systems (SAPS), and
- Open limestone channels & limestone beds.

There may be two more to add to the list: sulfide sequestration cells and iron terraces which might be considered a sub-set of aerobic wetlands.

Each component has its own expected geochemical or biogeochemical capability with respect to mitigating MIW. However, some of these components could exhibit capabilities that have heretofore not been considered within the context of the Periodic Table of Passive Treatment as first introduced in Gusek (2009).

In Gusek (2009), the oxidation/reduction potential (ORP) was the principal condition that would control whether or not a given MIW parameter would be addressed. This admittedly preliminary approach did not include adsorption phenomena or the displacement/replacement of the calcium ion in calcium carbonate by a metal. The same substitution process may be occurring with the carbonate ion when displaced by fluorine to form fluorite (CaF₂).

Adsorption Processes

Early research (Wildeman et al. 1993) suggested that adsorption processes contributed a small percentage of the overall divalent metal removal performance of passive treatment systems. More recent work by Tebo et al. (2004) and others suggest otherwise. For example, provided that interferences are addressed in pretreatment steps or are not present at all, many divalent metals and other MIW parameters will adsorb to manganese oxide (MnO₂) at neutral pH. Arsenic adsorption to iron oxyhydroxide (Fe[OH]₃) has be observed by many practitioners, including unpublished work by this author. Both phenomena have been found to be microbially facilitated: by Tebo et al. 2005 in the case of manganese and LaBlanc et al. (1996) in the case of iron oxyhydroxide. See Figs. 1a and 1b for graphical summaries of this process for iron and manganese, respectively. Space limitations preclude inclusion of references for each element. While a separate phenomenon, plant uptake and organic complexation of metals and some MIW parameters are included in this general process for simplicity of discussion.

Calcium Carbonate Alteration

The author suspected non-sulfate-reduction mechanisms were responsible for metal removal in one of two pilot scale BCR cells at the Brewer Mine which were described in Gusek (2000). Sulfate, calcium, and divalent metal mass balance calculations (unpublished) suggested that calcium present in the limestone portion of the BCR substrate was being displaced by some of the divalent metals present, including copper, iron, and zinc. This topic was addressed by Railsback (2010) who provides a thermodynamic stability/solubility plot of some carbonate minerals of divalent cations and an insightful discussion of the effects of atomic radii on this phenomenon. This topic is worthy of modeling investigations by geochemists followed by laboratory and field demonstrations.

An additional calcite/limestone alteration/replacement mechanism is discussed by Turner *et al.* (2005) for the sequestering of fluorine. Those authors note that some geochemical models (PHREEQ) are ill-equipped to handle this situation because both adsorption and precipitation mechanisms are involved. This process could be used in conjunction with anoxic limestone drains, limestone up-flow ponds, open limestone channels or limestone diversion wells. Equation 1 shows the alteration of calcite to the zinc carbonate mineral smithsonite in the presence of a neutral MIW containing dissolved zinc ions.

$$CaCO_{3} \text{ (calcite)} + Zn^{+2} \rightarrow$$
$$ZnCO_{3} \text{ (smithsonite)} + Ca^{+2} \tag{1}$$

A similar replacement reaction (equation 2) may be responsible for the alternation of calcite to the mineral fluorite.





Cd

TI Pb

1b Manganese Oxide Adsorption Tendencies



1c Calcium Replacement/Calcite Alteration

1d Carbon Adsorption/Complexation



Li

Be

92 U Column tests by Turner *et al.* (2008) suggest that pH control is essential for optimizing fluoride removal and that the effects of some interfering ions (*e.g.* sodium) appear to diminish with time. Also, increased partial pressure of CO_2 (1 atm) in the MIW (*e.g.* spent pot liner leachate from an aluminum smelting process) also improved the process efficiency. The results were supported by geochemical modeling (PHREEQ) and the process was considered appropriate for designing a permeable reactive barrier.

Periodic Table of Elements Review and Typical MIW Related Elements

Oriented horizontally, the PTE (Figs. 1a to 1d) is organized into seven periods or rows of elements and the Lanthanide and Actinide Series (omitted in Figs. 1a to 1d). Oriented vertically, there are 18 groups or columns of elements. The noble gases are found on the right side of the table; the hydrogen and the anions such as lithium, sodium, and potassium are found on the left side of the table. The elegance of this organization is that the elements of a single group tend to behave similarly in chemical reactions and that applies to behavior in passive treatment systems as well. Why this happens is typically not a concern to passive treatment system design engineers but the fact that it does may need to be more fully embraced.

Discussion

In Figs. 1a through 1d, tendencies of various elements associated with MIW to adsorb to, coprecipitate with, or complex with iron, manganese, calcium, and carbon are indicated by arrows. Due to space restrictions, it is not possible to address the many pre-conditions, interferences, adsorption sequences, that could be involved with these generalized relationships. Probably the most important precondition in most (but not all) adsorptive situations is circum-neutral pH. This is most certainly true in the case of manganese where the virtual absence of dissolved iron is an essential precondition. The partial pressure of carbon dioxide, P_{CO2}, and the presence of competing cations are important preconditions with respect to the kinetics and products of calcite replacement/alteration, respectively.

Due to space restrictions, specific references supporting the suspected or documented adsorptive relationships of selected MIW parameters are not included. The multiplicity of mechanisms for a given element suggests that competitive adsorption/replacement/alteration tendencies could make precise predictions with geochemical models difficult. This situation would be further compounded with potential interfering or enhancing conditions. Elevated P_{CO2} is one example of an enhancing condition with respect to limestone dissolution or alteration. Oxidation reduction potential (ORP) is another.

Turner et al. (2008) employed elevated P_{CO2} conditions in their work on fluoride removal. Sibrell et al. (2000) employed a similar strategy in enhancing the dissolution of limestone for generating alkalinity. It may be possible to take advantage of this phenomenon with respect to improving passive treatment system designs. Perhaps deep (>33 m) limestone diversion wells could be used to enhance the kinetics of carbonate replacement/alteration reactions at elevated P_{CO2} (P > \approx 3 atm). Maintaining these deep wells would involve periodically exhuming depleted limestone and replacing it with fresh material. Air lift pumping technology could be used to flushout depleted media. Industrial foams might also be considered for flushing and tremmie placement of fresh media (Masloff 2013).

Summary

The proposed revised Periodic Table of Passive Treatment (PT2) offers another view of the sometimes complicated picture of conflicting situations in treating MIW passively. This overview of a proposed revised PT2 should still be considered an intermediate point on the path to a more complete understanding of the complicated bio-geochemistry behind the passive treatment design process. It should be considered a logical expansion of the former USBM passive treatment decision tree and like Mendeleev's original work over 130 years ago, should be the focus of future enhancement, perhaps with the inclusion of interfering or enhancing conditions.

References

- Gusek JJ (2002) Sulfate-Reducing Bioreactor Design and Operating Issues: Is This the Passive Treatment Technology for Your Mine Drainage? presented at the National Association of Abandoned Mine Land Programs, Park City, Utah, September 15–18, 2002.
- Gusek JJ (2008) Passive Treatment 101: An Overview of the Technologies, presented at 2008 U.S. EPA/National Groundwater Association's Remediation of Abandoned Mine Lands Conference, Denver, CO, October 2–3, 2008.
- Gusek JJ (2009) Periodic Table of Passive Treatment. Paper was presented at the 2009 National Meeting of the American Society of Mining and Reclamation, Billings, MT. May 30 – June 5, 2009. RI Barnhisel (Ed) Published by ASMR, 3134 Montavesta Rd, Lexington, KY 40502.
- Railsback LB (2004) Accompanying text to An Earth Scientist's Periodic Table of the Elements and Their Ions: Geological Society of America Map and Chart Series 92, 7 p.
- Railsback LB (2010) Stability and solubility of carbonate minerals of divalent cations. Accessed from: www.gly.uga.edu/railsback/Fundamentals/Carb-MinsvRadii07.pdf March 2013.

- Robbins EI, DL Brant, Ziemkiewicz PF (1999) Microbial, Algal and Fungal Strategies for Manganese Oxidation at a Shade Township Coal Mine – Somerset County, Pennsylvania, presented at the 16th Annual Meeting of the ASSMR, Scottsdale, AZ, August 13–19, 1999.
- Sibrell, PL, BJ Watten, AE Friedrich, BJ Vinci (2000) ARD Remediation with Limestone in a CO₂ Pressurized Reactor. In Proceedings, 5th International Conference on Acid Rock Drainage, Society for Mining, Metallurgy, and Exploration, Denver, CO, pp 1017– 1026.
- Tebo B, MJR Bargar, BG Clement, GJ Dick, K Murray, D Parker, R Verity, SM Webb (2004) Biogenic Manganese Oxides: Properties and Mechanisms of Formation. Annu Rev Earth Planet Sci 32, p 287–328
- Tebo, B, M, HA Johnson, JK McCarthy AS Templeton (2005) Geomicrobiology of Manganese (II) Oxidation. Trends in Microbiology Vol 13 No 9 September 2005, p 421–428.
- Turner Brett D, P Binning, SLS Stipp (2005) Fluoride Removal by Calcite: Evidence for Fluorite Precipitation and Surface Adsorption. Environ Sci Technol 2005, 39, 9561–9568.
- Turner Brett D, PJ Binning, SW Sloan (2008) A calcite permeable reactive barrier for the remediation of Fluoride from spent potliner (SPL) contaminated groundwater. Journal of Contaminant Hydrology 95 (2008) 110–120.
- Wildeman TR, G Brodie, JJ Gusek (1993) Wetland Design for Mining Operations, BiTech Publishers, LTD, Richmond, BC, Canada, ISBN 0 021095 27 9.

Infiltration-Diverting Cap and Full-Scale Biochemical Reactor Operation at the Iron King/Copper Chief Mine, Arizona

James J. GUSEK¹, Ronald J. BUCHANAN, Jr.², Duff Sorells³

¹ Sovereign Consulting Inc., 5902 McIntyre Street, Golden, CO 80403 jgusek@sovcon.com
 ² Freeport-McMoRan Corporation, 333 N. Central Ave. Phoenix, AZ 85004 USA
 ³ Freeport-McMoRan Corporation, United Verde Branch, 300 Perkinsville Rd., Jerome, AZ 86331

Abstract A geomembrane and soil cap over a glory hole and a full-scale Passive Treatment System (PTS) including a biochemical reactor (BCR) were constructed at the Iron King/Copper Chief Mine near Cottonwood, Arizona, located on Mingus Mountain, as part of a voluntary remediation effort to mitigate mining influenced water (MIW) from two former, historic, underground copper mines. Construction of the glory hole area cap, designed to minimize or prevent rainfall and runoff infiltration into the underground mine workings, was completed in 2007. The borrow site that provided the earthen fill for cap construction created a bench for the subsequent construction of the PTS in the mountainous terrain.

Keywords ARD prevention, passive treatment, mining influenced water

Introduction

The Iron King/Copper Chief Mine (IK/CC) site is located in central Yavapai County, Arizona, approximately 6.5 km west of Cottonwood and 140 km north of Phoenix, Arizona, USA. Production from historic mining operations in the area began in 1904 and ended in 1945 (Clear Creek Associates 2001). There are two hydrologically distinct areas on the site: the Copper Chief/Upper Iron King (UIK), and the Lower Iron King (LIK; . Fig. 1). Three concrete bulkheads impound mining influenced water (MIW) from the two areas, creating two separate underground mine pools that exhibit different chemical characteristics.

Subsequent to the concrete bulkheads' installation, the MIW that was collected downgradient in the UIK and LIK was managed by pumping it back up to the glory hole (Fig. 1). The continued MIW management constituted



Fig. 1 Underground mine schematic cross section

a long-term maintenance issue and alternative remedies to pumping were considered. The passive treatment process was selected as the preferred alternative. Through the Voluntary Remediation Program (VRP), property owners investigate or clean up a contaminated site in cooperation with the Arizona Department of Environmental Quality (ADEQ). The VRP results in a streamlined process for program participants who work with a single point of contact at ADEQ to address applicable crossprogram remediation efforts. The ADEQ reviews these voluntary remedial actions and provides a closure document for successful site remediation that is accepted by all relevant ADEQ programs.

PTS construction commenced in the first quarter of 2009 and was concluded about 60 days later. The BCR design was based on the positive results of an in-field pilot study conducted in 2006. The BCR cell was configured as a top-fed vertical flow reactor; the feed to the system is commingled MIW from the two mines that is conveyed via a 500 m long subsurface pipeline. The BCR itself is also situated subsurface, with a lightweight fill cover consisting of plastic chambers and wood chips, a geomembrane liner, and topped off with 46 cm of plant growth medium which was hydroseeded. The BCR output reports to a small, concrete-lined mixing pond which feeds a multiterraced, aerobic polishing cell that is populated with native vegetation. The system was commissioned in mid-2009, is now fully functional and about three years of operational data has been collected, analyzed and will be related via this paper. Up to date operational data and the beneficial effects of the glory hole cover on mitigating MIW will be discussed.

Since March 2010, the PTS has operated in a "steady state" condition. This paper provides information on the glory hole cover and documents selected field and analytical data collected from the PTS as of the end of December 2012.

Glory hole cover objectives and description

Prior to construction of the glory hole cover, the IKCC site contained three principal MIW management-related features:

- Concrete bulkheads in the LIK adit, UIK adit, and the Copper Chief adit,
- Bulkhead seepage collection system located in the UIK adit with associated conveyance piping to the LIK adit pool, and
- LIK "primary" pump back system with associated piping to the glory hole.

The surface features of the glory hole area allowed rainfall and snowmelt to infiltrate into the UIK/Copper Chief mine workings. Subsidence cracks and surface depressions were also suspected of providing preferential pathways for rain water to percolate into the mine workings and recharge the UIK/Copper Chief mine pool, especially during the Arizona summer 'monsoon' season.



Fig.2 Glory hole construction photo (2007)

Fig. 3 Post-construction photo (2009)

Capping the glory hole area, sealing the mine subsidence features, and diverting runoff into natural drainages adjacent to the IK/CC site were obvious remedies to minimize the amount of MIW that the PTS would ultimately receive. While unable to prove in advance with any certainty, the glory hole area cover coupled with the cessation of pumping back bulkhead seepage might also result in improved MIW quality, especially in the UIK/Copper Chief mine pool.

A photo showing the geomembrane feature of the glory hole area cap under construction is provided in Fig. 2; a post-construction photo (2009) is provided in Fig. 3.

The key activities of the glory hole area cap and run-on diversion effort include:

- Placing native soil backfill to design subgrade (the borrow site for this material became the site for the subsequent construction of the PTS in 2009),
- Constructing diversion ditches above the highwall to divert run-on away from the o.8 ha capped zone,
- Placing 60 mm thick Linear Low Density Polyethylene (LLDPE) geomembrane (7,500 m²) sandwiched between protective geotextile,
- Rebuilding the glory hole for more easily receiving MIW pump-back from the LIK adit until the PTS was commissioned,
- Sealing the LLDPE to the power-washed rock face of the highwall with polyure-thane foam (PUF),
- Covering the geomembrane with: 12 in (25.2 cm) of native soil plant growth medium atop an identical thickness of borrow material fill (both harvested from the PTS/borrow site),
- PUF sealing of subsidence cracks,
- Re-grading surface depressions that could capture rainwater and enhance infiltration,
- Constructing geomembrane-lined diversion ditches across a secondary subsidence zone, and

 Implementing ancillary surface water drainage improvements (road culvert, riprap).

Passive treatment system objectives and description

The specific objectives of the PTS were to: remove target metals (*e.g.* iron, copper, zinc, cadmium, etc.) as sulfide precipitates, remove aluminum as a hydroxy-sulphate, remove sulfate by reduction to dissolved sulfide ion, add alkalinity to the MIW in the form of bicarbonate, precipitate manganese as an oxide (the common mineral pyrolusite [MnO₂]), and maintain the pH at a value of 6 or above.

The design of the PTS was based on the results from the bench-scale study, available site topography, and previous experience from other PTS design and construction projects. The PTS is designed to treat up to 26.5 L/min (7 gpm) of commingled MIW collected from both the UIK and LIK adits.

Prior to and during the PTS construction, MIW collected in both the UIK and LIK adits was pumped through a 76 mm (3 in) diameter HDPE pipeline to the existing glory hole that was rebuilt in conjunction with the glory hole area capping project in 2007.

In summary, the PTS consists of the following key components as shown schematically in Fig. 4:

- An underground "mixing and settling zone" inside the LIK adit,
- Buried pipelines to convey water (both treated and untreated) throughout the system year-round,
- A covered BCR, with cleanouts and sampling wells,
- A mixing pond, including a piping by-pass channel to prevent the possibility of embankment overtopping during a large rain event,
- A six-terraced aerobic polishing cell (APC) with irrigation water distribution and collection system, and



Fig. 4 Passive treatment system (PTS) schematic

• A storm water pond and associated storm water channel.

Details of the PTS design, construction, initial performance, and sampling point details are provided in Buchanan, *et al.* 2011.

Flow rate responses to rainfall

Estimating precise MIW flow data prior to the construction of the glory hole area cover was complicated by the pump back operations. However, site personnel recollections reflect a close and nearly instantaneous correlation of pumping effort in response to rainfall/ snowmelt. After the cessation of pump back operations and the draining of the IK/CC mine pools, flow rates were relatively steady at about 7.6 L/min (2 gpm). Interestingly, a 74 day dry interval in mid-2012 appeared to suppress the flow rate to the PTS to nearly zero. When the drought broke in mid-July 2012, the PTS influent flow rate response lagged the 47 mm (1.86 in) storm event by a week. However, the peak flow rate measured, 23.8 L/min (6.3 gpm), quickly declined to about a third of that value. The glory hole area cover and associated diversions appear to be functioning as intended from a physical perspective by moderating the flow volume requiring treatment.

Mine pool chemistry changes

Since the PTS commissioning, efforts to drain down the IK/CC MIW pools had been a project

priority to reach "steady state" operation. This condition was effectively achieved in the third and fourth quarters of 2010. It was interesting at the time to note that the MIW influent data for certain field parameters (pH and conductivity) improved in response to a decreasing contribution of Upper Iron King/Copper Chief MIW which had slowed to a relative trickle. This situation is also reflected in metals concentrations in PTS influent samples (collected every six months) as shown in Table 1.

Improvements in MIW influent chemistry are also attributable to source control measures (*e.g.* glory hole area cap, secondary subsidence zone sealing, and surface water diversion channels) that were implemented at the site in 2007 and the cessation of "primary" pump back activities to the glory hole as the PTS was commissioned. The metal contribution of UIK/Copper Chief MIW to the PTS influent did in fact decrease and the operational load on the BCR decreased as well. It is uncertain how the trend will continue as the iron and aluminum concentrations are negligible as of the end of 2012 and the PTS influent pH is 7.4.

Passive treatment system performance

The primary PTS performance parameters are those with typical elevated influent concentrations that contribute to mineral acidity; *i.e.* aluminum, iron, copper, zinc, cadmium, and manganese. Also included are sulfate and cal-

Parameter	Upper IK (Mar. '10)	Lower IK (Mar. '10)	Comb. UIK & LIK (Infl.) (Dec. '12)	BCR Effluent (Dec. '12)	APC (Terrace 1) (Dec. '12)
рН (—)	2.57	5.94	7.4	6.91	7.81
Aluminum	25.7	< 0.03	0.10	0.13	0.05
Iron	342	16.3	< 0.02	0.11	0.08
Copper	82.1	1.34	1.17	< 0.01	0.08
Zinc	96.4	15.4	14.0	< 0.01	0.58
Cadmium	0.22	0.077	0.047	< 0.005	< 0.005
Manganese	52.5	6.53	7.62	6.07	6.08
Calcium	465	253	287	326	287
Sulfate ¹	2600	890	1244	491	569

Table 1 Typical chemistry for primary parameters

¹Sulfate values are from March 2009 analyses (prior to PTS startup); units for ions in mg/L

cium as these parameters provide indicators relevant to the overall performance of the BCR portion of the PTS. Data listed in Table 1 reflect the MIW chemistries from the two mines in early 2010 (several months after start-up), the commingled PTS influent, and BCR effluent in December 2012.

pH improvements and metals removal in the PTS

Field pH values measured at the PTS influent, BCR effluent, and Irrigation Water observed on the APC terraces are shown on Fig. 5.

Data provided in Fig. 5 indicate that the PTS clearly improved the pH of the commingled UIK and LIK MIWs during the observation period. Also, the influent MIW chemistry appears to be improving. This improvement is visually evident at the PTS site in a v-notch weir that measures influent flow rate immediately up-gradient of the BCR. Staining on the weir has changed in appearance from a red, ironoxide dominated coloration to a turquoise color that is consistent with a lack of iron and/or aluminum and the continued presence of copper (Table 1).

Combined metal removal efficiencies for dissolved iron, aluminium, zinc, copper, and cadmium exhibited in the BCR have varied from 73 % to 97 % since start up; the average removal rate during the last two years of steady-state operation (five sampling events) has been 95.7 %. Recently, the decreasing presence of iron and aluminum in the influent has



Fig. 5 PTS pH data and trends

Wolkersdorfer, Brown & Figueroa (Editors)

resulted in a removal efficiency value of 93.1 % in the BCR which is representative of the combined removal of zinc, copper, and cadmium. Additional metal polishing also occurs in the APC feature of the PTS in the form of (oxidative) precipitated manganese (pyrolusite).

Sulfate removal in the BCR has been consistent since start-up. During the two years of steady- state operation, sulfate decreases of about 620 mg/L (ranging from 370 to 753 mg/L) have occurred in the BCR. Sulfate reduction rates were typically less than the benchmark 0.3 mol/d/m³ of substrate as cited by Wildeman *et al.* (1993). Sulfate reduction ranged from 0.08 to 0.04 mol/d/m³ during steady state operation. In comparison, metal loading during the same interval ranged from 0.05 to 0.0016 mol/d/m³; the lower value was derived from analytical data associated with the December 2012 sampling event.

BCR substrate longevity estimates

Organic carbon in the form of wood chips, sawdust and hay, and alkalinity in the form of limestone sand are the main consumable components of the BCR substrate. The carbon "reservoir" is estimated to be about 128t; the accompanying limestone mass is about 158t. Sulfate reduction rates and limestone dissolution rates (inferred from calcium concentration increases in the BCR effluent compared to the influent – Table 1) were used to estimate the longevity of the substrate with respect to carbon and alkalinity, respectively. Conservative estimates revealed that about 30 years of substrate functionality remain. The analysis further suggested that the carbon reservoir in the substrate will be depleted well before the limestone reservoir.

Performance summary

Key observations relative to PTS operation follow. Since start up in 2009 to December 2012:

• about 18,500 m³ (4.9 MUS.liq.gal) of MIW has been delivered to the PTS,

- dissolved removal efficiency of the BCR for the major MIW parameters (iron, aluminum, zinc, copper and cadmium, combined) ranged from about 73 % to 97 %,
- influent MIW pH improved from an initial value of about 2.5 to about 7.4, and
- during steady-state operation (Mar. '10 to Dec. '12), the PTS effluent chemistry exhibited only minor changes in response to improvements in the MIW influent chemistry, and
- during steady-state operation, APC samples exhibited a pH range of 7.0 to 8.0

Concluding remarks

The IK/CC PTS was completed under the ADEQ-VRP program in about six months at a cost of approximately \$US1.6 million. Since its commissioning three years ago, it has met expectations. Average analytical results indicate greater than 95 % attenuation of target metals under steady-state conditions. The sulfate reduction is consistent with metals loading and the design. The current estimated life cycle is about 30 years, which is about a decade longer than initial expectations. Generally, only routine maintenance has been required. With the improvement in MIW influent quality, previous influent pipeline scaling issues are expected to be minimal.

References

- Buchanan RJ Jr, Gusek JJ, Sorells D, Madden M (2011)
 Full-scale sulphate-reducing bioreactor at the Iron King/Copper Chief Mine, USA. In: Mine Closure 2011,
 Proceedings of the Sixth International Conference on Mine Closure, 18 – 21 September 2011, Lake Louise, Alberta, Canada.
- Clear Creek Associates (2001) Revised Work Plan, Iron King Dewatering and Treatment Project, dated June 20, 2001, Clear Creek Associates, Tucson, AZ.
- Wildeman TR, Brodie G, Gusek JJ (1993) Wetland Design for Mining Operations, BiTech Publishers, LTD, Richmond, BC, Canada, ISBN 0 021095 27 9.

Research on applicability of anaerobic passive bioreactor to acid mine drainage treatment in Japan

Takaya HAMAI, Takuya KODERA¹, Kousuke Такамото¹, Nobuyuki Masuda², Mikio Kobayashi³, Hajime Ikeda³, Takeshi Sakata³, Masatoshi Sakoda³, Hidekatsu Nakamura³, Hisatoshi Furuya³, Kazuya Sunada³, Manami Ikeda³, Takao Miura³

¹Metals Technology Center, Japan Oil, Gas and Metals National Corporation, Furudate 9–3, Kosakakouzan, Kosaka, Akita, Japan, furuya-hisatoshi@jogmec.go.jp ²International Center for Research and Education of Mineral and Energy Resources, Akita University, 1—1, Tegata Gakuen-cho Akita City ³Metals Environment Management Department, Japan Oil, Gas and Metals National Corporation, Toranomon 2-10-1, Minato-ku, Tokyo, Japan

Abstract In past experiments, the applicability of the treatment system for mine drainage with the anaerobic bioreactor containing rice husk and composted bark with cow manure was investigated. This time, the relationship between a metal removal process and ORP was figured out and moreover, it is cleared that anaerobic passive treatment for mine drainage can operate at lower cost using cheaper contents in bioreactors.

Keywords passive treatment, sulfate-reducing bacteria, anaerobic bioreactor, rice husk

Introduction

Passive treatment system which uses natural purification processes has attracted a lot of attention as a low cost and maintenance mine drainage treatment technology, and many research results of verification tests on the passive system have been reported mainly in the United States and Europe (e.g. Gusek et al. 1998, Younger et al. 2003). In Japan, however, no passive treatment system is actually introduced. All mine drainage treatment plants use active systems where neutralizer, electricity and daily maintenance are required. However, recently, from the viewpoint of cost reduction for the mine drainage treatment, the research on the applicability of passive treatment system in some domestic abandoned metal mine sites has been started by Japan Oil, Gas and Metals National Corporation.

In this research, some fundamental tests were carried out in order to design the treatment system with anaerobic bioreactors. In the bioreactor containing sulfate reducing bacteria (SRB), dissolved metal ions are capably removed as metal sulfides because sulfide is more insoluble compared with hydroxide.

We have succeeded to continuously treat the neutral pH mine drainage for over 800 days under the appropriate condition, water retention time for 50 hours and water temperature of over 15 °C, using the bioreactors filled with rice husk and composted bark with cow manure. Similar application has been experimentally and successfully utilized for the continuous treatment of acid mine drainage for over 500 days(Furuya *et al.* 2012).

As described above, It has been found that the passive treatment system using anaerobic bioreactor can be applied to mine drainage at various pH levels, although it is essential to further understand the detailed reaction mechanism for the design of the actual equipment.

This paper shows the relationship between oxidation-reduction potential (ORP) and metal ions removal phenomena in the reactor. Moreover, in order to reduce the material cost of anaerobic treatment system, the applicability of cheaper organic material for SRB has been investigated.

Methods

Mine drainage

The mine drainage for the continuous test was sampled at the abandoned mine in Akita prefecture located in the northern part of Japan. The concentrations of zinc, copper and iron in the drainage are shown in Table 1. The values exceed the national effluent standard, and so, the drainage has been selected as the sample in this investigation.

Apparatus

A schematic diagarm layout of the continuous experimental apparatus with the anaerobic column is shown in Fig. 1. The diameter and height of column is 10 cm and 45 cm, respectively, and 5 intake holes (numbered as 1st, 2nd, 3rd, 4th, and 5th from upper side to lower side in order) are equipped in the wall of the column. The column was filled with rice husk and com-

posted bark with cow manure as organic carbon resources for SRB and other microorganisms. These materials were found to be effective as organic carbon resources for the related microbes in the previous research (Furuya *et al.* 2011). Granular silicates and lime stones (diameter : $5 \approx 10$ mm) were utilized to maintain the inner structure of the reactor and to control pH respectively. The volume and weight fractions of each component in the bioreactor are shown in Table 2.

Process

The column was filled with the mixture of carbon resources and the mine drainage to the height of 40 cm. The contained SRB was incubated for 3 weeks in the mine drainage. SRB was supplied from the rice husk and composed bark with cow manure and no other bacteria source was added to the system. After then, the mine drainage was pumped up and introduced to pass the column from the top to the bottom with gravity flow. The hydraulic re-

	pН	Zn (mg/L)	Cu (mg/L)	Fe (mg/L)	SO ₄ ²⁻ (mg/L)
Mine drainage (min-max)	3.3-3.8	15—18	3—10	33—38	350—400
National effluent standard	5.8-8.6	2.0	3.0	10	



Table 1 Water quality of the mine drainage and the national effluent standard values.

"Reliable Mine Water Technology"

Rice husk	Composted bark with cow manure	
99.7	0.3	
95.0	5.0	
Crushed silica stone	lime stone	Table 2 Composition of mix
1050	300	ture in the hioreactor

tention time was 50 hours, which was calculated from the void volume, and the flow rate was 60 mL/h. The treated water was discharged from the silicone tube which extended from the bottom to a static water surface level.

Results and discussion

Relationship of ORP and metal removal

Before starting the treatment test, while SRB was incubated, the inside of the column was reductive. The upper part of the column subsequently changed into an oxidative condition in a week after starting to introduce the raw water, the sampled mine drainage (Fig. 2(a)). This could be mainly caused by the introduction of the raw water of which ORP was $400 \approx 500 \text{ mV}$ and the fast oxidation of ferrous ions by ironoxidizing bacteria at the upper part of the column. Although the upper part rapidly became oxidative as mentioned above, the lower part maintained the reductive condition with ORP of -100 \approx -200 mV for over 100 days. The pH of the lower part was kept at $6 \approx 7$. Therefore, the activity of SRB could be allowed long-term.

It was observed throughout the monitoring period that sulfate ions drastically decreased at the upper part of the column, 350 mg/L to 300 mg/L, and at the lower part, 280 mg/L to 220 mg/L (Fig. 2(b)). The first decrease at the upper part could not be mainly caused by sulfate reduction by SRB because the upper part of the column was in the oxidative condition. It could be possibly caused by sorption to lime stones and organic materials. However, the drastic decrease of sulfate ions at the lower part of the column could be probably considered to be caused by the sulfate reduction by SRB. Dissolved metal ions, especially zinc ions, drastically decreased from the middle part toward the lower part (Fig.2(c)). This result is well correlated with changes in the oxidation-reduction condition in the column. Zinc ions drastically decreased at reductive area where the activity of SRB was promoted, suggesting that most zinc ions passed through oxidative area without any chemical reaction and then zinc ions reacted with sulfide ions which were generated through sulfate ions reduction by SRB in the reduction condition, and finally removed as Zn sulfides. This was also correlated with the decrease of sulfate ions.

Sulfide ions were continuously detected from the outflow water. They were assumed to be generated by SRB, and surplus for the formation of metal sulfide. Removal of dissolved zinc ions continuously occurred even when almost all area of the column except for the lowermost part became oxidative. However, the concentration of total-zinc in the outflow water started to increase from around 100 days after the start of itroduction to the column, and exceeded the national effulent standards (2 mg/L) after 130 days.

Ferrous ions were removed through two-step process. Fig.2(d) shows that most of ferrous ions were removed at the upper part and the remaining portion were removed at the lower part. The first step removal, from the input to the 1st intake hole, was assumed to be oxidated by iron-oxidizing bacteria and removed as precipitates of ferric hydroxide. As the second step, from 4th to 5th, the remaining ferrous ions were supposed to be removed as ferrous sulfide.

Influence of leaking out of precipitates from the column

As described above, the concentration of totalzinc in the outflow water exceeded the national effulent standard 130 days after starting the introduction to the column(Fig.2(e)). However, the concentration of zinc ion became under the effulent standards after the filtration of the outflow water with 0.45 µm filter. This result was explained by suggesting that fine zinc sulfide precipitates were flowed out as a suspention form. composted bark with cow manure and rice husk were utilized as the source of SRB and orgnic carbon resource for SRB. Rice husk is a common agricultural waste in Japan and it is easily available without cost. However, composted bark is a little costly. Since the real operation of mine drainage treatment needs a large amount of composted bark, high initial cost would be problematic.

Therefore, in order to reduce the material cost, the applicability of the soil which is available from mine sites as an alternative for composted bark was investigated.

The investigation of cost reduction

So far, in the continuous treatment tests, the

Two polyethylene bottles were filled with 15 g rice husk, 15 g Lime stones, and 150 mL of



Fig. 2 Water quality changes in the column

the mine drainage containing sulfate ion. And then 1 g composted bark, or soil sampled from the mine site was added respectively. The ORP and the sulfate ions concentration of the solution in both bottles were regularly measured during the incbation.

As a result, both solutions almost became to be reductive conditions in around a same time (Fig.3(a)), and after 12days of incbation, the concentration of sulfate ion was also similar between both solutions (Fig.3(b)). This shows that the soil sampled from the mine site has the same effect as composted bark. Therefore, it would be probably expected that anaerobic passive treatment for mine drainage could operate with lower cost by using cheaper contents such as the soil at the mine site for bioreactors.

Conclusions

The correlation between the metal removal efficiency and the oxidation-reduction potential in the column was successfully evaluated. In fact, dissolved metal ions, especially zinc ions, reacted with sulfide ions which were generated through reduction of sulfate ions by SRB in the reduction condition. Moreover, the treatment of the acid mine drainage could be continued for 130 days. These results suggest the applicability of this system on acid mine drainage. Although leak-out of zinc sulfide precipitate was observed, the phenomena could be prevented by improving the stracture of the bioreactor. In addition, the experimental results showed that the appropriate soil at mine sites had almost same capability as composted bark. Therefore, it is expected that anaerobic passive treatment for mine drainage can operate with lower cost by using cheaper contents for the bioreactors.

References

- Furuya, H., Kodera, T., Takamoto, K., Masuda, N., Kobayashi, M., Osame, A., Asano, H., Sakata, T., Nakamura, H.,Okumura, Takahashi, T., Sunada, K., Manami, I. (2011) Research on applicability of anaerobic passive bioreactor to acid mine drainage treatment in Japan. Full Paper of International Mine Water Association Symposium (IMWA 2012) 30 Sep -4 Oct 2012, Bunbury Western Australia
- Furuya, H., Kodera, T., Sato, N., Masuda, N., Kobayashi, M., Osame, A., Asano, H., Takamoto, K., Nakamura, H., Okumura, M., Kurosaka, A., Takahashi, T., Sunada, K. (2011) On-site mine drainage treatment utilizing the passive bioreactor. Proceedings of 2nd international seminar on environmental issues in the mining industry (Enviromine 2011) 23–25 November 2011, Santiago, Chile, pp 92–93
- Gusek, J. J., T. R. Wildeman, A. Miller, J. Fricke, (1998) The challenges of designing, permitting, and building a 1,200 gpm passive bioreactor for metal mine drainage, West Fork, Missouri. Proceedings of 15th Annual Meeting of American Society for Surface Mining and Reclamation, 17–22 May 1998, St. Louis, MO, 203–212



Fig. 3 Comparing of capability between composted bark and soil

Younger, P.L., Jayaweera, A., Elliot, A., Wood, R., Amos, P., Daugherty, A.J., Martin, A., Bowden, L., Aplin, A.C.; Johnson, D.B. (2003) Passive treatment of acidic mine waters in subsurface-flow systems: exploring RAPS and permeable reactive barriers. Land Contamination & Reclamation 11(2): 127–135

Strategies for enhancing carbon sequestration in Mg-rich mine tailings

Anna L. HARRISON, Ian M. POWER, Gregory M. DIPPLE

Mineral Deposit Research Unit, Department of Earth, Ocean and Atmospheric Sciences, The University of British Columbia, 2207 Main Mall, Vancouver, British Columbia V6T 1Z4, Canada, ALH – aharriso@eos.ubc.ca; IMP – ipower@eos.ubc.ca; GMD – gdipple@eos.ubc.ca.

Abstract Mineralization of CO₂ within Mg-carbonate minerals in Mg-rich mine tailings provides the potential to render large mines greenhouse gas neutral. A potential strategy to enhance carbon fixation rates is through injection of CO₂-rich gas into tailings. Carbonation rates and CO₂ storage capacity must be sufficient to minimize CO₂ leakage to the atmosphere. Experimental carbonation rates of one tailings mineral, brucite, suggest that its carbonation can keep pace with mine emissions and that total carbon fixation rates are limited by tailings production. Because power consumption scales with tailings production, brucite contents of \approx 6.5 % are needed to offset point source mine emissions.

Keywords CO₂ sequestration, mine tailings, carbonate precipitation, tailings management strategies, carbon mineralization

Introduction

Anthropogenic greenhouse gas (GHG) emissions, particularly CO₂ emissions, have been identified as a cause of global climate change (IPCC 2007). Carbon sequestration is one of many potential strategies to stabilize CO₂ concentrations and prevent irreversible climate change while we transition to non-fossil fuel based energy sources (Broecker 2007; Pacala and Socolow 2004). Mineral carbonation. or carbon mineralization, is a method of carbon sequestration that involves dissolution of non-carbonate minerals (e.g. silicates, hydroxides, and oxides) to release cations, and the binding of these cations with CO₂ in carbonate minerals (Lackner 2003; Lackner et al. 1997, 1995; Seifritz 1990). Many industrial wastes, including mine tailings, are rich in minerals that provide suitable feedstock for mineral carbonation such as brucite [Mg(OH)₂], forsterite [Mg₂SiO₄], and serpentine group minerals [Mg₃Si₂O₅(OH)₄] (e.q. Bobicki et al. 2012: Renforth et al. 2011: Wilson et al. 2009). Carbonation of industrial wastes is advantageous as it exploits available waste materials that are typically fairly reactive under ambient

conditions, and it may decrease the hazardous nature of wastes such as asbestos mine tailings (e.g. Bobicki et al. 2012; Renforth et al. 2011). Carbon mineralization in mine wastes has been documented to occur passively under normal mining practices at both historic and active asbestos, diamond, chromite, and nickel mines globally (Bea et al. 2012; Beinlich and Austrheim 2012; Pronost et al. 2012; Wilson et al. 2011, 2010, 2009, 2006). Carbonation reactions are facilitated by high surface areas (Wilson et al. 2009), yet are limited by the uptake of CO_2 into solution (Wilson *et al.* 2010). Although the carbon sequestration capacity of ultramafic tailings is significant, rates of passive carbonation are insufficient to take full advantage of the carbon sequestration potential. For instance, complete carbonation of tailings produced annually at the Mount Keith Nickel mine (MKM) in Australia (≈11 Mt tailings per year; BHP Billiton 2005) would exceed annual mine emissions by more than a factor of ten. Yet passive carbonation rates currently offset annual emissions by only ≈15 % (Wilson 2009). Carbon mineralization in mine tailings could be accelerated by

increasing the exposure of tailings to CO_2 , such as by injection of CO₂-rich gas streams into tailings storage facilities. Here, we generalize the experimental results from our previous work (Harrison et al. 2013) investigating the potential for accelerated carbonation of brucite, a common and highly reactive tailings mineral, to evaluate CO₂ injection as a carbon sequestration strategy in mine tailings. Brucite is a Mg-hydroxide mineral that is typically present between 1 and 15 wt. % in ultramafic mine tailings and residues (Bea et al. 2012; Chrysochoou et al. 2009; Pronost et al. 2011). It is far more reactive than the more abundant silicate phases such as serpentine (e.g. Assima et al. 2013; Bales and Morgan 1985), and therefore provides a useful starting point for investigation of accelerated tailings carbonation strategies.

Methods

The effects of supplying CO₂-rich gas streams at ambient temperature and pressure (≈ 21 °C; 1 atm) on the carbonation rate of brucite was investigated experimentally in batch reactors, with geochemical conditions emulating those at MKM. Alkaline 3.0 L slurries containing 150 g brucite were supplied with gas streams with a range of CO_2 content (≈ 0.04 %, 10 %, 50 %, 100 % CO₂ by volume) at a rate of ≈ 270 mL/min (Harrison et al. 2013). Slurry samples were extracted periodically for measurement of pH, the stable carbon isotopic composition $(\delta^{13}C)$ of dissolved inorganic carbon (DIC), and cation and DIC concentrations. Solid samples were collected for measurement of mineralogical compositions and δ^{13} C. For further details regarding the experimental setup, refer to Harrison et al. (2013).

Results and Discussion

The experimental results indicated that brucite (brc) was carbonated to produce the hydrated Mg-carbonate mineral nesquehonite [MgCO₃·3H₂O] at a rate that increased linearly with CO₂ partial pressure (pCO₂) according to the following reaction (Harrison *et al.* 2013):

$$\begin{array}{l} Mg(OH)_{2(s)} + HCO_{3}^{-}(aq) + H^{+}(aq) + \\ H_{2}O_{(l)} \longleftrightarrow MgCO_{3} \cdot 3H_{2}O_{(s)} \quad (Eq. 1) \end{array}$$

A 2400-fold increase in CO₂ sequestration rate was achieved with an increase from atmospheric composition ($\approx 0.04 \% CO_2$) to pure CO_2 . Increasing the pCO_2 serves to enhance both brucite dissolution and carbonate precipitation. However, even at elevated pCO_2 the rate of CO₂ uptake into solution was found to be rate limiting. This is attributed to the relatively slow transformation from gaseous CO₂ to an aqueous form that can be mineralized (*i.e.* HCO_3^- and CO_3^{2-}) as indicated by chemical and isotopic disequilibrium between gaseous CO₂ and DIC during the carbonation reaction (Harrison et al. 2013). Nevertheless, the experimental carbonation rates would be sufficient to carbonate all the brucite produced annually at MKM (0.1-0.3 Mt brucite), offsetting total mine emissions by 20-60 % (Harrison et al. 2013). Therefore, accelerated carbonation of tailings minerals by supplying CO₂-rich gas streams is a promising method for reducing GHG emissions at mine sites with tailings that contain brucite. Power generation at mine sites often occurs at on-site power plants, which could provide a local point source of CO₂ emissions. Flue gas from power plants typically contains between 10-20 % CO₂ (Kikkinides et al. 1993; Uibu et al. 2011). These emissions provide a readily available source of CO₂-rich gas that could be injected into tailings storage facilities to accelerate brucite carbonation (Harrison et al. 2013). An alternative would be to circulate CO2-rich water, which could help to avoid the issue of slow CO₂ uptake into solution. However, the use of CO₂rich gas has the advantage that it would not increase the water consumption at mine sites, which can be an important concern particularly for mines in arid locations with high evaporative losses. A potential concern regarding CO_2 injection is its effect on the mobility of hazardous metals. Metals could be mobilized via dissolution of primary tailings minerals, yet secondary precipitates can incorporate these metals and limit their mobility depending on solution pH (Power *et al.* 2010). Therefore, further investigation is warranted to determine the potential side effects of CO₂ injection on tailings geochemistry.

If brucite carbonation via CO₂-rich gas injection were implemented at a mine site, tailings storage facilities would need to be designed to minimize leakage of injected CO₂ to the atmosphere. This requires that the rate of carbon mineralization in the tailings keep pace with the rate of CO₂ supply. The rate of CO₂ injection will be limited by the availability of the highly reactive phases such as brucite, as these will consume the majority of the CO₂ in the short term. Greater brucite content will accommodate higher injection rates, as well as provide greater total sequestration capacity. The sequestration or 'reactive capacity' (Eq. 2) of brucite is calculated by assuming complete conversion to nesquehonite; this equates to 0.75 g CO₂ stored per gram brucite. In order to prevent CO₂ leakage, the rate of CO₂ supply must not exceed the reactive capacity at any given time, and should therefore balance the rate of brucite deposition according to the reaction stoichiometry.

The rates achieved in the brucite carbonation experiments employing 10 % CO₂ were considered representative of reaction in mine tailings. The predicted brucite carbonation rate using flue gas is thus $\approx 0.3 \text{ mol CO}_2/\text{m}^2$ brc/a (after Harrison et al. 2013). Due to the relatively high reactivity of brucite, it is assumed that the rate of CO₂ mineralization is dictated primarily by the brucite carbonation rate rather than carbonation of the less reactive silicates. The reactive capacity provided by brucite and the time before CO₂ venting at a given CO₂ injection rate can then be calculated according to Equations 2 and 3. Carbonation rates in the field will be affected by water content distribution (e.g. Assima et al. 2013), surface passivation effects (e.g. Jeen et al. 2006), and the hydraulic properties of the porous medium. Quantification of the extent to which these effects will alter carbonation rates requires further experimentation. As such, for the purposes of this study, it is assumed that CO_2 supply is the primary rate-limiting factor; therefore Equation 3 applies only when the maximum rate of carbonation (Eq. 4) is less than the rate of CO_2 supply.

Reactive capacity
$$(C_r) = \frac{m_t F_{brc}}{GFW_{brc}}b$$
 (Eq. 2)

Time to
$$CO_2$$
 venting $= \frac{C_r}{r_{CO_2}}$ (Eq. 3)

Maximum brucite carbonation rate = $m_t F_{brc} S_{brc} r_{brc}$ (Eq. 4)

Where, C_r is the reactive capacity (mol CO₂), m_t is the mass of tailings (g), F_{brc} is the brucite content of the tailings as a fraction of tailings mass, b is a stoichiometric coefficient for the carbonation of brucite, GFW_{brc} is the molar mass of brucite (g/mol), r_{CO2} is the rate of CO₂ supply (mol CO₂/a), S_{brc} is the surface area of brucite (m²/g), and r_{brc} is the 'flue gas' rate of brucite carbonation measured in batch reactors (mol CO₂/m² brc/a).

At MKM, approximately 0.5 m of tailings are deposited annually, assuming they are evenly distributed across the $\approx 16.6 \text{ km}^2$ tailings storage facility, with historic tailings reaching depths of up to \approx 19 m (after Wilson 2009). The total annual CO₂ equivalent emissions at MKM are reported to be 0.37 Mt CO₂ (BHP Billiton 2005). GHG emissions from mining operations are typically divided between fossil fuel combustion from distributed sources like trucks and mining equipment, and emissions from electricity generation. It is estimated that ≈ 64 % of emissions are from electricity generation, and \approx 36 % are from distributed sources (USEPA 2008). This suggests that at MKM, approximately 0.24 Mt CO₂/year is produced from point sources. If CO₂ were injected at a rate equal to the rate of point source CO_2 emissions ($\approx 328 \text{ mol } CO_2/\text{year}/\text{m}^2$ tailings; after BHP Billiton 2005), current brucite production rates are nearly sufficient to offset point source CO₂ emissions (fig. 1A). Higher injection rates could be initially applied to carbonate historic tailings. For instance, it would



Fig. 1 Time to CO_2 venting versus tailings deposition rate (A) and historic tailings depth (B) at various brucite contents with a CO_2 injection rate equal to the estimated rate of point source CO_2 emissions at the Mount Keith Nickel mine ($\approx 238 \text{ mol } CO_2/\text{year}/\text{m}^2$ tailings; after BHP Billiton 2005). Shaded areas indicate range of brucite content and tailings depth and deposition rate applicable to the Mount Keith Nickel mine.

take up to 20 years for CO_2 to vent from the deepest tailings at MKM at this CO_2 injection rate (fig. 1B). For highly reactive minerals like brucite, the reactive capacity rather than the mineral carbonation rate will likely limit the maximum CO_2 injection rate.

At mines with high tailings production rates that produce power on-site, such as MKM, it is estimated that a minimum brucite content in tailings of ≈ 3 wt. % would be required to offset point source mine emissions, or ≈ 64 % of total emissions, if brucite is the primary sink for CO₂ (figs. 1A and 2). Smaller 'off-grid' mines produce greater CO₂ emissions per tonne of tailings produced, and would require in excess of 6.5 wt. % brucite to offset estimated point source emissions (fig.2). Regardless of electricity source or mine size, accelerated carbonation of even minor amounts of brucite (e.g. 2.5 wt. %) could provide >4-fold acceleration over passive carbonation rates (fig. 2). In the case of a carbon tax or cap-and-trade system, offsetting GHG emissions would be financially beneficial for mining companies. Economically marginal deposits that possess significant carbon capture potential, such as high brucite content, may therefore become financially viable (*e.g.* Bobicki *et al.* 2012).

Although accelerated brucite carbonation would provide significant offsets of mine emissions, in order to take full advantage of the sequestration capacity offered by mine tailings, Mg-silicate carbonation must also be enhanced (fig. 2). Passive carbonation of serpentine has been documented in tailings with and without brucite (Wilson 2009; Wilson et al. 2006, 2009). This demonstrates that despite being less reactive than brucite, Mg-silicate carbonation is possible in a tailings environment. Injection of CO₂-rich gas into tailings will not only exploit the sequestration potential of brucite, but may also help carbonate the more abundant Mg-silicates. Due to the lower reactivity of Mg-silicates in comparison to brucite, more aggressive methods are often employed in mineral carbonation processes to accelerate dissolution, such as the use of strong acids (e.g. Alexander et al. 2007). Hence, it is unlikely that injection of CO₂-rich gas alone will allow sufficient acceleration of Mgsilicate carbonation to take full advantage of



Fig. 2 Comparison of range of passive annual carbonation rates at Diavik Diamond Mine, Northwest Territories, Canada, Clinton Creek Chrysotile mine, Yukon, Canada, and the Mount Keith Nickel Mine (MKM), Western Australia (circles) with annual GHG emissions at mine sites of various size and power sources (stars). Open and filled stars represent estimated point source and total CO₂-equivalent emissions, respectively. Total reactive capacity including Mg-silicate carbonation is indicated by the black vertical dashed-dot line. The reactive capacity per tonne tailings based on brucite carbonation alone at

various brucite contents is indicated by the grey vertical dashed lines at 2 wt. % brucite intervals (modified after Harrison et al. 2013).

the CO₂ sequestration potential. As research to enhance Mg-silicate carbonation continues, deployment of accelerated brucite carbonation strategies in the interim will help guide the development of Mg-silicate carbonation techniques for mine tailings, while providing an immediate and significant GHG benefit.

Conclusions

Experimental results indicate that passive rates of carbonation could theoretically be accelerated to offset \approx 20-60 % of total CO₂ emissions at the Mount Keith Nickel Mine in Australia. This could be achieved via injection of CO₂-rich gas into tailings, such as flue gas from mine site power plants, to completely carbonate brucite and partially carbonate Mg-sili-

cates. Mines that contain >6.5 wt. % brucite in their tailings may have the potential to completely offset point source CO₂ emissions via brucite carbonation alone. Carbonation of the more abundant Mg-silicates could capture >10-fold the scale of mine emissions at a large mine such as MKM. Deployment of accelerated brucite carbonation strategies would offer a first step towards the development of methods that take advantage of the total CO₂ sequestration capacity of mine tailings, while providing an immediate GHG benefit.

Acknowledgements

This research was funded by grants held by GMD from the Carbon Management Canada National Centre of Excellence and the Natural Sciences and Engineering Research Council of Canada (NSERC). IMP was funded by an NSERC Postdoctoral Fellowship. ALH was funded by a University of British Columbia Four Year Fellowship.

References

- Alexander G, Maroto-Valer MM, Gafarova-Aksoy P (2007) Evaluation of reaction variables in the dissolution of serpentine for mineral carbonation. Fuel 86:273–281
- Assima GP, Larachi F, Beaudoin G, Molson J (2013) Dynamics of carbon dioxide uptake in chrysotile mining residues – Effect of mineralogy and liquid saturation. Int J Greenhouse Gas Control 12:124–135
- Bales RC, Morgan JJ (1985) Dissolution kinetics of chrysotile at pH 7 to 10. Geochim Cosmochim Acta 49:2281–2288
- Bea SA, Wilson SA, Mayer KU, Dipple GM, Power IM, Gamazo P (2012) Reactive transport modeling of natural carbon sequestration in ultramafic mine tailings. Vadose Zone J 11
- Beinlich A, Austrheim H (2012) In situ sequestration of atmospheric CO_2 at low temperature and surface cracking of serpentinized peridotite in mine shafts. Chem Geol 332-333:32–44
- BHP Billiton (2005) Mt Keith Nickel Operations: Environmental Data. BHP Billiton Sustainability Reports, BHP Billiton, http://hsecreport.bhpbillton. com/wmc/2004/performance/mko/data

- Bobicki ER, Liu Q, Xu Z, Zeng H (2012) Carbon capture and storage using alkaline industrial wastes. Prog Energy Combust Sci 38:302–320
- Broecker WS (2007) CO2 Arithmetic. Science 315:1371
- Chrysochoou M, Fakra SC, Marcus MA, Moon DH, Dermatas D (2009) Microstructural analyses of Cr(VI) speciation in chromite ore processing residue (COPR). Environ Sci Technol 43:5461–5466
- Harrison AL, Power IM, Dipple GM (2013) Accelerated carbonation of brucite in mine tailings for carbon sequestration. Environ Sci Technol 47:126–134
- IPCC (2007) IPCC Climate Change 2007: Synthesis Report, An Assessment of the Intergovernmental Panel on Climate Change, www.ipcc.ch/pdf/assessment-report/ar4/syr/ar4_syr.pdf
- Jeen S-W, Gillham RW, Blowes DW (2006) Effects of carbonate precipitates on long-term performance of granular iron for reductive dechlorination of TCE. Environ Sci Technol 40:6432–6437
- Kikkinides ES, Yang RT, Cho SH (1993) Concentration and recovery of CO₂ from flue gas by pressure swing adsorption. Ind Eng Chem Res 32:2714–2720
- Lackner KS (2003) A Guide to CO₂ Sequestration. Science 300:1677–1678
- Lackner KS, Butt DP, Wendt CH (1997) Progress on binding CO₂ in mineral substrates. Energy Convers Manage 38:S259–S264
- Lackner KS, Wendt CH, Butt DP, Joyce EL, Sharp DH (1995) Carbon dioxide disposal in carbonate minerals. Energy 20:1153–1170
- Pacala S, Socolow R (2004) Stabilization wedges: Solving the climate problem for the next 50 years with current technologies. Science 305:968–972
- Power IM, Dipple GM, Southam G (2010) Bioleaching of ultramafic tailings by Acidithiobacillus spp. for CO₂ sequestration. Environ Sci Technol 44:456–462
- Pronost J, Beaudoin G, Lemieux J-M, Hebert R, Constantin M, Marcouiller S, Klein M, Duchesne J, Molson JW, Larachi F, Maldague X (2012) CO₂-depleted warm air venting from chrysotile milling waste (Thetford Mines, Canada): Evidence for in-situ carbon capture from the atmosphere. Geology 40:275–278

- Pronost J, Beaudoin G, Tremblay J, Constantin M (2011) Carbon sequestration kinetic and storage capacity of ultramafic mining waste. Environ Sci Technol 45:9413–9420
- Renforth P, Washbourne C-L, Taylder J, Manning DAC (2011) Silicate production and availability for mineral carbonation. Environ Sci Technol 45:2035–2041
- Seifritz W (1990) CO_2 disposal by means of silicates. Nature 345:486
- Uibu M, Kuusik R, Andreas L, Kirsimäe K (2011) The CO₂binding by Ca-Mg-silicates in direct aqueous carbonation of oil shale ash and steel slag. Energy Procedia 4:925–932
- USEPA (2008) Quantifying greenhouse gas emissions from key industrial sectors in the United States. http://www.epa.gov/sectors/pdf/greenhouse-report.pdf
- Wilson SA (2009) Mineral traps for greenhouse gases in mine tailings: A protocol for verifying and quantifying CO₂ sequestration in ultramafic mines. PhD Dissertation, The University of British Columbia, Vancouver, British Columbia
- Wilson SA, Barker SLL, Dipple GM, Atudorei V (2010) Isotopic disequilibrium during uptake of atmospheric CO_2 into mine process waters: Implications for CO_2 sequestration. Environ Sci Technol 44:9522– 9529
- Wilson SA, Dipple GM, Power IM, Barker SLL, Fallon SJ, Southam G (2011) Subarctic weathering of mineral wastes provides a sink for atmospheric CO₂. Environ Sci Technol 45:7727–7736
- Wilson SA, Dipple GM, Power IM, Thom JM, Anderson RG, Raudsepp M, Gabites JE, Southam G (2009) Carbon dioxide fixation within mine wastes of ultramafic-hosted ore deposits: Examples from the Clinton Creek and Cassiar chrysotile deposits, Canada. Econ Geol 104:95–112
- Wilson SA, Raudsepp M, Dipple GM (2006) Verifying and quantifying carbon fixation in minerals from serpentine-rich mine tailings using the Rietveld method with X-ray powder diffraction data. Am Mineral 91:1331–1341

Temperature Independent Removal of Iron in a Passive Mine Water System

Robert S. Hedin

Hedin Environmental, 195 Castle Shannon Blvd, Pittsburgh, PA 15228, USA, bhedin@hedinenv.com

Abstract The Marchand passive system treats a 7.1 m³/min flow of coal mine drainage containing 72 mg/L Fe to a final effluent with 1 mg/L. Fe removal in this aerobic system is by oxidative mechanisms. The system has not displayed a significant seasonality in effectiveness, despite kinetic considerations that indicate that iron oxidation should differ by an order magnitude between cold and warm periods. Year-round sampling of the treatment ponds revealed a negative correlation between water temperature and pH. Because pH has a positive influence on Fe²⁺ oxidation, this offsets the negative influence of kinetics. The results demonstrate the complexity of iron chemistry in passive treatment systems and caution against their modeling with static chemical assumptions.

Keywords IMWA 2013, passive treatment, iron oxidation, coal mine drainage

Introduction

The treatment of mine water containing elevated ferrous iron (Fe²⁺) requires oxidation of Fe²⁺ to Fe³⁺ and settling of the ferric oxyhydroxide solids. In passive systems the oxidation is usually considered the rate-limiting step (Dempsey et al. 2001). The kinetics of the oxidation are strongly affected by temperature. In climates where air temperatures vary widely, Arrhenius-based calculations indicate that oxidation kinetics will vary tenfold between cold and warm seasons (Stumm and Morgan 1996). This kinetic penalty would make passive treatment impractical in northern latitude temperate climates where stringent effluent limit must be satisfied. In reality, such severe seasonal variation is not commonly observed. Many passive treatment systems have been constructed in the northern latitudes that are effective year-round. One of the best studied systems is the Marchand passive system in Pennsylvania (USA) where a large Fe-contaminated deep mine discharge is consistently treated to < 3 mg/L Fe (Hedin 2008). This paper describes the treatment performance of the Marchand System over the

last six years and presents unexpected chemical correlations with temperature that balance the kinetic penalty.

Background

The Marchand Mine passive treatment system is shown in Fig. 1. The system was installed in 2006 to treat a large Fe-contaminated discharge from a flooded underground coal mine and consists of six 1.3 m deep serially-connected ponds followed by a 0.2 - 0.3 m deep constructed wetland. The ponds were constructed in compacted clay (no organic substrate) and have retained an open-water environment. The wetland was constructed with the best available soil (obtained onsite) and planted with a mix of aquatic plant species.

Methods

The system has been sampled approximately monthly since its construction. The final effluent has been sampled 97 times, the influent 67 times, and the effluent of each of the ponds 23 times. Measurements were made in the field of pH, temperature, conductivity, dissolved oxygen, and alkalinity. Raw and acidified sam-



Fig. 1 Marchand passive treatment system on August 29, 2012. Arrows show flow paths. Circles are sampling points. The system location is 40°14'4.81" N; 79°45'55.63" W.

ples were collected for laboratory measurements of acidity, Fe, Al, Mn, sulfate and total suspended solids using standard methods (Clesceri *et al.* 2005). On 14 occasions dissolved metals were measured on an extra filtered (0.22 µm) sample. Dissolved Fe was assumed to approximate Fe^{2+} because Fe^{3+} is sparingly soluble at the circumneutral pH found at all stations. CO₂ fugacity was calculated using The Geochemist's Workbench[®] (Aqueous Solutions LLC). Flow rates were measured with a velocity meter at the piped influent to the first pond.

Results

Table 1 shows the average conditions at the sampling stations since it was constructed. The

influent flow rate ranged between 4.8 m³/min and 9.4 m³/min and averaged 7.1 m³/min (Fig. 2a). The influent had a constant water temperature of 14 °C, which is typical of deep mine discharges in this region. As water flowed through the system its temperature changed in response to ambient air conditions, which can range between -15 °C in winter and +35 °C in summer. The temperature of the influent to the last pond (F) ranged between 4 °C and 24 °C. The ponds never froze and retained open water conditions year-round. The temperature of the system's final discharge ranged between 1 °C and 31 °C. Portions of the wetland froze every winter and the wetland surface was largely ice covered during extended cold weather.

	Flow	Temp	DO	pН	HCO ₃ -	Fetot	Fedis	Mntot	SO4tot	TSS	CO ₂
	m ³ /min	C°	mg/L	s.u.	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	fugacity
Influent	7.1	13.9	0.8	6.30	407	72.4	66.8	1.2	1,036	25	0.163
A out	na	13.9	4.1	6.46	367	62.7	51.2	1.2	1,109	60	0.106
B out	na	13.8	6.1	6.59	342	54.5	35.7	1.2	1,110	60	0.078
C out	na	13.7	7.0	6.70	316	40.7	20.8	1.2	1,074	50	0.056
D out	na	13.5	7.5	6.82	294	30.0	12.4	1.2	1,083	37	0.042
E out	na	13.3	8.0	6.93	288	19.3	4.9	1.2	1,115	25	0.032
F out	na	13.3	9.3	7.10	281	12.4	1.4	1.1	1,117	16	0.022
Effluent	na	14.5	16.8	7.76	262	1.0	0.1	0.5	1,160	<6	0.0045

Table 1 Average conditions at the Marchand Mine passive treatment system, Jan 2007 – Dec 2012. TSS is total suspended solids. Al concentrations were <0.1 mg/L for all stations.</th>



Fig. 2 Treatment performance by the Marchand system. A) Flow rate at system influent; B) Total Fe at the system influent (○) and effluent (●) stations

The mine water was strongly alkaline, anoxic with high CO₂, and contaminated with Fe. The influent Fe concentrations ranged between 54 mg/L and 89 mg/L and averaged 72 mg/L (Fig. 2b). As water flowed through the system, the major effects on water chemistry were decreased Fe, alkalinity and CO₂ and increased pH and dissolved oxygen. The changes in Fe and alkalinity were stoichiometricly consistent with the carbonate neutralization of acidity produced by Fe oxidation and hydrolysis.

The system decreased Fe concentrations to an average 1 mg/L. Of 96 measurements of Fe in the final effluent, only 4 were higher than 3 mg/L and the highest measurement was 6.0 mg/L. The treatment system was effective year round. A cold weather decline in the removal of Fe was not evident (Fig. 2b). Table 2 shows correlations between water temperature and chemical parameters. Fe removal was not correlated with water temperature. Water temperature was negatively correlated in the ponds with pH and positively correlated with alkalinity. The temperature-pH correlations increased with flow through the ponds and reached a maximum in Ponds E and F.

Discussion

Temperature affects the oxidation of Fe^{2+} in the Marchand system through competing impacts on kinetics and concentrations of key chemical parameters. The removal of Fe at circumnueutral pH is generally assumed to be controlled by an abiotic oxidation process where the Fe^{2+} oxidation rate is first order with

				Fe removal					CO ₂
	Flow	рН	Alk	Fe(tot)	Fe(dis)	Fe(tot)	Fe(dis)	Mn	fugacity
Influent		-0.25	0.49*	0.33	0.38			0.16	0.31
A out	0.17	-0.59*	0.24	-0.23	-0.19	0.25	0.21	-0.38	0.68*
B out	0.15	-0.65*	0.26	-0.01	-0.31	-0.41	0.02	-0.34	0.74*
C out	0.22	-0.76*	0.43*	0.28	-0.01	-0.27	-0.29	-0.34	0.84*
D out	0.22	-0.80*	0.47*	0.43	0.15	-0.23	-0.35	-0.22	0.85*
E out	0.22	-0.87*	0.45*	0.02	0.11	0.34	0.09	-0.33	0.90*
F out	0.18	-0.85*	0.45*	0.23	0.15	-0.14	0.03	-0.12	0.85*
Effluent	0.22	-0.34	-0.13	-0.15	-0.17	0.14	0.10	-0.73*	0.36

Table 2 Temperature correlations for measured and calculated parameters. Correlations significantat the P = 0.05 level are labeled with *.



Fig. 3 Temperature relationships at Pond E Effluent for Fe, CO₂, and pH. The fourth panel shows temperature relationships for k_1 calculated from $e^{(-Ea/RT)}$ where Ea is 23 kcal/mol K, pH calculated from a second order rate relationship where pH values determined from pH-T regression, and $k_1/[H^+]^2$. The plotted values are relative to the average effluent temperature of Pond E.

respect to Fe^{2+} and O_2 and second order with respect to pH (Stumm and Morgan 1996) as follows:

$$d(Fe^{2+})/d(t) = k_1[Fe^{2+}] [O_2]/[H^+]^2$$

Arrhenius calculations indicate that the kinetic constant (k) changes tenfold over a 15 °C change in water temperature. It would appear that the treatment system should oxidize iron on cold winter days at 5–10 times slower rates than warm summer days. The kinetic effect is, however, offset by a concentration effect resulting from the inverse relationship between water temperature and pH. Fig. 3 shows key temperature relationships at the Pond E effluent. Fig. 3d shows the calculated variation of k_1 , [H]², and the combined factor, $k_1/[H]^2$, with temperature. The graph shows changes relative to the average temperature at the Pond E

effluent. The offsetting effects of k_1 and $[H]^2$ result in little change to $k_1/[H]^2$ over the temperature range observed in Pond E. This result explains the absence a temperature penalty for Fe²⁺ oxidation and hence bulk Fe removal by the treatment system over a wide range in temperature.

The pH in circumneutral mine water systems is largely controlled by carbonate chemistry. CO_2 , which is present in excess at Marchand and in most mine waters, degasses to the atmosphere, causing an increase in OH^- and hence pH.

$$HCO_3^- \rightarrow CO_2 (gas) + OH^-$$

Because of the strong dependence of Fe oxidation on pH and the demonstrated ability of accelerated CO_2 degassing to increase iron oxidation rates (Cravotta 2007; Kirby *et al.*

IMWA 2013

2009), mechanical aeration is a common practice in conventional treatment systems (Younger et al. 2002). Variable CO₂ degassing in passive treatment systems is an unrecognized phenomenon that appears to influence iron dynamics in a similar manner. The degassing of CO₂ in the Marchand ponds was strongly temperature dependent with lower CO₂ fugacities occurring when water temperatures were colder. The direct relationship between CO₂ fugacity and water temperature in the ponds was unexpected because CO₂ solubility increases with decreasing water temperature. The simplest explanation for the inverse relationship between water temperature and CO₂ is that the ponds mix more thoroughly at colder temperatures. When the air temperature is lower than water temperature, the surface waters are continually being cooled and sinking due to density gradients. The mixing continually refreshes the surface with deeper water that is more supersaturated with CO₂ which prompts degassing. Water temperatures in the ponds never fell below 4 °C where mixing stops and ice forms. When air temperatures are warmer than the pond water temperature, the warmer less dense surface water floats and mixing is poor. The surface is not refreshed and gas exchange processes are slowed.

All temperature correlations weakened in the wetland. While the ponds never froze, the wetlands commonly froze in cold weather. The ice cap presumably lessened gas exchange processes. While the ponds are largely devoid of plant growth, the wetlands contained emergent plants and large blooms of the alga Chara vulgaris during several spring and summer seasons. The shallow water depths combined with seasonal biological activity create a more dynamic system where temperature relations are more complex and unpredictable than in the simple oxidation ponds.

Conclusions

The Marchand system has provided highly effective treatment of a large flow of alkaline Fecontaminated mine water for six years. Iron removal was not correlated with water temperature, despite Arrhenius-based calculations that predict iron oxidation rates 10 times slower in cold seasons than warm seasons. The kinetic penalty was offset by a strong inverse relationship between pH and temperature which appears to be caused by increased CO₂ degassing at lower temperatures. The findings caution against evaluations of the treatment system performance where temperature effects are predicated based on static chemical conditions and kinetic considerations.

Acknowledgements

The Marchand System was constructed by Sewickley Creek Watershed Association with funding provided by the Pennsylvania Department of Environmental Protection Growing Greener Program. Sewickley Creek Watershed Association provided access to the system. Analytical costs were supported by the Western Pennsylvania Coalition for Abandoned Mine Reclamation, Pennsylvania Department of Environmental Protection, and Trout Unlimited Eastern Abandoned Mine Program.

References

- Clesceri LS, Greenberg AE, Eaton AD (2005) Eds. Standard Methods for the Examination of Water and Wastewater, 21st Edition; American Public Health Assoc., American Water Works Assoc, and the Water Environment Federation: Washington, DC
- Cravotta CA III (2007) Passive aerobic treatment of netalkaline, iron-laden drainage from a flooded underground anthracite mine, Pennsylvania, USA. Mine Water Env. 26:128–149
- Dempsey BA, Roscoe HC, Ames R, Hedin R, Jeon BH (2001) Ferrous oxidation chemistry in passive abiotic systems for treatment of mine drainage. Geochemistry, Exploration, Environment, Analysis. 1:81–88
- Hedin RS (2008) Iron removal by a passive system treating alkaline coal mine drainage. Mine Water Environ 27:200–209
- Kirby CS, Dennis A, Kahler A (2009) Aeration to degas CO2, increase pH, and increase iron oxidation rate for efficient treatment of n*et al.* kaline mine drainage. Applied Geochemistry 24:1175–1184

Stumm W, Morgan JJ (1996) Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters, 3rd Edition; John Wiley and Sons, New York, NY, 1022 pp
Younger PL, Banwart SA, Hedin RS (2002) Mine Water: Hydrology, Pollution, Remediation, Kluwer Aca-

demic Publishers, Dordrecht, The Netherlands, 442 pp

Carbon Sequestration Through Oceanic Fe Fertilization: Opportunity for Mine Water?

Benjamin C. HEDIN, Robert S. HEDIN

Hedin Environmental, 195 Castle Shannon Blvd., Pittsburgh, Pennsylvania, USA, ben.hedin@hedinenv.com

Abstract John Martin first proposed the iron hypothesis in 1990 which suggests that ocean iron concentrations impact phytoplankton growth which impact global climate. Subsequent experiments have confirmed this hypothesis and demonstrated unique ocean conditions that are suited for sequestering atmospheric carbon and increasing the productivity of local food chains. In this paper, we review the literature of ocean iron fertilization experiments and perform calculations to evaluate the opportunity for using mine drainage by-products in future geoengineering proposals.

Keywords IMWA 2013, iron fertilization, carbon sequestration, mine water

Introduction

Large portions of oceans have low productivity despite available nutrients. These areas, called high nutrient low chlorophyll (HNLC), characteristically have an abundance of macronutrients, such as nitrate and phosphorous, yet phytoplankton populations are relatively small and rarely bloom. These conditions persist because of iron limitations. John Martin first made the connection between chronically low iron concentrations and low productivity in 1990 when he proposed the iron hypothesis which states that ocean iron concentrations impact phytoplankton populations which affect global climate (Martin 1990). Specifically, that during the last glacial maxima, aerosol iron concentrations were 50 times higher than the last interglacial period. This increase in iron likely affected atmospheric CO₂ concentration quickly, in just a few hundred years. The specific mechanism of the carbon sequestration was the sinking of phytoplankton to ocean sediments.

Martin also acknowledged the possibility of iron fertilization as a geoengineering option to sequester CO_2 from the atmosphere into ocean sediments. Recent CO_2 sequestration interests have raised the profile of ocean iron fertilization (OIF) projects. Because mine water professionals commonly deal with large excesses of iron, the purpose of this paper is to review the best iron fertilization information currently available and provide calculations that assess the opportunity for mine water or mine water solids to increase CO₂ sequestration and the productivity of ocean ecosystems.

Background

The major natural source of iron to pelagic environments is wind-blown dust. Iron is used by phytoplankton, cyanobacteria and bacteria for fixing atmospheric nitrogen, reducing nitrate and chlorophyll synthesis (Martin 1990). Lab experiments have shown that very little iron is needed for substantial phytoplankton growth and C:Fe molar ratios ranging from 140,000 to 500,000 have been reported (Buesseler & Boyd 2003). Where iron is limiting, such as HNLC waters, the addition of iron can have a huge impact on primary productivity.

To date, thirteen OIF experiments have been conducted around the globe in various ocean conditions. Between 350 and 10,000 kg of iron sulfate dissolved in acidified sea water have been discharged into the ocean in pulsed doses, similar to episodic dust events. Although fertilization typically increases local Fe concentrations by less than 1 mmol/m² and

raises Fe concentrations to no more than 10 µg/L Fe, the result is phytoplankton blooms that persist for weeks. Monitoring vessels have collected data on blooms for only a few days to over a month. Unfortunately no vessel has monitored a bloom's complete development and collapse. Often, OIF experiments are carried out in eddies because they can be identified by satellites and the waters inside and outside an eddy, to a large extent, do not mix, allowing for comparison between fertilized and unfertilized conditions over a small area. During a bloom many variables are monitored to allow for the calculation of chlorophyll concentration, nutrient concentrations (nitrate, dissolved inorganic carbon, particulate organic carbon and silicon), particulate organic carbon concentration and dominant phytoplankton as well as zooplankton, among others (Boyd et al. 2007).

OIF experiments have demonstrated that iron fertilization increases productivity, decreases dissolved inorganic carbon and decreases nutrients. The composition of the plankton blooms has varied. Of eleven OIF experiments that produced a bloom, diatoms emerged as the dominant organism in seven. Diatoms are phytoplankton encased in silica which not only allows them to avoid predation, but causes them to sink after death, exporting particulate organic carbon to the ocean floor where it is considered isolated for centuries (Boyd *et al.* 2007; Coale *et al.* 2004).

Carbon Sequestration Potential

About 20 % of the worlds' oceans are characterized as HNLC areas. A major HNLC area is the Southern Ocean which is generally defined to be south of 60° latitude, with an area of approximately 20 Mkm² (Fig. 1). In this area, a large amount of unused surface macronutrients are returned to the deep ocean. Four OIF experiments have been performed in the Southern Ocean, all resulting in phytoplankton blooms, confirming that iron limits primary production (Buesseler & Boyd 2003; Smetacek *et al.* 2012).

The most detailed OIF experiment in the Southern Ocean was the 2004 European Iron Fertilization Experiment (EIFEX). The experiment consisted of two fertilizations of 7 t of iron sulfate each, separated by 14 days. Over the 37 day experiment, water chemistry was measured over a vertical depth gradient of up to 3,000 m. Surface concentrations of nitrate, nitrite and dissolved inorganic carbon decreased inside the fertilized patch yet remained stable outside the patch. Additionally, surface concentrations of chlorophyll, particulate organic carbon, particulate organic nitro-



Fig. 1 Areas of the ocean with abundant nitrate are deemed HNLC areas. Data from www.geos.ed.ac.uk/homes/s 0675905/MScBSc.html

Wolkersdorfer, Brown & Figueroa (Editors)

gen and biogenic silica all increased inside the fertilized patch yet remained stable outside (Fig. 2). All of these variables indicate a Fe-induced phytoplankton bloom, of which 97 % was due to large diatom proliferation because of available silica (Smetacek *et al.* 2012).

The research team recorded particulate organic carbon concentrations throughout the depth gradient as an indicator of sinking and possibly sequestered of carbon. Around 24 days after initial fertilization, particulate organic carbon stocks increased sharply below 200 meters depth as diatoms died en masse and formed sinking aggregates. Increases in particulate organic carbon from 300 to 3,000 m were accompanied by decreases near the surface (Smetacek *et al.* 2012).

The authors calculated an iron induced increase in C fixation by phytoplankton of 2.4 mol/m², of which 1.2 mol/m² sank below 1,000 m. The resulting C:Fe molar ratio of iron induced carbon export was 6,667. The authors consider these measurements underestimates because the bloom had not yet reached an iron limiting state, enhanced primary production and carbon flux continued after monitoring had ended and chlorophyll concentrations inside the patch were still above pre fertilization and outside-patch concentrations (Smetacek *et al.* 2012).

Increasing Productivity

Iron fertilization of silica deficient water also induces large phytoplankton blooms, but diatoms are a small percentage. To investigate the role of silicon in the iron hypothesis, simultaneous OIF experiments in silicon rich and deficient portions of the Southern Ocean were conducted in 2002. Although both fertilization events resulted in phytoplankton blooms, diatoms made up less than half of the low silicon bloom and most of the high silicon bloom. The maximum primary productivity rate in the silicon deficient bloom was double that of the silicon rich bloom. Although limited carbon was exported to the ocean floor due to lack of diatoms in the silicon deficient bloom, proliferation of other phytoplankton could have impacts several levels up the trophic chain (Coale et al. 2004).

Among the ten OIF's that measured an increase in chlorophyll, half recorded an increase in zooplankton stocks suggesting that increasing oceanic primary productivity could affect the local food chain (Boyd *et al.* 2007). Such is illustrated in a recent 2009 OIF experiment in a silicon deficient portion of the south-western Atlantic. A short initial non-diatom phytoplankton bloom produced a zooplankton bloom that kept the phytoplankton population in check (Mazzocchi 2009).



Fig. 2 High chlorophyll concentrations inside the fertilized patch (a) and low outside of the patch (b). Silicate concentrations decreased inside the fertilized patch (c) but stayed stable outside (d) Smetacek et al. 2012.

Geoengineering

The results of all OIF experiments to date indicate that iron fertilization initiates a phytoplankton bloom that could sequester carbon as well as enhance the entire local food chain. As mentioned before, certain areas of the ocean are conducive for each respective task. Here, we will present rough calculations that explore sequestering carbon and increasing productivity on a large scale.

Accepting the iron hypothesis, geoengineering of our current climate by sequestering carbon into ocean sediment is possible. Based on the 2004 EIFEX data, the authors calculated the sequestration of 1.2 mol C/m^2 from a single iron fertilization event. Extrapolating this result to half of the Southern Ocean (10.15 Mkm²) suggests that 161 Mt of carbon could be sequestered through the application of 113,000 t of Fe. During the course of the EIFEX bloom, silic acid concentrations halved and nitrate + nitrite concentrations only slightly decreased. Therefore, assuming silicon is the limiting nutrient in diatom blooms, sequestered carbon could double to 323 Mt. Although the complete collapse of the diatom bloom was not observed during the 37 day EIFEX experiment, a decline was evident from decreases in surface particulate organic carbon stocks and increases of deep particulate organic carbon stocks late in the experiment. Assuming the bloom was close to collapsing, iron fertilization could take place every 4 months to allow HNLC conditions to be reestablished. Thus, a regular OIF regime in 50 % of the Southern Ocean could sequester 1.29 Gt of carbon per year (table 1). For context, the total C emissions of the world's cement industry are about 1 Gt of carbon per year.

A consistent and large scale OIF, such as the one mentioned above, would require 901 kt of iron per year based on a C sequestered: Fe added weight ratio of 1,434. This is a huge amount of Fe. Estimates of the amount of Fe produced annual by mine water systems worldwide are unknown to the authors, but are suspected to be much less than this quantity. The authors are familiar with iron production by mine water systems in the coalfields of the eastern US. The largest iron-producing passive system in the eastern U.S. creates 292 t/a Fe (Hedin 2006). The authors estimate that in southwestern Pennsylvania, the annual iron discharge from flooded coal mines is approximately 10,000 t/a Fe (100,000 gpm [6.31 m³/s] at 50 mg/L Fe). While this iron loading is only a fraction of the total shown in Table 1, it is enough to theoretically sequester 14 Mt of carbon.

The value of large ocean iron fertilization efforts depends on the value of sequestered carbon and the value of increased ocean productivity. The value of carbon sequestration can be estimated from carbon credit markets. Although, the carbon market is quite unstable at this time, carbon credits currently sell for approximately \$10/t C in California, \$4/t C in Europe and \$0.14/t C in New Zealand. Based on these prices, and the sequestration scenario shown in Table 1, the gross value yielded from

	Value	Source
Iron induced carbon sequestration	14.4 g C/m^2	Smetacek <i>et al.</i> 2012
Area of Southern Ocean	20.3 Mkm ²	www.worldatlas.com
Carbon sequestration with fertilization of half of	161 Mt C	Calculation
Southern Ocean (one event)		
All available silicon used for diatom growth (one	323 Mt C	Assumption
event)		
Sequestration at 4 events per year	1.3 Gt C	Assumption
C sequestration: Fe fertilization, mass ratio	1,434	Smetacek <i>et al.</i> 2012
Fe fertilization requirement per year	901 kt Fe	Calculation

 Table 1 Carbon sequestration potential of the Southern Ocean.

a ton of iron used in ocean fertilization ranges between \$430/t (New Zealand) and \$14,340/t (California).

Although fertilization of ocean waters low in silica does not sequester much carbon, the increase in primary productivity could be useful for stimulating the local food chain. Authors of the 2004 EIFEX study calculated that one ton of iron stimulated 2,868 t of carbon uptake. Based on previously mentioned OIF experiments, high temperature and low silicon concentrations can double primary productivity rates in the Southern Ocean and promote non-diatom phytoplankton growth (Coale et al. 2004). A doubling of primary production results in a carbon to iron ratio of 5,735. Proliferation of non-diatom phytoplankton leads to increases in zoo plankton populations and, presumably, higher trophic level organisms. Although no scientific experiments have examined OIF potential in this regard, a recent unscientific OIF off of British Columbia, Canada, attempted to increase productivity of the local salmon fishery. Table 2 shows calculations for the impact of an OIF where the target is predatory fish atop a five trophic level food chain that has 10 % C transfer between trophic levels. The calculations suggest that one pound of iron could result in 0.57 lb (0.3 kg) of predatory fish. The wholesale price for salmon in California in 2012 was \$4-6/lb. One ton of iron fertilization theoretically yields 0.57 t salmon which has wholesale value of \$4,560 - \$6,840.

The cost of supplying iron for OIF's depends on the source of iron. Iron oxide pro-

Trophic Level	C:Fe ratio
1 (Primary Producer)	5,735
2 (Zooplankton)	573.5
3 (Predatory Zooplankton)	57.35
4 (Grazers)	5.74
5 (Predatory Fish)	0.57

Table 2 Tentative calculations of impact of OIFon local trophic chains.

duced from coal mine drainage in Pennsylvania currently sells for \$575 per ton Fe. High purity synthetic iron oxide sells for \$1,150/t Fe. Iron sulfate heptahydrate, the product used in most OIF experiments sells for \$500/t Fe.

Conclusion

OIF experiments confirm Martin's iron hypothesis that adding iron to ocean environments will increase primary productivity. However, specific ocean chemistry is required to sequester carbon or increase food chain productivity. HNLC areas, specifically those high in silicon, such as the Southern Ocean, are required to promote diatom blooms that can sequester atmospheric carbon in ocean sediments. Fertilization of low silicon, warm ocean waters can promote a non-diatom phytoplankton bloom with possible impacts to the local food chain.

The potential for stimulation of the ocean's productivity with iron is huge. A concerted effort to increase the productivity of the Southern Ocean could consume 900 kt of iron annually. The amount of iron produced by active and closed mining operations is unknown, but it appears to be much less than this quantity.

The value of large scale OIF was estimated from the results of EIFEX and the current market value for carbon credits and salmon. The highly volatile carbon credit market yields values of \$430 – \$14,340 per ton Fe. Stimulation of a salmon fishery, assuming that the increased fish can be captured, yields a value of \$4,560 – \$6,840 per ton Fe. The current cost to produce an iron oxide product from mine drainage is \$575/t Fe, while the cost for iron sulfate is \$500/t Fe.

References

Boyd PW, Jickells T, Law CS, Blain S, Boyle EA, Buesseler KO, Coale KH, Cullen JJ, de Baar HJW, Follows M, Harvey M, Lancelot C, Levasseur M, Owens NPJ, Pollard R, Rivkin RB, Sarmiento J, Schoemann V, Smetacek V, Takeda S, Turner S, Watson AJ. (2007) Mesoscale Iron Enrichment Experiments 1993-2005: Synthesis and Future Directions. Science 315:612-617.

- Buesseler KO, Boyd PW (2003) Will Ocean Fertilization Work? Science 300:67-68.
- Coale KH, Johnson KS, Chavez FP, Buesseler KO, Barber RT, Brzezinski MA, Cochlan WP, Millero FJ, Falkowski PG, Bauer JE, Wanninkof RH, Kudela RM, Altabet MA, Hales BE, Takahashi T, Landry MR, Bidigare RR, Wang X, Chanse Z, Strutton PG, Friederich GE, Gorbunov MY, Lance VP, Hilting AK, Hiscock MR, Demarest M, Hiscock WT, Sullivan KF, Tanner SJ, Gordon RM, Hunter CN, Elrod VA, Fitzwater SE, Jones JL, Tozzi S, Koblizek M, Roberts AE, Herndon J, Brewster J, Ladizinsky N, Smith G, Cooper D, Timothy D, Brown SL, Selph KE, Sheridan CC, Twining BS, Johnson ZI. (2004) Southern Ocean Iron Enrichment Experiment: Carbon Cycling in High- and Low-Si Waters. Science 304:408-414.
- Hedin RS (2008) Iron removal by a passive system treating alkaline coal mine drainage. Mine Water Env. 27:200-209

- Martin JH (1990) Glacial-Interchange CO2 Change: The Iron Hypothesis. Paleoceanography 5(1):1-13.
- Mazzocchi MG, González HE, Vandromme P, Borrione I, d'Alcalá MR, Gauns M, Assmy P, Fuchs B, Klaas C, Martin P, Montresor M, Ramaiah N, Naqvi W, Smetacek V. (2009, October) A non-diatom plankton bloom controlled by copepod grazing and amphipod predation: Preliminary results from the LO-HAFEX iron-fertilisation experiment. GLOBEC International Newsletter 15(3):3-6.
- Smetacek V, Klaas C, Strass VH, Assmy P, Montresor M, Cisewski B, Savoye N, Webb A, d'Ovidio F, Arrieta JM, Bathmann U, Bellerby R, Berg GM, Croot P, Gonzalez S, Henjes J, Herndl GJ, Hoffman LJ, Leach H, Losch M, Mills MM, Neill C, Peeken I, Röttgers R, Sachs O, Sauter E, Schmidt MM, Schwarz J, Terbrüggen A, Wolf-Gladrow D. (2012) Deep carbon export from and Southern Ocean iron-fertilized diatom bloom. Nature 487:313-319.

Assessment of glycerol-enhanced bacterial sulfate degradation in lignite mining sediments by stable isotope investigations

Christina Jeschke¹, Kay Knöller¹, André Simon², Martin Gast³, Nils Hoth²

¹Helmholtz Centre for Environmental Research – UFZ,-Theodor-Lieser-Str. 4, 06120 Halle (Saale), Germany, christina.jeschke@ufz.de

²Technical University Bergakademie Freiberg, Institute of Drilling Engineering and Fluid Mining, Gustav-Zeuner-Str. 1A, 09596 Freiberg, Germany

³LUG Engineering GmbH, Dissenchener Str. 50, 03042 Cottbus, Germany

Abstract The generation of acid mine drainage (AMD) is known to create significant impact on the hydrochemical conditions in lignite mining sediments. Especially high loads of acidity, iron and sulfate pose an immense risk to adjacent ground- and surface water bodies. Bacterial sulfate reduction (BSR) is the only natural process that can counteract those major effects of AMD contamination.

Often, BSR is limited due to a low supply of organic carbon, acting as an electron donor. Therefore, the injection of additional electron donors into the aquifer may stimulate the sulfate degradation. Glycerol is particularly suitable due to its chemical properties, *e.g.* low freezing point. So it is possible to use easily degradable substrate with defined quantity over the whole year. This technique was tested in a lignite mine dump aquifer section in the Lusatian lignite mining district, Germany.

Glycerol was added to the groundwater via injection wells and channelized by a funneland-gate system. The decision whether sulfate reduction is occurring in the investigated aquifer section was based on the observation of the stable isotopic composition and concentration of sulfate. The sulfate concentration showed significant changes in the wells, sometimes with little alteration in the isotopic composition. Therefore, part of the sulfate concentration changes seem to be due to transport phenomena such as dispersion and dilution. Only samples with changed isotope signatures provide the evidence for the occurrence of BSR. The significant enrichment of both heavy sulfur and heavy oxygen in the remaining sulfate pool can be interpreted as a direct result of the activity of sulfate-reducing bacteria. The preferable reactive zone for microorganism is relatively fixed to the location the glycerol injections. Groundwater sulfate is being reduced stepwise as it progresses through the reactive zone. Subsequently, the residual sulfate is transported with the groundwater flow and appears at certain times at the different wells. The temporal variability of the process intensity and transport of reaction products in the groundwater flow affect the sulfate concentrations and sulfate isotope signatures and lead to a spatially heterogeneous distribution. Also, the residence time of the groundwater in the reactive zone and the availability of the electron donor influence the extent of sulfate degradation.

Regardless of the inhomogeneous distribution, the overall turnover of sulfate by sulfate reducing bacteria justifies the injection of glycerol and proves the applicability of this enhanced natural attenuation method to handle the restoration of aquifers contaminated with AMD.

Keywords bacterial sulfate reduction, isotope fractionation, glycerol, lignite mining
Bioremediation of V⁵⁺ and Ni²⁺ by indigenous *Marinobacter Goseongensis* isolated from South African Vanadium Mine Waste

Ilunga Каміка; Maggy NB Момва

Department of Environmental, Water and Earth Sciences, Faculty of Science, Tshwane University of Technology, Arcadia Campus, Private Bag X680, Pretoria 0001, South Africa. mombamnb@tut.ac.za

Abstract Study assessed the bioremediation of V⁵⁺ and Ni²⁺ in wastewater by an indigenous bacterial species. Bacterial species was isolated from mine water and characterized by sequencing. The isolate appeared to tolerate V⁵⁺ and Ni²⁺ separately at concentrations ranging between 650 to 700 mg/L and 250 and 300 mg/L (24h-LC₅), respectively. Removal of V⁵⁺ and Ni²⁺ in the media was inversely proportional to the test metal concentrations. *Marinobacter goseongensis* could remove more than 99.99 % of both metals at 50 mg/L at below the maximum permissible limit of 0.1 mg/L. This indigenous bacterial isolate can be used in V⁵⁺ and Ni²⁺ bioremediation.

Keywords Mine water, microbial diversity, *Marinobacter*, vanadium, nickel, pollution, bioremediation

Introduction

Mine water remains one of the major problems of concern, not only in South Africa, but also worldwide. This is due to its environmental, socio-economic and public health impacts (Oelofse 2009). In South Africa in particular, mining activities have a long history and have played a major role in both economic development and environmental pollution countrywide (Adler et al. 2007). Although significant progress has been made to address mine water management, environmental pollution due to the disposal of untreated mine water still remains a challenge. Microorganisms, due to their ubiquitousness, have been viewed as one of the best ways to deal with this problem. Due to their ability to survive, grow and reproduce in such harsh environments, an interest in microorganisms was aroused among researchers worldwide (Zhou et al. 2010). Nevertheless, their presence in extreme environments such as mine water affects their species diversity (Wang et al. 2011). Wang et al. (2011) have pointed out that extreme conditions can be defined by levels of environmental factors, the effects of which pose difficulties for the survival of specific

taxa or all taxa. In addition, both Johnson and Hallberg (2003) and Imarla et al. (2006) have also reported that a microbial community composition is largely bound to geochemical parameters such as pH and metal ion concentrations. As a result, microorganisms isolated from such environments are considered to constitute a valuable tool in the treatment of highly polluted mine water. Knowing that microorganisms, with bacteria in the lead, represent the largest reservoir of undescribed biodiversity (Tekere et al. 2011); their study has proved to be of great importance to science. This study aims at assessing the resistance and bioremediation ability of indigenous bacterial isolate to both V⁵⁺ and Ni²⁺ in a modified wastewater mixed liquor.

Methods

The *Marinobacter* species was isolated according to Huu *et al.* (1999) using Halomonas elongata (HMC) medium. Prior to be used, the isolate was identified by sequencing thereafter exposed to V^{5+} and Ni^{2+} ions at various concentration (from 50 to 800 mg/L) in the modified mixed liquor (Kamika and Momba 2011). Prior to assessing the metal tolerance ability

of the isolates, the optimum growth temperature of MWI-1 was determined by incubating the isolates at various temperatures (25 °C, 30 °C and 35 °C) and in the HMC broth. Sample flasks as well as positive controls were inoculated with the isolates (approximately 100 cfu/mL) incubated at 30 °C \pm 2 °C for 4 days. The median lethal concentration (LC_{50}) of the test metal for each of the test microbial isolates was determined as described by previous investigators (Kamika and Momba 2011). The minimum inhibitory concentration (MIC) of the test metal (referring to the smallest concentration of an antimicrobial agent necessary to inhibit growth of microorganisms) was determined according to Shirdam et al. (2006). MIC values were noted when the isolates failed to grow on the plates. After incubation, the microbial isolates were classified as being sensitive or tolerant to Ni²⁺ according to the inhibition of growth cells.

The genera *Marinobacter* were isolated (MWI-1) from the mine water samples and assessed for their possible ability to resist V⁵⁺ and Ni²⁺. The phylogenetic analysis using the neighbour-joining method with a bootstrap

value of 100 replicates indicated that an MWI-1 [AB793286] isolate belonged to the genus *Marinobacter* and was most closely related to *Marinobacter goseongensis* strain En6 [EF660754.1 and NR044340.1] at a similarity of approximately 97 % (fig. 1).

During the study the growth curves of the MWI-1 in a metal-free medium (HMC broth) revealed a lag-phase between time 0 to 2 followed by an exponential phase from time 2 h to 8 h when inoculated at 25 °C, 30 °C and 35 °C with bacterial counts of 7 log CFU/mL, 8 log CFU/mL and 7 log CFU/mL, respectively. At 30 °C, MWI-1 indicated a second exponential growth (10 logCFU/mL) from time 16 h to the end of the experiment, whereas a death phase was observed at 25 °C and 35 °C, repectively.

As MWI-1 grew very well at 30 °C, its tolerance to V^{5+} and Ni^{2+} in the modified mixed liquor was tested at the said temperature and at pH 7.2 ± 0.2. The growth performance of this isolate in the modified mixed liquor containing either V^{5+} or Ni^{2+} or both at two different concentrations in order to highlight the difference of the toxic effect between the two metals (fig. 2).



^{0.001}

Fig. 1 Phylogenetic tree using the neighbour-joining method, constructed and based on the bacterial 16S rRNA gene sequence detected in the present study along with similar sequences detected from the NCBI and RDP databases.



Fig. 2 Growth performance of MWI-1 in a medium containing either V^{5+} (A) or Ni^{2+} (B) or both (B) at 100 mg/L and 200 mg/L, 30 °C, pH 7.2±0.2.

In general, the growth of the isolates decreased with the increases of the metal concentrations. The MWI-1 was able to significantly grow in the presence of V^{5+} at 100 mg/L (9 log CFU/mL) and 200 mg/L (8 log CFU/mL),

while in the presence of Ni²⁺ MWI-1 could only grow at 100 mg/L. Concomitantly, Ni²⁺ toxicity was able to inhibit the growth in all the volume ratios. Statistical evidence revealed a significant difference (p<0.05) in terms of growth performance between the positive controls and those samples treated with Ni²⁺ while no significant difference (p>0.05) was indicated for MWI-1 treated with V⁵⁺. Another significant difference was also noted for positive controls when compared with those samples treated with both metals concomitantly.

A general observation indicated that the MWI-1 isolate was more tolerant to V⁵⁺ than to Ni²⁺ in the modified mixed liquor (Table 1). The MWI-1 isolate could resist V⁵⁺ up to 650-700 mg/L (MIC) and only reached 200–250 mg/L in the presence of Ni²⁺. The tolerance or sensitivity of the MWI-1 isolate was also revealed by its ability to remove V5+ and Ni2+ (Table 1 and 2). In the presence of V^{5+} or Ni^{2+} separately, the MWI-1 was able to remove up to 99.95 % of 100 mg/L V⁵⁺ and 86.42 % of 100 mg/L Ni²⁺. When in concomitance with each other (Table 2), the Ni²⁺ toxicity disturbed the removal of V⁵⁺ in the modified mixed liquor. In consortium, none of the metals (V^{5+}/Ni^{2+}) was removed at a percentage of over 30 %, with the exception of V⁵⁺ (30.15 %) that was removed at a ratio of 1:1 (100 mg/L/100 mg/L).

Due to their abundance, the *Marinobacter* genus of the *Proteobacteria phylum* was isolated in the present study and assessed for their tolerance to and removal of V⁵⁺ and Ni²⁺ in the modified mixed liquor. The isolate (MWI-1) was firstly sequenced and found to be closely related to *Marinobacter goseongensis*.

ι,	Tolerance	limit (mg/I	-)	Percentage removal (%)				
Experi ment	24h-LC50 (V ⁵⁺)	MIC (V ⁵⁺)	24h-LC50 (Ni ²⁺)	MIC (Ni ²⁺)	100 mg/L V ⁵⁺	200 mg/L V ⁵⁺	100 mg/L Ni ²⁺	200 mg/L Ni ²⁺
1^{st}	550	700	250	350	99.95	96.38	81.36	47.28
2^{nd}	500	650	200	300	99.98	91.28	86.25	43.95
3^{rd}	500	700	200	350	98.97	94.65	79.64	39.78
	500-550	650-700	200-250	300-350	99.63	94.10	82.42	43.67

Table 1 Tolerance limit and removal ability of MWI-1 in the modified mixed liquor containing V^{5+} and Ni^{2+} separately.

	100/100 (mg/	'L) [V ⁵⁺ /Ni ²⁺ ,	200/100 (mg/l	L) [V ⁵⁺ /Ni ²⁺ ,	100/200 (mg/L) [V ⁵⁺ /Ni ²⁺ ,		
		v/v]		v/v]		v/v]	
	V ⁵⁺ (%)	Ni ²⁺ (%)	V ⁵⁺ (%)	Ni ²⁺ (%)	V ⁵⁺ (%)	Ni ²⁺ (%)	
1^{st}	27.05	26.15	16.31	11.07	9.87	3.68	
2^{nd}	25.13	21.08	18.05	13.12	7.38	5.28	
3^{rd}	38.27	24.65	17.15	10.24	11.28	9.17	
	30.15	23.96	17.17	11.48	9.51	6.04	

Table 2 Removal ability of MWI-1 in the modified mixed liquor containing V^{5+} and Ni²⁺ in consortium.

This MWI-1 showed very good growth at 30 °C in the HMC broth, while at 25 °C and 35 °C a prompt die-off was noted when inoculated in a metal-free media. Findings of this study corroborated those of Roh et al. (2008) who reported that the optimum temperature for Marinobacter goseongensis sp. nov. should be between 25 °C and 30 °C. When inoculated in modified mixed liquor, culture media containing V^{5+} and Ni^{2+} , separately or combined and incubated at 30 °C, reveals a significant growth (p<0.05) of the MWI-1 in the media with V⁵⁺ when compared to the media with Ni²⁺. The MWI-1 bacterial isolate was more tolerant towards V⁵⁺ than towards Ni²⁺ (Table 1). The toxicity of the test metals in MWI-1 appeared to have a relatively negative effect on the metalremoval ability of the test isolate in the modified mixed liquor with V⁵⁺ indicating the highest level of removal (Table 1). It has been reported that bacterial strains can be characterised as being tolerant towards metal such as Ni²⁺, if it is capable of expressing growth at concentrations higher than 100 mg/L of the metal (Gikas 2008).

Zucconi *et al.* (2003) stated that isolating microorganisms from extreme environments represent an appropriate practice to select metal-resistant strains that could be used for metal removal and bioremediation purposes. Since it has been reported that most of the species of the genus *Marinobacter* are halophilic, heterotrophic neutrophiles and living under extreme environmental conditions such as pH and high salinity, they have been isolated from several habitats such as seawater, petroleum refineries, oil-refineies, and so forth (Guo *et al.* 2007). According to Brito *et al.* (2006), the *Marinobacter* species are the best degraders of hydrocarbons and have been associated with the removal of hydrocarbons in seawater. Owing to their ability to grow under extreme habitats, strains found in *Marinobacter* could have the ability to remove metal in the environment. Researchers have reported that several strains of *Marinobacter spp.* such as *Marinobacter aquaeolei* possess iron transport capabilities and are also capable of oxidising iron (Amin *et al.* 2012).

Conclusion

This study revealed that highly contaminated and toxic mine water effluents are a reservoir of novel microbial species which can adequately be used for the removal of metals in highly polluted effluents. The MWI-1 isolate, closely related to Marinobacter goseongensis, demonstrates high tolerance to both V⁵⁺ and Ni²⁺. Further studies on geochemistry and microbial diversity need to be conducted in order to unveil how the chemistry of the effluent from the vanadium mine in South Africa can affect the microbial diversity of the environment. Furthermore, studies carried out on microbial diversity in extreme environments such as mine water are needed in order to isolate novel hyper-tolerant microbial species for the removal of metals.

Acknowledgement

The authors are grateful to the National Research Foundation (NRF) for the funding of this project (Grant number: M590) and to the South African mining industries for allowing the researchers to use their mine water samples.

References

- Adler R.A., Claassen M, Godfrey L, Turton AR (2007) Water, mining, and waste: an historical and economic
- perspective on conflict management in South Africa. Economics of Peace and Security J 2(2): 33–44.
- Amin SA, Green DH, Al Waheed D, Gardes A, Carrano CJ (2012) Iron transport in the genus *Marinobacter*. Biometals 25(1): 135–147.
- Brito EMS, Guyoneaud RM, Goñi-Urriza M, Ranchou-Peyruse A, Verbaere A, Crapez MAC, Wasserman JCSA, Duran R (2006) Characterization of hydrocarbonoclastic bacterial communities from mangrove sediments in Guanabara Bay, Brazil. Res. Microbiol 157 (8): 752–762.
- Gikas P (2008) Single and combined effects of nickel (Ni(II)) and cobalt (Co(II)) ions on activated sludge and on other aerobic microorganisms: A review. J Hazard Mater 159(2–3): 187–203.
- Guo B, Gu J, Ye Y-G, Tang Y-Q, Kida K, Wu X-L (2007) *Marinobacter segnicrescens* sp. nov., a moderate halophile isolated from benthic sediment of the South China Sea. Int J Syst Evol Microbiol 57: 1970– 1974.
- Huu NB, Denner EBM, Ha DTC, Wanner G, Stan-Lotter H (1999) *Marinobacter aquaeolei* sp. *nov.*, a halophilic bacterium isolated from a Vietnamese oil-producing well. Int J Syst Bacteriol 49: 367–375.
- Imarla T, Hector SB, Deane SM, Rawlings DE (2006) Resistance determinants of a highly arsenic-resistant strain of *Leptospirillum ferriphilum* isolated from a commercial biooxidationtank. Appl Environ Microbiol 72: 2247–2253.
- Johnson DB, Hallberg KB(2003) The microbiology of acidic mine waters. Research in Microbiol 154: 466–473.

- Kamika I, Momba MNB (2011) Comparing the tolerance limits of selected bacterial and protozoan species to nickel in wastewater systems. Sc Total Environ 410: 172–181.
- Oelofse SHH (2009) Mine water pollution–acid mine decant, effluent and treatment: a consideration of key emerging issues that may impact the state of the environment. In: Krishna, C.S. (ed) Mining: Environment and health concerns, 1st edn. The Icfai University Press, India, pp 84–91.
- Roh SW, Quan ZX, Nam YD, Chang HW, Kim KH, Rhee SK, Oh HM, Jeon CO, Yoon JH, Bae JW (2008) Marinobacter goseongensis sp. nov., from seawater. Int J Syst Evol Microbiol 58(Pt 12): 2866–2870.
- Shirdam R, Khanafari A, Tabatabaee A (2006) Cadmium, nickel and vanadium accumulation by three strains of marine bacteria. Iran J Biotechnol 4(3): 180–187.
- Tekere M, Lotter A, Olivier J, Jonker N, Venter S (2011) Metagenomic analysis of bacterial diversity of Siloam hot water spring, Limpopo, South Africa. African Journal of Biotechnology, 10(78): 18005– 18012.
- Wang J, Yang D, Zhang Y, Shen J, Van Der Gast C, Hahn MW, Wu, Q (2011) Do Patterns of bacterial diversity along salinity gradients differ from those observed for macroorganisms. PLOSOne, 6(11): e27597.
- Zhou M, Liu Y, Zeng G, Li X, Xu, Fan T(2007). Kinetic and equilibrium studies of Cr(VI) biosorption by dead Bacillus licheniformis biomass. World J. Microbiol Biotechnol, 23: 43–48.
- Zucconi L, Ripa C, Alianiello F, Benedetti A, Onofri S (2003) Lead resistance, sorption and accumulation in a *Paecilomyces lilacinus* strain. Biology and Fertility of Soils, 37: 17–22.

Effect of nickel on nutrient removal ability of selected indigenous protozoan species in wastewater systems

Ilunga Каміка; Maggy NB Момва

Department of Environmental, Water and Earth Sciences, Faculty of Science, Tshwane University of Technology, Arcadia Campus, Private Bag X680, Pretoria 0001, South Africa. mombamnb@tut.ac.za

Abstract This study compared the effect of Ni²⁺ on nutrient-removal efficiency of four indigenous wastewater protozoan species. Isolates could simultaneously remove phosphate (66.4-99.36 %), nitrate (56.19-99.88 %) and Ni²⁺ (45.98-85.69 %) with *Peranema* sp. having the highest removal of nutrients (Phosphate-99.36 % and Nitrate-99.88 %) and *Paramecium* sp. the highest Ni²⁺-removal: 85.69 %. Increase in Ni²⁺ concentration had a significant effect on nutrient-removal efficiency of these indigenous isolates. Although Ni²⁺ appeared to be toxic to isolates, its effect at low concentration (10 mg-Ni²⁺/L) towards test isolates can be used to enhance the wastewater treatment process for nutrient- removals. *Peranema* sp. is candidate in bioremediation of wastewater systems.

Keywords wastewater, metal, nickel, bioremediation, protozoa, phosphate, nitrate, phosphate, pollution

Introduction

Human activities such as industrialisation, mining operations and urbanisation have been reported to negatively impact not only on the use of available water resources, but also on aquatic life (Kamika and Momba 2011). Metals are among these pollutants discharged in water resources. They have been reported as being capable of affecting the removal of other pollutants such as nitrate and phosphate during the biological treatment of wastewater (Ochoa-Herrera et al. 2011). However, little has been known regarding the protozoan ability to simultaneously remove/take up nitrate and phosphate in wastewater mixed liquor under metal stress. This study assessed the effect of Ni²⁺ on the simultaneous uptake of nitrate and phosphate by four protozoan isolates (Aspidisca sp., Peranema sp., Paramecium sp. and Trachelophyllum sp.).

Materials and Methods

Test organisms

The indigenous protozoan species used in this study included *Aspidisca* sp., *Paramecium* sp.,

Trachelophyllum sp. and *Peranema* sp. These protozoan species were isolated from wastewater mixed liquors collected from the aeration tanks of the Daspoort Wastewater Treatment Plant (Pretoria, South Africa). They have demonstrated the ability to successfully remove nitrate and phosphorus in modified mixed liquor media (Akpor *et al.* 2008) and also to tolerate V⁵⁺ and Ni²⁺ separately (Kamika and Momba 2011). The preparation of these protozoan species was carried out according to Akpor *et al.* (2008).

Sample collection and preparation of the culture medium

Wastewater samples (5 L) were collected on a monthly basis between November 2011 and May 2012 from the anaerobic and aerobic zone of the Northern Wastewater Treatment Works in Johannesburg. Modified mixed liquor (culture medium) from the collected wastewater samples was prepared as reported by Kamika and Momba (2011) and screened in terms of chemical oxygen demand (COD), dissolved oxygen (DO), pH, phosphate, nitrate and metal presence (Ni²⁺). Nickel nitrate [Ni(NO₃)₂] was used as a source of Ni²⁺ ions. The stock solution of Ni²⁺ at a concentration of 1000 mg/L was prepared using deionised water. A 200 mL wastewater mixed liquor medium was prepared with Ni²⁺ at a concentration of 10 to 50 mg/L Ni²⁺ (increased at a geometric scale of 10 mg/L). Nickel concentration was confirmed using ICP-OES. To maintain the nutrients in solution, the pH of the modified wastewater mixed liquor was maintained as acidic (6.5 ± 0.3) by adding 1.0 M HCl and 1.0 M NaOH (Merck, SA). The ICP-OES was used to confirm the Ni²⁺ concentrations in the wastewater mixed liquor media, while nitrate and phosphate concentration were confirmed using the standard methods (APHA 2001).

Determination of Ni²⁺ effects on nutrient removal

The experiments were conducted in 250 mL Erlenmeyer flasks containing 200 mL of the modified mixed liquor. The flasks were aseptically inoculated with a fresh culture of protozoan (≈ 100 Cells/mL) isolates separately. For each microbial isolate, positive and negative controls were used in this experimental study. The positive control flask contained the mixed liquor without Ni²⁺ and the negative control had the mixed liquor with 50 mg/L Ni²⁺. The negative control was used to assess any external contamination in the samples during the experimental study. To check the effect of Ni²⁺ on the ability of microbial isolates to remove nutrient, the protozoan isolates were separately inoculated in the culture media containing the mixture Ni²⁺. All the inoculated samples as well as the controls were incubated at 30 $^{\circ}C \pm 2 ^{\circ}C$ for four days. After each 24 h period, samples were homogeneously shaken, an aliquot of 30 mL was taken, and analyses for growth/die-off of the microbial isolates, pH, COD and DO, phosphate, nitrate concentrations were performed. The Ni^{2+} median lethal concentration (LC₅₀) was estimated according to the inhibition concentration approach. The first-order die-off rate of microbial species was calculated using the formula reported by Peng *et al.* (2008), whereas the growth rates were calculated according to by Kamika and Momba (2011). The data were statistically analysed using the Stata computer software.

Effect of Ni²⁺ on nitrate and phosphate removal in wastewater

Fig. 1 illustrates the percentage removal of nitrate by specific test organisms in the modified wastewater mixed liquor containing various concentrations of Ni²⁺. In general, the nitrate uptake was observed throughout the experimental study in both the positive control and the inoculated mixed liquor media. While a gradual increase in the nitrate uptake was observed over the incubation period in each of the culture media. an increase in the Ni²⁺ concentration resulted in a decrease in the rate of nitrate removal by protozoan isolates. The nitrate removal in the modified wastewater mixed liquor without Ni²⁺ (Positive controls) ranged from 42.12 to 96.98 % for Peranema sp., 35.03 to 87.36 % for Paramecium sp., 21.44 to 97.81 % for Trachelophyllum sp. and from 17.32 to 96.91 % for Aspidisca sp. However, in the mixed liquor media containing Ni²⁺, the ranges were as follows: 0.85 to 99.88 % for Peranema sp., 0.02 to 83.92 % for Paramecium sp., 0.03 to 68.84 % for Trachelophyllum sp. and 0.02 to 56.19 % for Aspidisca sp. Overall, significant differences were noted between the removal efficiency of protozoan isolates inoculated in the controls and those inoculated in the mixed liquor with Ni^{2+} (10 to 50 mg/L). The removal efficiencies of the isolates were significantly higher in the controls than in the mixed liquor with Ni²⁺. Although higher nitrate removal efficiency of all the isolates was significantly noted during day 4 of exposure (p < 0.05), Peranema sp. was found to have the highest nitrate uptake and Aspidisca sp. the lowest nitrate uptake in the mixed liquor with Ni²⁺. Even though the highest nitrate removal efficiency of all the isolates occurred in the mixed liquor containing 10 mg-Ni²⁺/L, this nickel concentration appeared to significantly enhance the ability of *Peranema* sp. to uptake more nitrate compared to other protozoan isolates. Furthermore, *Peranema* sp. was the only protozoan isolate able to remove more than 30 % of nitrate concentration in the modified wastewater mixed liquor containing 30 mg-Ni²⁺/L. While the nitrate uptake abilities of other protozoans decreased considerably in the nickel mixed liquor containing up to 50 mg-Ni²⁺/L, the removal efficiency of *Peranema* was still palpable (fig. 1).

Similar to the nitrate uptake, the phosphate uptake was observed throughout the experimental study in both the positive control and the mixed liquor media treated with Ni²⁺ (fig. 2) with Peranema sp. having the highest phosphate-removal efficiency (6.91 to 99.36 %) and Aspidisca sp. the lowest (0.27 to 66.40 %). However, statistical evidence revealed no significant difference (p>0.05) between the removal efficiency of the isolates. In addition, the phosphate-removal efficiency of all test isolates appeared to be higher in the mixed liquor media treated with 10 mg-Ni²⁺/L. When comparing the uptake of nitrate and phosphate by test isolates, Ni²⁺ toxicity appear to affect the nitrate uptake more than the phosphate uptake.

Determination of 24 h-LC50 of Ni²⁺ to and growth/die-off rate of test organisms

Fig. 3 illustrates the effect of Ni²⁺ on the growth responses of each test isolate in the modified wastewater mixed liquor. A general decrease in growth response was observed with an increase of Ni²⁺ concentration throughout the experimental study. Over the period of exposure, the growth response in the mixed liquor not treated with Ni²⁺ ranged from 2 to 5log₁₀ Cells/mL for Peranema sp., 2 to 6log₁₀ Cells/mL for Paramecium sp., 2 to 5 log₁₀ Cells/mL for Trachelophyllum sp. and 2 to 6 log₁₀ Cells/mL for Aspidisca sp. However, in the mixed liquor treated with Ni²⁺, the growth response of protozoan isolates ranged from 2 to 4 log₁₀ Cells/mL for Peranema sp., 2 to 5 log₁₀ Cells/mL for Paramecium sp., 2 to 4 log₁₀ Cells/mL for Trachelophyllum sp. and 2 to 3 log₁₀ Cells/mL for Aspidisca sp. with an increase in growth rate ranging from 0.02 to 2.03 d⁻¹, 0.27 to 4.04 d⁻¹, 0.05 to 1.31 d⁻¹ and 0.04 to 0.50 d⁻¹, respectively. All protozoan isolates appeared to exhibit a low growth rate with *Paramecium* sp. (4.04 d^{-1}) being the isolate with the highest growth of all the protozoan isolates. Peranema sp. was the only isolate that showed the growth rate as being



Fig. 1 Percentage removal of nitrate by test organisms inoculated in the modified wastewater liquor and incubated at 30 °C, pH 6.5 for 4 days in the presence of various concentrations of Ni²⁺. (Initial concentration of nitrate in the mixed liquor: 97.15 mg/L, Positive control: Flask with 0 mg-Ni²⁺/L and inoculated with test isolates).



higher than its respective positive control (1.98 d^{-1}) in culture media containing 10 Ni²⁺.

Furthermore, protozoan isolates exposed to Ni²⁺ appeared to be sensitive when comparing their growth to that of respective positive controls (fig. 3). After one day of incubation, a significant percentage die-off rate of 46.41 % was revealed in the modified wastewater mixed liquor inoculated with *Peranema* sp. (24 h-LC₅₀: 50 mg-Ni²⁺/L), while *Paramecium* sp., *Trachelophyllum* sp. and *Aspidisca sp* showed die-off rate of approximately 38.12 % (24 h-LC₅₀ between 40–50 mg-Ni²⁺/L), 62.62 % (24 h-LC₅₀ between 30–40 mg-Ni²⁺/L) and 62.94 % (24 h-LC₅₀ between 20–30 mg-Ni²⁺/L), respectively.

As evident in Table 1, all test isolates were able to remove Ni²⁺ from the modified wastewater mixed liquor. Whereas, a general decrease of Ni²⁺ removal was observed throughout the experimental study in the mixed liquor. Similarly to the removal of nutrients, the Ni²⁺ removal ability of isolates appeared to decrease with an increase in the Ni²⁺ concen-

Ni ²⁺ , mg/L	Peranema	Paramecium	Tachelophyllum	Aspidisca
10	84.02	85.69	79.36	45.98
20	79	82.31	45.65	35.32
30	75.3	79.65	26.25	30.28
40	67	70.69	11.29	5.32
50	65.32	69.32	3.68	1.78

Table 1 Average percentage removal of nickel inthe modified wastewater mixed liquor incubatedat 30 °C, pH 6.5 (n=3)

tration in the culture media. *Paramecium* sp. (85.69 %) was the protozoan isolates with the highest percentage removal of Ni²⁺ in the culture media, followed by *Peranema* sp. (84.02 %). However, *Aspidisca* sp. could not remove more than 50 % of the Ni²⁺, with the highest (45.98 %) removal rate being from the wastewater mixed liquor containing 10 mg-Ni²⁺/L.

For COD variation (Table 2), a general increase in COD concentrations was observed in the mixed liquor without Ni^{2+} (positive control) and the mixed liquor treated with Ni^{2+} . However, COD concentration gradually decreased with the gradual increase of Ni^{2+} in the treated mixed liquor media. In the mixed liquor media without Ni^{2+} , COD concentration varied from 267.8 to 916.64 mg/L for *Peranema* sp., 281.28 to 903.52 mg/L for *Paramecium* sp., 274.04 to 560.88 mg/L for *Trachelophyllum* sp. and 257.98 to 604.32 mg/L for *Aspidisca* sp.

While in the mixed liquor media with Ni²⁺, the COD concentration varied from 219.04 to 968.32 mg/L (increase: 366.08 %) for *Peranema* sp., 226.88 to 937.6 mg/L (increase: 335.56 %) for *Paramecium* sp., 231.98 to

464.96 mg/L (increase: 204.32 %) for Trachelophyllum sp. and 199.17 to 541.04 mg/L (increase: 218.22 %) for Aspidisca sp. A significant difference was noted between the COD variation in the treated and untreated mixed liquor media with Peranema sp. and Paramecium sp. exhibiting a higher COD increase in the treated sample than in the untreated ones (positive controls). An overall observation of COD variation in the treated mixed liquor revealed the highest COD increase in mixed liquor with 10 mg-Ni²⁺/L. Moreover, the antimicrobial action of Ni²⁺ was evident by the decrease of DO uptake with the gradual increase of Ni²⁺ concentrations (Table 3). In the untreated mixed liquor (positive controls), the DO-percentage uptake varied from 0 to 91.14 % for Peranema sp., 0 to 95.85 % for Paramecium sp., 0 to 65.97 % for Trachelophyllum sp. and o to 43.93 % for Aspidisca sp.

However, in the mixed liquor media with Ni²⁺, the DO-percentage uptake varied from 0 to 97.58 % for *Peranema* sp., 0 to 86.18 % for *Paramecium* sp., 0 to 52.34 for 68.84 % for *Trachelophyllum* sp. and 0 to 41.27 % for *Aspidisca* sp. In general, the test isolates were able to remove above 50 % of DO in the culture media containing low Ni²⁺ concentrations with exception of *Aspidisca* sp (41.27 %).

A slight difference (p>0.05) however, was observed in the DO uptake by the positive controls and the mixed liquor treated with 10 mg-Ni²⁺/L. No explanation could be given for *Tachelophyllum* sp. displaying a higher DOpercentage uptake in the mixed liquor con-

Ni ²⁺ , mg/L	Peranema		Paramecium		Tacheloph	yllum	Aspidisca	
	Initial	final	Initial	Final	Intial	Final	Initial	Final
0	267.8	916.64	281.28	903.52	274.04	560.88	257.98	604.32
10	231.76	968.32	303.04	937.6	236.87	464.96	295.53	541.04
20	276.56	715.92	226.88	701.04	254.98	528.56	199.93	416.56
30	219.04	724.32	278	647.83	314.74	394.88	237.01	267.6
40	291.21	368.32	276.64	297.63	231.98	316.64	199.17	245.12
50	300.69	282.56	300.64	280.75	234.98	280.32	298.01	297.52
50	300.09	202.30	300.04	200.75	234.90	200.32	296.01	297.52

Table 2 Average concentration of COD release in the modified wastewater mixed liquor incubated at30 °C, pH 6.5 (n=3).

Ni ²⁺ , mg/L	Peranema	Paramecium	Tachelophyllum	Aspidisca	
0	91.14	95.85	65.97	43.94	Table 3 Average percentage
10	97.58	86.18	52.34	41.27	of DO untake in the modi-
20	54.38	47.05	68.84	40.76	fied wastewater mixed
30	55	46.26	36.79	37.07	liquor incubated at 20 °C
40	29.67	27.05	28.7	30.8	$\frac{11}{10} \frac{1}{10} $
50	14.16	33.18	2.25	15.11	рн 6.5 (<i>n=3)</i> .

taining 20 mg-Ni²⁺/L when compared to other concentrations and their specific positive control. *Peranema* sp. was the only isolate able to reach a 50 % of DO removal in the samples containing 30 mg-Ni²⁺/L. Findings of the present study corroborate those of Awasthi and Rai (2005), who investigated the toxicity of Ni²⁺ and Cd²⁺ to nitrate uptake in free and immobilised cells of *Scenedesmus quadricauda*. Tsai *et al.* (2006) pointed out that Cd²⁺ at 2 mg/L could affect the biological reaction of phosphate removal, while at 5 mg/L, the Cd²⁺ removal efficiency of total nitrogen and nitrification dropped substantially.

Conclusion

The overall aim of the study was to assess the effect of Ni²⁺ on the simultaneous uptake of nitrate and phosphate by indigenous protozoan isolates. Nickel antimicrobial action negatively affects the nutrient-uptake ability of all the protozoan isolates. Nitrate and phosphate removal appears to gradually decrease with a gradual increase of Ni²⁺ concentrations in the modified wastewater mixed liquor over the period of exposure. Peranema sp. was the isolate with the highest removal efficiency of nutrients. At 10 mg/L, Ni²⁺ could enhance the nutrient-removal ability of Peranema sp. Nickel uptake is also observed in the modified wastewater mixed liquor with Paramecium sp. (85.69 %) which demonstrates the highest uptake compared to other protozoan isolates. This study suggests that protozoan isolates, especially Peranema sp., is a potential candidate for the bioremediation of pollutants such as nitrate and phosphate in mine water containing Ni²⁺. Further studies are needed to identify more protozoan species able to simultaneously remove nutrients and metals during the treatment of wastewater.

References

- Akpor OB, Momba MN, Okonkwo JO (2008) Protozoan biomass relation to nutrient and chemical oxygen demand removal activated sludge mixed liquor. Biotechnol J. 3(8): 1083–1087.
- APHA (2001) Standard methods for the examination of water and wastewater. 20th ed. American Public Health Association (APHA), Washington DC.
- Awasthi M, Rai LC (2005) Toxicity of nickel, zinc, and cadmium to nitrte uptake in free and immobilized cells of Scenedesmus quadricauda. Ecotox Environ Safe 61(2): 268–272.
- Kamika I, Momba MNB (2011) Comparing the tolerance limits of selected bacterial and protozoan species to nickel in wastewater systems. Sci Total Environ 410: 172–181.
- Ochoa-Herrera V, Leon G, Banihani Q, Field JA, Sierra-Alvarez R (2011) Toxicity of copper ions to microorganisms in biological wastewater treatment systems. Sci Total Environ 412: 380–385.
- Peng X, Murphy T, Holden NM (2008) Evaluation of the effect of temperature on the die-off rate for Cryptosporidium parvum oocycts in water, soils, and feces. Appl Environ Microbiol 74(23): 7101–7107.
- Tsai Y-P, You S-J, Pai T-Y, Chen K-W (2006) Effect of Cd(II) on different bacterial species present in a single sludge activated sludge process for carbon and nutrient removal. J Environ Eng 132(2): 173–180.

Leaching pattern of metals from historic sulphidic mine waste upon addition of bark compost

Stefan Karlsson, Viktor Sjöberg, Anna Grandin, Bert Allard

Man-Technology-Environment Research Centre. Örebro University, 701 82 Örebro, Sweden, stefan.karlsson@oru.se

Abstract The drainage water from pot experiments where Agrostis capillaris was grown on a mixture of 70 % (volume) sulphidic mine waste and 30 % (volume) bark compost was monitored for general hydrochemical parameters, dissolved metals and organic carbon during two years. During the first months there was a significant release of DOC from the bark compost that decreased from 80 mg L^{-1} to 10 mg L^{-1} at week 1 and 14, respectively. During the second year the DOC remained at some 10 mg L^{-1} . In the early stage the DOC consisted of molecules in both the fulvic acid size range (80 % of DOC concentration) and that of humic acids (20 % of DOC concentration). The quantitative impact of the humic substances was indicated by correlation coefficients larger than 0.9 with several metals (Al, Cd, Cu, Fe, K, Mg, Mn, Na, Ni and Zn) and principal anions (Cl⁻ and F⁻). For SO_4^{2-} , Ca and Pb there was no or weak correlation with DOC and their concentrations increased with time. The change in pH from 3.7 to 4.2 during the time of the study would have had a limited impact on the stability of any metal humic complexes. Hence the lowered metal mobility is attributed to adsorption of the metal-fulvate complexes. These results illustrate that addition of bark compost and its leachable humic substances influence the mobility of metals from the sulphidic mine waste but not always in a theoretically predictable manner. Hence, the properties of an organic additive should be determined experimentally before use.

Keywords Historic sulphidic mine waste, grass cover, solution chemistry

Introduction

In Sweden historic sulphidic mine waste is a common problem because of a mining history that began almost some 1000 years ago, although the highest amount was produced after circa 1700. Although "historic" is a relative term it usually refers to waste that was produced before the Second World War. The typical site is small (some ha), with a high metal content (usually %) and acid generating potential and it is found far from modern infrastructure such as roads and electricity (SEPA 2013). This combination makes it very costly to use the standard procedures with either dry or wet covers why other strategies are required. Among these, the establishing of vegetation covers is probably a good alternative since it would stabilize the surface from erosion and reduce infiltration of rain water (Ahn *et al.* 2011; Nathanail and Bardos 2004). With this approach it is difficult to fully prevent the production of leachate so it is probably necessary to include some kind of passive water treatment system with long term sustainability. However, just reducing the production of contaminated water might be sufficient on many sites.

In boreal environments the impact of local climate must be added to the more common challenges such as low water holding capacity and limited access to nutrients in the waste. In central Sweden, where the majority of small waste piles are found, the soil is frozen from mid-November until early May. In addition, in late autumn and early spring there are several weeks with daily cycles of freezing and thawing which adds another stress factor to vegetation. Also summer poses some serious threats. The waste sites are usually free from all kind of vegetation why temperatures around 60-70 °C are reached at solar noon on a typical summer's day. At night it is not too uncommon to find frost, at least until the end of June. Finally, the toxic properties of the waste must be considered.

In this harsh environment we are evaluating how the UMBRELLA concept (UMBRELLA 2013) performs when establishing a grass cover with Agrostis capillaris var. metallica and if growth can be sustained over several seasons. In brief, this strategy uses an optimized assembly of microorganisms to supply the plants with nutrients. No fertilizers or biocides are used why a minimum of maintenance is required. In principle, this approach is also suitable for phyto-extraction and stabilization. Because of the poor conditions for growth in the material from the Ljusnarsberg mine waste site (Sartz 2010) that served as the substrate in this study we evaluated the impact of increased water holding capacity by mixing it with compost and addition of carbonaceous refuse in the root zone. During the first growth season in 2011 the plants survived although the growth was quite limited (Karlsson et al. 2012a, b). The best growth was found in a treatment with water works granules combined with mycorrhiza. Concentrations of dissolved organic carbon and all metals studied, except calcium and lead, decreased with up to one order of magnitude. Here we report on the composition of the solution phase with focus on organic constituents and metal concentrations as a function of treatment during the first two years of the experiment.

Methods

The methodology that was used in this study has been described elsewhere (Karlsson et al. 2012b) but a summary is given here for the readers' convenience. Sieved (< 5 mm) mine waste from the Ljusnarsberg mine site, Sweden, was mixed with commercially available bark compost by 30 % (volume) to improve its water holding capacity. After homogenization the mixture was put in ordinary plastic flower pots. Each pot contained some 1.8 L of the substrate and all amendments were mixed into the top 5 cm, according to table 1. The amendments consisted of i) mycorrhiza for improved nutrient availability; ii) water works granules (wwg; Ca/Mg carbonate from water softening) to increase pH in the root zone and iii) Aspen (Populus tremula) shavings to support the heterotrophic community of microorganisms. The pots were sown with Agrostis capillaris and put outdoor. Water was administered weekly (10 mm) during dry periods. Sampling of the drain water was made after rain falls or watering. The samples were frozen immediately.

The analytical protocol included electrical conductivity, pH, principal anions (Ion chromatography) and metals (ICP-MS; Agilent 7500 cx). Dissolved organic constituents were analyzed as: i) Total organic carbon (TOC) with a Shimadzu TOC-V CPH instrument; ii) Molecular weight distribution by size exclusion chromatography (Toso Haas TSKgel 2000 SW and Agilent SEC-5 columns) and iii) as low molecu-

Treatment	Function	Material
1	Reference	No additions
2	Increase pH	Water works granules (wwg)
3	Nutrient availability (reference)	Mycorrhizaª, dead
4	Nutrient availability	Mycorrhiza ^a
5	Nutrient availability and pH (reference)	Mycorrhiza ^a (dead) and wwg
6	Nutrient availability and pH	Mycorrhiza ^a and wwg
7	Easily accessible carbon	Aspen (Populus tremula) shavings

^a Kindly provided by Prof K Turnau, Jagiellonian University, Krakow, Poland

Table 1 Additives in the pot experiments.

	El Cond.	pН	F-	Cl-	SO42-	Na	Mg	Al
	mS cm ⁻¹		mg L-1					
Mine waste	2.40	3.22	98.0		2275	1.18	95.6	59.6
Compost	0.57	7.20		113	21	29.3	12.2	0.40
	К	Са	Mn	Fe	Cu	Zn	Cd	Pb
	mg L-1	mg L-1	mg L-1	mg L-1	mg L-1	mg L-1	μg L-1	mg L-1
Mine waste	1.2	547	11.9	3.72	8.92	133	391	1.20
Compost	96.4	59.4	0.10	0.05	0.09	0.06	0.30	0.02

Table 2 General composition of water extracts (L/S 10) of mine waste and bark compost.

lar weight carboxylic acids (Dahlén *et al.* 2000). All chromatograms and interpherograms were evaluated manually.

Results and discussion

The composition of the leachate water from the waste has previously been determined in long term leaching systems on the field site (Sartz 2010) as well as in several short term leaching with water at a liquid to solid ratio (L/S) of 10 (table 2).

It is evident that the two materials released different concentrations of all ions and that the compost buffered pH at near neutral. The concentrations of DOC in the leachate from the compost had a concentration around 100 mg L⁻¹ whereas those from the mine waste were below detection, i.e. lower than 0.05 mg L⁻¹. From the long term leaching experiments on the field site DOC concentrations varied from below the limit of detection to some 1 mg L⁻¹. The origin of this DOC is uncertain but high microbial weathering activity might release organic carbon. However, it is fair to conclude that the pot systems discussed here are influenced by the compost not only concerning the water holding capacity but also from qualitative features of the released DOC.

The quality of the DOC in the water leaching experiment, according to the SEC analysis, was dominated by two size classes. Average molecular weight estimates, UV/Vis spectra and SUVA index as well as their fluorescence spectra indicate the presence of humic and fulvic acids. Since these estimators are not definitive, the presence of *e.g.* peptides and proteins in these size ranges is possible. The absolute concentrations of the two humic substances were not determined since it involves a rather extensive procedure for cleanup but their absorbance properties indicate a ratio of 20 % and 80 % of humic and fulvic compounds, respectively.

The compost also released low molecular weight organic compounds (LMWOC) in the water leaching but at a rather low DOC concentrations, seldom more than 1 mg L⁻¹. Screening with CE showed that this fraction was dominated by acetic acid, possibly indicating that the compost had been stored in plastic bags until it was bought.

Both the compost itself and the released DOC had a large impact on metal distribution (Karlsson *et al.* 2013; Sjöberg *et al.* 2013) by adsorption to the solid matter as well as complexation in the solution phase. Hence, the qualitative impact in the pot experiments can be expected to influence not only adsorption controlled metal distribution but also solubility equilibria.

In the pot experiments all systems behaved in a similar way and there was a high release of ions during the first weeks, as illustrated by the electrical conductivity (Fig. 1). During the following weeks the ion content of the solution phases were approximately halved, and then returned to their initial levels during the second summer. The large decrease in July 2012 illustrates the impact of heavy rain events, resulting in a temporary dilution.

DOC behaved in a different manner and no increase was found during the second summer (Fig. 1). Instead the concentrations remained at some 10 mg L^{-1} , just as at the end of



Fig. 1 Electrical conductivity (mS cm⁻¹) and DOC (mg L⁻¹) as a function of time in treatments 1 and 6.

the first summer. The reasons are not clear in detail but it is likely that heterotrophic microbial activity released the DOC at this steady state concentrations. The quality of the DOC has also changed and no humic acid sized compounds could be detected. Instead the LMWOC fraction increased up to some 5 mg L⁻¹ C and contained several carboxylic acids indicative of heterotrophic activity.

In many acidic mine waters there is a high correlation between electrical conductivity and element concentrations in the dissolved phase and so is the case for the long term leaching experiments of this mine waste (Sartz 2010). In the pot experiments, however, a different pattern of correlations emerged (Table 3). The correlation coefficients between the dissolved metal concentrations and the electrical conductivity are essentially lower than those for DOC. This pattern was also found for the dominating mineral forming elements such as aluminum and iron. Calcium and lead behaved differently and their concentrations followed more the development of electrical conductivity. These results illustrate that the electrical conductivity is a poor estimator for the concentrations of dissolved metals when sulphidic mine waste is mixed with bark compost.

Among the most toxic elements discussed here lowered concentrations were found for Cu, Zn and Cd but also Ni behaved in a similar way, contrary to the development of electrical conductivity. The concentrations of



Fig. 2 Concentrations ($\mu g L^{-1}$) of copper and zinc as a function of time in treatments 1 and 6.

uranium were lowered but its relationship to DOC was less evident than for the previous elements. Geological modeling indicated undersaturation of all transition elements and aluminum whereas the concentrations of Pb were influenced by formation of anglesite. The

	El.cond.	DOC	Na	Mg	Al	К	Са	Fe	Mn	Cu	Zn	Cd
El.cond.	1											
DOC	0.52	1										
Na	0.49	0.92	1									
Mg	0.55	0.98	0.95	1								
Al	0.64	0.90	0.86	0.90	1							
К	0.60	0.95	0.95	0.96	0.89	1						
Са	-0.37	-0.38	-0.42	-0.39	-0.21	033	1					
Fe	0.77	0.85	0.71	0.82	0.80	0.74	-0.36	1				
Mn	0.51	0.97	0.96	0.99	0.90	0.96	-0.36	080	1			
Cu	0.78	0.86	0.77	0.87	0.92	0.80	-0.22	090	0.87	1		
Zn	0.84	0.95	0.92	0.98	0.96	0.95	-0.28	078	0.98	0.89	1	
Cd	0.52	0.93	0.92	0.95	0.94	0.92	-0.20	076	0.97	0.90	0.99	1
Pb	0.26	-0.40	-0.44	-0.44	0.23	-0.33	0.81	-027	-0.47	-0.10	-0.18	-0.42

Table 3 Correlation coefficients for some quality parameters for all treatments in leachates 2011-2012.

Wolkersdorfer, Brown & Figueroa (Editors)



Fig. 3 Concentrations ($\mu g L^{-1}$) of aluminum and iron as a function of time in treatments 1 and 6.

modeling also indicated a high impact of their respective fulvate complexes. Assuming that the humic substances have an average carbon content of 50 % and a cation-exchange capacity of 10 meq g⁻¹ they accounted for a complexing capacity in the range of 5 – 50 meq L⁻¹. Such complexes have a highly different pH dependent adsorption. In general, adsorption is increased in the low pH range but lowered in the high pH range. Hence, under the solution conditions in this study there are reasons to assume a lower mobility of these complexes through adsorption.

At present the nature of the adsorbing phase is not known. The mine waste itself is a complex mixture of primary and secondary minerals, including silicates and oxides and would require a thorough characterization in order to estimate its pH dependent adsorption capacity. In general, (hydr)oxide surfaces would mainly carry a positive pH dependent charge under the conditions in this study why adsorption of negatively charged fulvate complexes would be enhanced (Stumm 1992). The conditions are more complex concerning the silicates.

Preliminary studies on the properties of the bark compost indicate a specific adsorption capacity of Cu(II) in the range of 0.1 meq g^{-1} at pH 5. A slightly lower capacity was found for zinc while for lead it was only 0.001 meq g^{-1} . These findings support the observations from the pot experiments where the lead concentrations increased with time. The speciation of both copper and lead in the solution phase would be dominated by their complexes with humic substances according to geochemical modeling. At this point of the study the only plausible explanation for their different behavior would be that they associate with organic ligands that are retained differently in the substrate. Hence, more attention is paid to the chemical properties of potential organic ligands but also to their physical stability. In the pot experiments the ionic strength, and particular the calcium concentrations, are high enough to induce coagulation/aggregation of high molecular humic substances. Therefore also the potential physical entrapment of the carrier phases must be evaluated

After the first summer the different treatments had very limited impact on the composition of the leachates and the bark compost dominated the composition (Karlsson *et al.* 2012a b). During the second summer there are indications for more complex quality differences of the DOC between the treatments. In general there is a tendency for a higher abundance of metabolically derived LMWOC. This raises the question whether they originate from microbial decomposition of the compost that would limit the systems adsorption capacities.

Conclusions

The UMBRELLA concept proved to sustain the growth of Agrostis capillaris on historic sulphidic mine waste, so far for a minimum of two seasons. Addition of bark compost lowered the concentrations of dissolved Al, Cd, Cu, Fe, Mn, Ni and Zn significantly. The DOC concentrations governed the behavior of the elements and the major component in the DOC had a molecular weight in the fulvic acid range. The concentrations of Ca and Pb increased nearly to those in leachates from unamended waste.

Acknowledgements

The authors express their gratitude to all participants in the UMBRELLA project for valuable cooperation. The study was by financed by FP7 contract 226870.

References

- Ahn JS, Song H, Yim GJ, Ji SW, Kim JG (2011) An engineered cover system for mine tailings using a hardpan layer: A solidification/stabilization method for layer and field performance evaluation. J Hazard Mater 197:153-160
- Dahlén J, Hagberg J, Karlsson S (2000) Analysis of low molecular weight organic acids in water with capillary zone electrophoresis employing indirect photometric detection. Fresenius Journal of Analytical Chemistry, 366:488-493
- Karlsson S, Sjöberg V, Grandin A, Allard B (2012a) Revegetation of historic acidic mine waste with Agrostis capillaris – Impact on leachate composition in pot experiments. In In McCullough CD, Lund MA, Wyse L (Eds.) International Mine Water Symposium, Bunbury, Australia, p 489-497
- Karlsson S, Sjöberg V, Grandin A, Allard B (2012b) Revegetation of historic acidic mine waste with Agrostis capillaris – Remediation strategy. In McCullough CD, Lund MA, Wyse L (Eds.) International Mine Water Symposium, Bunbury, Australia, p 317-325
- Nathanail CP, Bardos RP (2004) Reclamation of contaminated land. Wiley and Sons Ltd., 238 pp
- Sartz L (2010) Alkaline by-products as amendments for remediation of historic mine sites. Örebro Studies in Environmental Science 15, Dissertation, Örebro University, Sweden
- SEPA (2013) http://www.naturvardsverket.se/upload/ sa-mar-miljon/mark/avfall/Inventering-av-gruvor/Forteckning-nedlagda-anlggningar-120427.pdf.
- Sjöberg V, Karlsson S, Grandin A, Allard B (2013) Establishing Agrostis capillaris on historic sulphidic mine waste – Impact on solution chemistry (submitted)
- Stumm W (1992) Chemistry of the solid-water interface. Wiley, 428 pp
- UMBRELLA (2013) http://www.umbrella.uni-jena.de/ cms/index.php?option=com content&view=article&id=3&Itemid=11

A Global Perspective on Boron Removal: Treatment Technologies and Practical Applications

Karla Kinser¹, Stephanie Sansom², Douglas S. Oliver³

¹MWH Global 1801 California Street, Suite 2900, Denver, Colorado 80202, USA, karla.j.kinser@mwhglobal.com ² MWH Global 1801 California Street, Suite 2900, Denver, Colorado 80202, USA, stephanie.j.sansom@mwhglobal.com ³Rio Tinto Technology and Innovation 4700 Daybreak Parkway, South Jordan, Utah 84095, USA, douglas.oliver@riotinto.com

Abstract Proposed mining of a borate orebody has led to increased investigation into water treatment options for pumped mine water with high concentrations of boron and arsenic. Concentrations of boron vary by region, but can be found as high as 1,000 mg/L or higher at some locations. Although there are a number of technologies that are suitable for removing low boron concentrations (<10 mg/L), these technologies are not always suitable for removing high boron concentrations (>100 mg/L). A literature review was performed to evaluate the most common commercial methods for removing boron from source water. Evaluated technologies include pre- or post-treatment, thermal-based, pressure-driven membrane, electric potential driven membrane and alternative technologies.

Keywords Boron, treatment technologies, mine water, global

Introduction

The purpose of this task was to develop conceptual treatment plans for treatment of water from mining sites. A literature review of various treatment technologies was performed, and a summary proposed for the removal of boron and arsenic from a proposed borate mine, as these compounds are expected to exceed discharge limits significantly. The processes were then used to prepare process flow diagrams and the development of cost estimates.

Boron Deposits

Boron is a relatively rare element, with over 60 % of the world reserves located in Turkey. Boron is also mined in other Eastern European countries (*e.g.* Serbia), along with the United States and South America (Chile, Argentina, Peru and Bolivia), with the largest boron mine located in Boron, California. This mine ac-

counts for nearly half of the world's boron production. After extraction, boron ore is refined and used for the production of glass and ceramics, detergents, semiconductors, magnets and other pharmaceutical and biological applications.

Common borate minerals include borax, ulexite, kernite, ezcurrite, searlesite, and colemanite. These borate minerals are often found in lacustrine and evaporate deposits.

Common Water Quality Issues

The concentration of boron in groundwater in and adjacent to borate deposits is related to the lithology and mineralogy of the area. Often associated with high boron concentrations in these types of deposits, are high concentrations of arsenic, which can be difficult to remove from water. Silica and phosphates are also commonly associated with these deposits, which can cause scaling in treatment processes such as reverse osmosis. Although the act of mining excavation itself does not result in pollution of the groundwater, it is the discharge of this water without additional treatment that can cause detrimental effects to the surrounding environment (Okay *et al.* 1985). Additionally, large volumes of boron and arsenic contaminated water can be generated as a result of dewatering for mining applications.

Treated Water Quality Requirements

Discharge limits vary by region and the endsource location for discharge. A review of the literature yielded varying degrees of required treatment; a limited number of global standards are summarized in Table 1.

Literature Review

A literature review was performed to evaluate the most common commercial methods for removing boron from source water. Evaluated technologies include pre- or post-treatment technologies, thermal-based technologies, pressure-drive membrane technologies, electric potential driven membrane technologies and alternative technologies.

Treatment technologies used for low concentrations of boron (<10 mg/L), include flocculation, sedimentation, oxidation, filtration and advanced treatment processes including ion exchange, reverse osmosis and electrolytic recovery.

Although many of these technologies have been evaluated for the treatment of boron, many of these technologies have only been tested on waters with concentrations as high as 10 mg/L (*e.g.* activated alumina). Additionally, some of these technologies have only been evaluated at the bench scale stage, and require additional testing, either in pilot scale or full scale, prior to being considered a viable technology for the removal of boron (*e.g.* electrocoagulation). Based on a comprehensive literature review, the maximum removal for boron using a variety of process technologies is summarized in Table 2.

Options Evaluation

Three options have were been identified as potential process trains for the treatment of water with high boron concentrations:

- **1.** Softening followed by pH adjustment and reverse osmosis
- **2.** Softening followed by metals precipitation and ion exchange
- **3.** Thermal treatment followed by ion exchange.

Option 1 – Softening/Clarification/Reverse Osmosis

Option 1 includes softening to remove hardness upstream of the RO system to prevent scaling. Softening will be accomplished through lime softening, which will also assist in the removal of boron and other metals like iron and manganese as well as phosphates and silica. The slurry produced by the reaction is contacted to a flocculent and fed to a clarifier for solid/liquid separation. The sludge is collected from the bottom of the clarifier and can be either pumped to a storage area or pressure-filtered to increase its density prior to transport. The combination of lime softening and clarification for pretreatment is extensively used in industrial water treatment applications.

pH will be adjusted upstream of the RO system in order to ensure that all of the boron present in the flow stream is in the borate ion form, which is a highly soluble charged ion, and more easily removed through the membranes (Xu and Jiang 2008). The RO system is a 2-pass system in which permeate from the first pass is sent through an additional set of RO membranes due to the very high boron and arsenic concentrations. RO concentration from both passes of RO will be combined and will require additional treatment prior to disposal.

In addition to boron removal, other constituents of concern, including arsenic,

Parameter (mg/L)	Michigan, United States ¹	WHO (2011 provisional)	South America (Agricultural)	South America (Mining Specific)
Arsenic (As)	0.05	0.01	0.05	0.1 / 0.82
Boron (B)	0.5	2.4	0.56	
Iron (Fe)	2.0		1.0	2.0 / 1.6
Nitrate (NO ₃)	10.0	50.0	10.0	
Nitrite (NO ₂)		3.0	0.06	
Ammonia (NH ₃)	10.0			TBD

1. Kennecott Eagle Minerals 2006

2. Maximum / Yearly Average

Table 1 Global Treatment Requirements for Selected Parameters in Mining

Technology	Boron Removal (%) ¹	Arsenic Removal (%) ²
Lime Softening	60	90
Metals Precipitation	87	95
Adsorption	65	95
Ion Exchange (Basic)	96	95
Ion Exchange (Boron Selective)	99	
Electrodialysis	75	60
Reverse Osmosis	99	60 (as As(III))
		>95 (as As(IV))
Liquid-liquid Extraction		
Electrocoagulation	50 ³ / 99 ⁴	
Evaporation / Crystallization	5	

1. Removal percentages collected from various literature reviews

2. USEPA 2000

3. At bench scale level testing only

4. At concentrations of 100 mg/L and below

5. A set percentage removal was not provided by GE, however it was indicated, via personal correspondence (GE 2012) that an effluent limit of 0.3 could be achieved through thermal treatment

Table 2 Maximum Constituent Removal through Various Technologies

nitrate/nitrite, ammonia/ammonium and iron will also be removed through this proposed treatment train. While iron may be co-precipitated through the lime softening process (the high pH allows iron to oxidize and precipitate out of solution), nitrate/nitrite will be removed through the RO system along with ammonia/ammonium.

Option 2 – Softening/Clarification/Metals Precipitation/Ion Exchange

Option 2 includes softening to remove hardness followed by metals precipitation and ion exchange for polishing.

In addition to boron removal, other constituents of concern, including arsenic, nitrate/nitrite, ammonia/ammonium and



Fig. 1 Option 1 – Proposed Flow Schematic.



Fig. 2 Option 2– Proposed Flow Schematic.



Fig. 3 Option 3 – Proposed Flow Schematic.

iron will also be removed through this proposed treatment train. While iron may be co-precipitated through the lime softening process (the high pH allows iron to oxidize and precipitate out of solution), nitrate/nitrite will be removed through the RO system along with ammonia/ammonium.

Option	CAPEX	OPEX	\$/1,000 L
Option 1 – Softening / Clarification / Reverse Osmosis	\$14,000,000	\$1,950,000	50
Option 2 – Softening / Clarification / Metals Precipitation / Ion Exchange	\$6,100,000	\$1,370,000	23
Option 3 – Ion Exchange / Thermal Treatment	\$18,000,000		

1. "--" = Not calculated

Table 3 Option 1 – Preliminary Cost Estimate

Option 3 – Ion Exchange/Thermal Treatment Option 3 includes ion exchange for softening followed by thermal treatment.

Cost Comparison

The cost estimates for these conceptual designs were based on a Class 5 Opinion of Probable Construction Cost (OPCC) estimate and are summarized in Table 3. These cost estimates assume an influent boron concentration of >100 mg/L at a flow rate of approximately 10 L/s. Although cost estimates for treatment processes for lower influent concentrations are not presented in this report, they are expected to be significantly lower, due to the less complex systems required to achieve discharge limits.

Conclusions

The general conclusion is that a three-step unit process treatment scheme is needed to achieve the set effluent goals. Essentially, on one end of the spectrum is a treatment train based on RO and on the other a train based on precipitation. Thermal processes and IX are both viable options which might offer less labor, less chemical and less generation of waste streams. However, there are a host of unknowns which must be characterized in the water quality, bench-scale testing, and detailed process design to determine if these processes can be applied. None of the treatment train options have previously proved to treat such high levels of boron or arsenic.

References

- Chiara T (2012) Personal communication with GE Water and Process Technologies
- Kennecott Eagle Minerals (2006) Eagle Project Groundwater Discharge Permit Application
- Okay O, Güçlü H, Soner E, Balkaş T (1984) Boron Pollution in the Simav River, Turkey and Various Methods of Boron Removal. Water Res. Vol 19. No. 7. pp 857–862
- Xu Y, Jiang J (2008) Technologies for Boron Removal, Ind. Eng. Chem. Res., 47, 16–24
- United States Environmental Protection Agency (2000) Technologies and Costs for Removal of Arsenic from Drinking Water, EPA 815-R-00-028, December 2000

A comparative study of lime doser treatment

Natalie Alyssa Kruse Daniels¹, Jennifer R. Bowman¹, Amy L. Mackey², Dina Lopez¹

¹Ohio University, Athens, Ohio, United States of America, krusen@ohio.edu ²Raccoon Creek Partnership, Athens, Ohio, United States of America

Keywords active treatment, acid mine drainage, stream recovery, sediment deposition.

Extended Abstract Alkaline dosing is a common treatment strategy in rural areas affected by acidic waters from abandoned mine. The efficacy of these systems is dependent upon many natural and anthropogenic factors. Without a clear understanding of what will lead to either success or failure of a treatment system and what the ultimate goals of the treatment system are, system designs are hit or miss.

In southeastern Ohio, lime dosers have been selected to treat four mining impacted watersheds with varying results. The Carbondale Doser and Jobs Hollow Dosers were both installed in 2004 (NPS 2011), while the Thomas Fork Doser was installed in 2012 and the Pine Run Doser was installed in early 2013. Their siting was determined through a combination of sufficient treatment space, appropriate land ownership or availability, sufficient hydraulic head and consistent flow to drive the doser. The chemical and biological recovery varies between each stream, Carbondale has been the most effective, while lobs has been a mixed success. So far, Thomas Fork has not been consistently effective. The physical and chemical characteristics of each stream (Monday Creek, Hewett Fork and Thomas Fork) were evaluated to determine what leads to success or failure of doser treatment. The stream flow and velocity to transfer the treatment waters, as well as additional acid sources and natural alkalinity sources along the flow path were considered. The lessons learned from this assessment have been used to create a conceptual model for successful treatment. The model has been applied to the newly constructed Pine Run system to assess its potential for success.

Several major factors affect success of treatment in the streams studied. Results suggest that, for successful doser treatment, acid sources must be close together, ensuring that the alkalinity from the doser is transported to the acid sources before secondary minerals are formed or is being consumed prematurely. Sufficient velocity is vital to carry unreacted lime downstream. In systems with insufficient velocity to carry material downstream, lime may build up within the stream channel and not be transported far enough to ameliorate downstream acid sources. A low velocity zone downstream of acid sources allows metal precipitates to settle. In some cases, natural alkalinity sources lead to further recovery and can add as much if not more alkalinity to the stream as a doser.

The Carbondale Doser in Raccoon Creek has been intensively studied (e.g. Kruse et al. 2012) and serves as the foundation for the conceptual model. Carbondale treats three key acid sources, Carbondale Mines, Carbondale Creek and Trace Run. They are clustered within two stream kilometers in the headwaters of Hewett Fork. The stream maintains sufficient power throughout the year to entrain alkaline material long enough to be consumed by the three major acid sources. Downstream of Trace Run, the alkalinity from the doser has been consumed. Further downstream, there are two key features that lead to effective watershed restoration: a low velocity depositional area for metal precipitates and large natural alkalinity sources from groundwater as

well as alkaline tributaries (Kruse *et al.* in review). The analysis presented in Fig. 1 further shows that at the beginning of the dry season in June, a critical time for biological impacts, there is little pH variability downstream of the doser, while in October, at the end of the dry season, large variations can be seen. These variations happen at a less critical time in the life of aquatic fauna that are evaluated during the summer biological sampling index period (K.S. Johnson 2013 personal communication).

Downstream of the Jobs Hollow Doser in the headwaters of the Monday Creek Watershed, there is a short zone of recovery, but large acid sources downstream limit recovery (NPS 2011). The watershed was extensively mined; most tributaries to the mainstem are acid sources. Only one, Little Monday Creek, is a significant alkalinity source and it is approximately 25 km downstream of the Jobs Hollow Doser (e.g. Pool et al. 2013). While sparse data is available, as shown in Fig. 1, the Jobs Doser maintains a near neutral pH in the stream channel at the end of the dry season, as the flow rate and velocity of the stream begin to increase. At the beginning of the dry season, however, low velocity leads to pH variability. This key early summer time period is particularly critical to aquatic life since it is at the beginning of the growing season. Multiple acid sources with few natural alkalinity sources alongside pH variability in early summer limit the effectiveness of the lobs Doser. However, treatment of acid sources in the headwaters is an important strategy for watershed restoration.



Fig. 1 pH profiles downstream of the Carbondale Doser in Hewett Fork (HF), the Jobs Hollow Doser in Monday Creek (MC) and the Thomas Fork Doser in Leading Creek (LC) for the beginning and end of the dry season. The seasonal variability in pH can limit biological recovery, especially when low pH occurs during key times in the lifecycle of aquatic fauna.

The Thomas Fork Doser in the Leading Creek Watershed is plagued by low velocity which does not allow unreacted lime to travel downstream far enough to treat acid sources further downstream. As shown in Fig. 1, when there is insufficient flow at the beginning of the dry season, large pH variability is seen during the critical time period, while at the end of the dry season, there is sufficient stream power to carry the alkaline material downstream and buffer acidity in the Thomas Fork. Beyond the lack of velocity during the dry season, there are several other large acid sources along Thomas Fork that may limit the dosers effectiveness, despite the natural buffering capacity added to the stream by the East Branch of Thomas Fork.

This analysis suggests a conceptual model for success includes: acid sources located close to the doser, sufficient velocity to carry alkaline material, a depositional area downstream of acidity sources to collect metal precipitates and additional alkalinity sources.

The Pine Run Doser, in the West Branch of Sunday Creek, that was installed in early 2013 may not be effective based on the conceptual model developed here. The site is plagued by insufficient flow which is unlikely to carry lime downstream to treat the multiple acid sources located downstream in Pine Run making the stated goal of treatment ambitious (Shaw 2011). The buffering capacity added to the system by the doser may, however, accrue positive results many kilometers downstream due to additional treatment systems in the West Branch of Sunday Creek.

This study has allowed for better understanding of additional factors that ought to be considered when siting a doser. The conceptual model can be applied to siting and design of treatment to maximize recovery.

References

- Kruse NK, Bowman JR, Mackey AL, McCament B, Johnson KS (2012) The lasting impacts of offline periods in lime dosed streams: A case study in Raccoon Creek, Ohio. Mine Water and the Environment 31(4):266-272
- Kruse NK, DeRose L, Korenowsky R. Bowman JR, Lopez DL, Johnson KL, Rankin E (in review) The role of remediation, natural alkalinity sources and physical parameters in stream recovery. Journal of Environmental Management
- NPS (2011) 2011 Non-Point Source (NPS) Monitoring Project for Acid Mine Drainage. Voinovich School of Leadership and Public Affairs, Ohio University.
- Pool JR, Kruse NA, Vis ML (2013) Assessment of mine drainage remediated streams using diatom assemblages and biofilm enzyme activities. Hydrobiologia 709:101–116
- Shaw M (2011) Pine Run Characterization and Treatment Exploration Project. Unpublished Masters Thesis, Ohio University, Athens, Ohio, USA.

Habitat and watershed characteristics that limit stream recovery after acid mine drainage treatment

Natalie Alyssa Kruse Daniels¹, Kelly S Johnson², Jennifer Bowman¹

¹Voinovich School of Leadership and Public Affairs, Ohio University, Athens, Ohio, USA, krusen@ohio.edu ²Department of Biological Sciences, Ohio University, Athens, Ohio, USA

Abstract Treatment of acid mine drainage (AMD) often meets with mixed results. Recovery of chemical quality is not always sufficient for recovery of macroinvertebrates and fish. Mixing zones downstream of treatment systems, episodic acidification and habitat degradation can limit biological recovery. Here, we report on three streams impacted by AMD that have been monitored for chemistry and biology for a decade. Improvement or limited improvement has been seen in the biological quality of Monday Creek and Raccoon Creek, but no change has been seen in Huff Run. This paper suggests mechanisms for these differences and provides recommendations for prioritizing treatment expenditure.

Keywords biological recovery, coal mine, mine reclamation, stream restoration

Introduction

A key aim of acid mine drainage (AMD) treatment and mine land reclamation is the restoration of the ecosystems damaged by mining. While this may remain an overarching goal, it is not always a result of specific AMD treatments, which typically focus primarily on water chemistry targets (NPS 2011). While chemical water quality targets are both valid and necessary, they only reveal the quality at the moment that the sample is taken. Biological quality, however, more fully integrates the chemical, physical and functional aspects of the aquatic ecosystem. Good chemical water quality is not always enough to achieve biological recovery. In Ohio, the goal of AMD treatment in the coal bearing region of Ohio is full attainment of Warm Water Habitat (WWH) use designation. WWH represents the biological community expected to be present in the 25th percentile of reference sites that do not support cold water taxa (i.e. salmon, trout). In order to achieve this, both the fish and macroinvertebrate community metrics (Index of Biotic Integrity and Invertebrate Community Index) must meet thresholds developed for each eco-region based on comparison to reference sites (Karr 1981, OEPA 1988).

The abandoned mine land program in Ohio has focused efforts on four watersheds: Raccoon Creek, Monday Creek, Huff Run and Sunday Creek. Each was extensively mined before state or federal regulations were in place (pre-1950's). Over \$22 million has been spent across the four watersheds on reclamation, stream captures and passive and active treatment projects (NPS 2011). The stream kilometers of mainstem recovered in each watershed, in terms of water chemistry and biological quality, varies, with greater success in some watersheds than others.

The purpose of this analysis it to use these patterns of recovery to suggest factors that lead to successful AMD treatment and those that limit stream recovery. Specifically, the role of in-stream physical habitat, the abundance and location of acid sources and their treatments, and the role of natural alkalinity sources will be examined. We focused on the mainstem sections of the watershed for ease of comparison. These 'lessons-learned' can be used to prioritize treatment dollars to maximize stream miles restored.

Methods

Three watersheds (fig. 1) were assessed to determine factors that limit stream recovery.

While \$1.9 million has been spent in the fourth watershed, Sunday Creek, it is not included in this analysis because two large mine discharges remain untreated and impact a large portion of the watershed biology.

Raccoon Creek flows through six counties in southern Ohio, Hocking, Athens, Vinton, Jackson, Gallia and Meigs, and drains directly to the Ohio River in Gallia County. The mainstem of Raccoon Creek is 180 km long and the watershed drains 1,771 m². Approximately 20,000 ha of the watershed were mined for coal; about half the mines were underground mines and half were surface mines. The majority of the mines were abandoned before reclamation laws were in place. Abandoned mines in the watershed are concentrated in the headwaters of Raccoon Creek and in the Little Raccoon Creek subwatershed (NPS 2011).

Monday Creek flows through Athens, Hocking and Perry Counties to its confluence with the Hocking River. The mainstem is 43.5 km long and the watershed drains 300 m² of land. The watershed was extensively mined for coal. Major acid sources to the mainstem include Lost Run, Snake Hollow and Snow Fork (NPS 2011).

Huff Run flows through Carroll and Tuscarawas Counties in Eastern Ohio to its confluence with Conotton Creek just south of Mineral City, Ohio. The mainstem of Huff Run is short, only 16 km long and the watershed covers 36 m². The downstream two thirds of the watershed (west of State Route 542) has been extensively mined for coal and some limestone and clay. In addition to AMD, Huff Run is impaired from agricultural runoff, untreated sewage and poor riparian buffers (NPS 2011).

The number of stream kilometers in each watershed meeting two targets, full biological attainment and pH > 6.5, in 2009, are shown in Table 1. Biological attainment was estimated from scores from a rapid macroinvertebrate bioassessment metric, the Macroinvertebrate

Aggregate Index for Streams (MAIS; Smith and Voshell 1997). A MAIS score of '12' is a good estimator of the biological quality needed to meet Warm Water Habitat criteria (Johnson 2009).

To more accurately measure biological improvement, linear regression analysis of MAIS scores from baseline conditions (2001 in Monday Creek 2005 in Raccoon Creek and 2005 in Huff Run) to 2011 conditions were performed. Sites were designated as 'improved' if they received a positive regression score significant a p < 0.05, and 'somewhat improved' if the significance of the regression was between p < 0.05 and p < 0.10. After the streams were determined to be successfully recovered or recovering using full attainment of WWH based on IBI and ICI scores, where available, and MAIS scores as metrics, the following factors were compared to find which were the most closely associated with stream recovery:

- Habitat (using the Qualitative Habitat Evaluation Index (QHEI); Rankin 1989);
- Abundance and Location of Acid Sources
- Abundance and Location of Natural Alkalinity Sources
- Stream Kilometers Downstream of Acid Sources and Treatment Systems
- Proximity of Treatment Systems to Mainstem
- Known Acidification Events

Results and Discussion

As shown in Table 1, the level of success of watershed-scale treatment varied among the watersheds assessed. Both Raccoon Creek and Huff Run have a large percentage of stream kilometers achieving the pH target of 6.5, while Monday Creek has fewer stream kilometers meeting the pH target. This difference is due to several factors. Mining in Raccoon Creek Watershed was concentrated in Little Raccoon Creek and the headwaters of Raccoon Creek; this has allowed for clustered treatment projects with many kilometers of stream to accrue the benefits of treatment. In Huff Run,

Watershed	Projects	Total Costs	Total Acid Load Reduction (kg/d)	km Meeting WWH	km Meeting pH Target	km Monitored	Mean Mainstem QHEI
Raccoon Creek	14	\$9,710,495	2,461	67.1	166	188	65
Monday Creek	18	\$5,871,172	1,762	0	34	61	68.5
Huff Run	12	\$4,678,279	439	0	16	16	62

Table 1 Summary of stream recovery in three watersheds evaluated in 2011: Raccoon Creek, MondayCreek, and Huff Run (NPS 2011).



Fig. 1 Watershed maps depicting treatment and reclamation project locations with red stars, a) Raccoon Creek, b) Monday Creek, c) Huff Run. Scales are not consistent between maps (NPS 2011).

mining was all to the west of highway 542 (fig. 1c), impacting about 10 km of stream, within those 10 km, 12 projects have been installed to ameliorate AMD. This has allowed for successful pH adjustment in the mainstem of Huff Run. Monday Creek, on the other hand, has significant acid sources in virtually every tributary, some of which are treated and some remain either partially or fully untreated (NPS 2011).

Despite pH improvement, attainment of biological recovery goals has not been consistent. As shown in Table 1, neither Monday Creek nor Huff Run has had any stream kilometers of the mainstem meeting full attainment status, whereas over 67 km of Raccoon Creek now meet WWH status (NPS 2011). While none of the mainstem sites in Monday Creek are in full attainment of WWH, nine of the thirteen mainstream sites assessed using the MAIS show statistically significant improvement, while one shows slight improvement, between the 2001 baseline and 2011. The seven sites assessed on the mainstem of Huff Run. however, show no significant change in MAIS scores, between the 2005 baseline and 2011, despite nearly \$6 million of investment (fig. 2). In Raccoon Creek, while a large number of stream kilometers now meet WWH designation when compared to the IBI and ICI baseline in 2001, only four of the twelve sites assessed on the mainstem of Raccoon Creek and Little Raccoon Creek have shown significant improvement in MAIS scores between the 2005 baseline and 2011. Nearly half of the stream kilometers that have improved since baseline in Raccoon Creek improved before 2005, so the assessment may be skewed.

It is clear from the analysis that Huff Run has achieved chemical improvement without



Fig. 2 Baseline versus 2011 MAIS scores along the mainstem of Huff Run (NPS 2011).

biological improvement, while Monday Creek has achieved some chemical and some biological improvement and Raccoon Creek has had significant chemical and biological improvement. The mechanisms that drive this difference are varied.

The analysis presented here suggests that the overall habitat assessment used in Ohio. the QHEI (shown in Table 1), suggests that the habitat of the mainstem of Monday Creek is better than Raccoon Creek and Huff Run. In addition, the watersheds have different quantities and locations of natural alkalinity sources-Raccoon Creek has many natural alkalinity sources often downstream of acid sources that lead to some natural attenuation of AMD. Monday Creek has only a few alkaline tributaries that are far outweighed by the acid sources. Huff Run has alkaline sources upstream of the acid sources that, along with treatment projects, leads to circum-neutral pHs and slightly alkaline conditions along the mainstem.

Acid sources in the three watersheds have three spatial patterns. Acid sources in Raccoon Creek are clustered in Little Raccoon Creek and the headwaters of Raccoon Creek; they allow for treatment of water bodies and many kilometers of stream in which to accrue the biological benefits of chemical improvement. Acid sources in Monday Creek are distributed throughout nearly every tributary; there is some improvement downstream of treatment and reclamation projects, but it is not continuous due to continued acidification. In Huff Run, the acid sources are clustered in the lower two-thirds of the watershed in tributaries, but in close proximity to the mainstem.

Treatment projects installed in each watershed have varied proximity to the mainstem of each watershed (fig. 1). In Raccoon Creek and Monday Creek, the watersheds are larger with longer tributaries. The treatment projects are installed in the tributaries with stream reaches in which metal precipitates deposit rather than introducing precipitates to the mainstem. The furthest downstream treatment project in Raccoon Creek is 91.2 km upstream of the mouth. while the furthest downstream treatment project in Monday Creek is in a tributary, 4.5 km upstream of the mouth. The tributaries in Huff Run Watershed are shorter due to the narrow shape of the watershed; by necessity, the treatment projects are located close to the mainstem or on the mainstem and clustered in the lower reaches of the watershed: the furthest downstream treatment project is on the mainstem, only 2 km from the mouth. This can lead to both sedimentation and periodic acidification of the mainstem of the watershed, limiting biological recovery. The short length of the mainstem of Huff Run means that there is no space in which to accrue the benefits of treatment within Huff Run and the receiving stream Conotton Creek is impounded along its length and has had historically poor biological quality that does not further deteriorate downstream of Huff Run. Conotton Creek's poor biological community may restrict recolonization of Huff Run

Conclusions

The mechanisms for improvement and limitations on recovery vary by watershed. In Monday Creek watershed, \$5.8 million of treatment has been installed, including 18 projects with an acid load reduction of 1762 kg/d. The major acid sources in Monday Creek are in tributaries and are found along all 43 stream kilometers. In Raccoon Creek watershed, \$9.7 million of treatment was installed by 2011, including 14 projects with an acid load reduction of 2461 kg/d. The major acid sources in Raccoon Creek are found in headwaters tributaries and in Little Raccoon Creek in the upper 122 km of the 180 kilometer-long mainstem. In both watersheds, treatment systems have limited acid sources reaching the mainstem and have decreased episodic acidification in many reaches of the streams. In Huff Run watershed, \$4.6 million in treatment has been installed, consisting of 12 projects with a total acid load reduction of 438 kg/d along 16 stream kilometers. The acid sources are all clustered in the lower 10 km of the watershed and treatment systems are physically close to the mainstem (<1 km). The lower reaches have historically degraded habitat and high erosional sediment loads. The limited recovery in Huff Run is due to historical habitat degradation, the extension of treatment system mixing zones into the mainstem and insufficient natural attenuation to mitigate episodic acidification and accrue the benefits of treatment.

These results suggest that recovery is dependent upon connected improvement in the mainstem not interrupted by the sedimentation and habitat degradation and that treatment funds should be used preferentially in cases that will lead to greater recovery. Further work is needed to find thresholds for the factors identified here and to explore the role of episodic acidification.

Acknowledgements

The authors thank the Appalachian Watershed Research Group, the Raccoon Creek Partnership for ongoing research collaborations. Chemical and biological data was collected with the assistance of the Monday Creek Restoration Project, the Sunday Creek Watershed Group and the Huff Run Watershed Restoration Partnership and many of their volunteers. Chemical and biological data collection was supported by the Ohio Department of Natural Resources Division of Mineral Resources Management and data analysis was supported by the American Electric Power Foundation.

References

- Johnson KS (2009) Performance of a family-level macroinvertebrate index (MAIS) for assessing acid mine impacts on streams in the Western Allegheny Plateau. Final report for Ohio Department of Natural Resources. Ohio University, Athens.
- Karr JR (1981) Assessment of biotic integrity using fish communities. Fisheries 6(6):21–27
- NPS (2011) 2011 Non-Point Source (NPS) Monitoring Project for Acid Mine Drainage. Voinovich School of Leadership and Public Affairs, Ohio University.
- Ohio Environmental Protection Agency (1988) Biological criteria for the protection of aquatic life: users manual for biological field assessment of Ohio surface waters. Ecological Assessment Section, Division of Water Quality, vol II, Columbus
- Rankin, ET (1989) The Qualitative Habitat Evaluation Index [QHEI]: Rationale, Methods and Application. Ecological Assessment Section, Division of Water Quality, Ohio Environmental Protection Agency, Columbus, Ohio
- Smith EP, Voshell JR (1997) Studies of benthic macroinvertebrates and fish in streams within EPA Region 3 for development of biological indicators of ecological condition, Part 1, Benthic macroinvertebrates. Report to US EPA, Cooperative Agreement CF821462010. USEPA, Washington
Optimising mine pit dewatering treatment techniques to meet production deadlines

Tim Lilley

Pall Corporation, Portsmouth, UK

Abstract Mine operators use membrane technology to treat wastewater for discharge or reuse. Membrane characteristics and their respective separation capabilities are contrasted apropos waterborne contaminants and how pH adjustment, precipitation and microfiltration can offer economic treatment solutions for the reduction of metals in mine wastewater applications. A case study describes dewatering a mine pit to allow continued production of the mine. The water was contaminated with cadmium, manganese and nickel amongst other species and was treated with chemical addition and MF alone to achieve the pit dewatering volumetric target of > 35 % and metals reduction to within discharge standards.

Keywords microfiltration, membrane, water treatment

Introduction

Mine operators are facing increasingly challenging water management targets. Stringent discharge controls are demanding improvements in water treatment methods be employed and water scarcity is driving operators to review treatment technologies for prospective water reuse for processes and shift maintenance.

Conventional water treatment techniques continue to provide solutions to these challenges but recent advances in membrane technology has greatly extended the scope and performance of water processing plant. Experiences gained in integrating established chemical methods with membrane systems have greatly enhanced the performance of the conventional techniques. Furthermore, the use of membranes introduces a degree of design flexibility that allows treatment selection and sizing to be matched to specific economic operational targets.

A detailed understanding of the waterborne contaminants and the corresponding treatment targets together with an in-depth knowledge of membrane capabilities and chemical processes is central to the effective economic solution to a given application.

Characterisation of waterborne contaminants and membrane separation processes

Water will act as a host for a range of contaminants and the first step in devising a treatment process to remove them is to understand whether these contaminants exist in either suspended or dissolved forms. Materials that dissolve in water will do so according to their own individual chemical properties and that of the host water. Consequently, the level and form of which all dissolved species exist in water will depend on the physical and chemical characteristics of the solution. When a substance dissolves in water, it imparts new chemical properties to the solution and can create potentially damaging environmentally characteristics. Consequently, the principal discharge treatment standards are generally focused on these dissolved components. In contrast, suspended materials will mix indiscriminately with the host water and, importantly, these constituents will not significantly change the chemical characteristics of the resulting mixture and will largely retain their original structure and properties.

Suspended material can be removed from water by filtration though a porous medium or membrane; in contrast dissolved components

can be removed by the diffusional process of reverse osmosis (RO; Lorch 1981). Where treated water targets are based on dissolved materials and RO membranes are to be used, it will be necessary to remove the suspended components prior to the RO to enable the latter stage to perform its design function of chemical separation; this protection can be achieved with a microfiltration (MF) membrane. Failure to do so will result in inefficient RO performance and an unacceptable maintenance burden. However, by adjusting the chemical environment of the solution. dissolved constituents can be precipitated as a suspended form for subsequent separation by physical means. Indeed, separation of dissolved contaminants from waste streams has historically been brought about with conventional chemical treatments (Plasari and Muhr 2007). These techniques involve pH adjustment of the solution or oxidation/reduction of species to reduce solubility; separation of the resulting solid can then be achieved by settlement or filtration. Fig. 1 indicates how the solubility of some common metals changes with the pH of the host water (Freeman 1989). In this case, the pH can be increased with the addition of a base and the metals precipitate as the corresponding hydroxide.

However, Fig. 1 indicates that certain metals exhibit complex solubility characteristics as pH increases. In the Figure, chromium and zinc have a minimum solubility as pH increases above which points the metals have increasing solubility. In such cases it is necessary to use stage wise pH adjustment and filtration to avoid re-dissolving previously precipitated metals. Alternatively, where such mixtures exist it can be advantageous to use additional metal precipitants. As discussed above, the behaviour of dissolved species is dependent upon other components within the solution and the coexistence of certain metals and sulphide ions results in precipitation of the corresponding metal sulphide. Sodium sulphide is a soluble solid and can be used in such a way. Fig. 2 indicates the sparingly soluble characteristic of nickel, zinc and cadmium sulphides (Freeman 1989) - metals that were of particular importance in a pit lake water treatment application of the following case study.

By using these chemical properties, separation of certain contaminates, principally metals can be achieved with chemical additions and single stage membrane microfiltration. The 0.1 micron rating and durability of the correct MF membrane will result in a filtrate of exceptional quality. Moreover, the efficiency of solids removal will be maintained for many years with performance verified for operational and regulatory compliance by routine, non-destructive membrane integrity testing.





Fig. 2 Solubility of metal sulphides vs. pH.

6

pH

10

8

12

Ì٢

10

1

0.1

0.01

0.001

0.0001

0.00001

concentration (mg/L)

The selection of the MF membrane is particularly important when the feed water exhibits the variability of those from chemical precipitation processes. This front-end treatment represents a very demanding duty and an exceptionally robust membrane construction will be central to economic long term efficacy of the whole system. An example of a high efficiency MF membrane is illustrated in Fig. 3.

This PVDF (polyvinylidene fluoride) 0.1 µm rated filtration membrane is the wall of a hollow fibre where feed water filters from the outside to the inside of the filtration medium. In doing so, the often high and variable suspended solids in the feed including the precipitated target contaminants collects on the upstream surface of the membrane resulting in an increase in transmembrane pressure (TMP) as the contaminants are retained. This process necessitates frequent back flushing cleaning cycles which typically include air-scrubbing agitation and reverse flow (backwash) with previously filtered water. Periodically, chemical cleaning in place (CIP) will further enhance membrane flux maintenance. It has been shown that physically robust and chemically inert polymer chemistry is a critical feature of the MF stage (Liu 2007). Otherwise, fibre degradation will result in deterioration in filtrate quality and compromise the treated water quality with the passage of target contaminants.



Fig. 3 Homogeneous PVDF MF membrane

Design considerations and technology selection

Application of these principles and that of tailoring a system to suit given performance and economic targets is exemplified in a site example from a barite mine in Nevada, USA. It was necessary to partially dewater a 150,000 m³ pit lake against a tight time schedule to allow continued operation of the mine. The water was contaminated with approximately 2000 mg/L of total dissolved solids (TDS) made up primarily of sulphate but also metals including cadmium, manganese and nickel.

The volumetric targets and timescale demanded a plant that was capable of processing >50 m^3/h for a period of two months with water quality targets being dependent on treated water destination options. Water utilisation options can include surface water course or aquifer reinjection discharge, process reuse or irrigation. Discharge to surface water course or aquifer typically requires tight water quality standards be met as these are generally subsequent drinking water sources. For the barite mine pit lake water makeup TDS and dissolved metal reduction to local regulatory standards would be required. As referenced earlier, in a membrane context reduction of dissolved contaminants requires RO together with the associated MF to protect the RO construction. Also distribution pipework would be required in this particular case, all of which would be additional sources of contamination and cost. Considering the discharge options, water for irrigation would require only metals reduction from the pit lake composition as TDS and sulphate were already within applicable standard limits (NDEP Profile 1, 2012).

Figs. 1 and 2 illustrate the solubility dependence on pH of the relevant species of the barite pit lake water. As can be seen, all critical metal species can be precipitated with chemical adjustment and can therefore be subsequently filtered with single stage MF thereby offering considerable application cost reductions over the alternative of MFRO technolo-



gies. However, the specific combination of metals meant that simple pH adjustment was not the most efficacious route as pH would have to be increase to around 10 for the hydroxide precipitation of nickel and, as discussed earlier, at such levels, re-solubilising zinc would be likely to take place (Fig. 1). Therefore the combination of pH adjusted hydroxide precipitation of aluminium, oxidation of manganese and sulphide precipitation of nickel, cadmium and zinc would be the optimum route. Particularly dissolved cadmium and zinc can be reduced to target levels at significantly lower pH than the hydroxide precipitation alternative route. The conceptual process chemistry as described in the following sequence was explored with bench scale testing to ensure dose rates and reaction time was optimised.

- Pit lake neutralised and pH adjusted with Ca(OH)₂
- Manganese oxidised Mn(II) > MnO₂ with H₂O₂
- Aluminium precipitated and Al(OH)₃ at $pH \approx 7$
- Nickel, cadmium & zinc precipitated as sulphides with NaHS addition at $pH \approx 10$
- pH reduced to \approx 7 with H₂SO₄

The schematic process flow diagram is illustrated in Fig. 4.

In the context of generic membrane water treatment methodology there are aspects to the design presented here that suited the economic goals of the specific project which may not be ideal for a permanent installation. This exemplifies the earlier point of the degrees of flexibility that the use of membranes systems enables. This temporary, partial dewatering target allowed aggressive use of chemicals in the use of hydrogen peroxide for the oxidation of manganese, simultaneous precipitation of metals and final pH adjustment to discharge limits with sulphuric acid. This latter stage being acceptable as the sulphate and TDS discharge limit did not apply in this case.

The temporary plant illustrated in Figs. 4 and 5, ran from mid-August until early October 2012 at a flowrate of 60 m³/h and achieved a pit dewatering volumetric target of >35 % which exceeded the required target to allow production at the minesite to continue. The process acheived continuous metals reduction to 1 µg/L cadmium, < 0.1 mg/L manganese and < 0.05 mg/L nickel. A more detailed summary of water quality is presented in Table 1.



Fig. 5 Pit dewatering site installation

"Reliable Mine Water Technology"

Parameter (mg/L or –)	Pit water	Discharge Standard (NDEP Profile 1)	Treated Water	
Aluminum	1.7	0.2	0.045	
Cadmium	0.66	0.005	0.001	
Manganese	11.0	0.1	0.09	
Nickel	1.8	0.1	0.04	
Zinc	10.0	5.0	0.02	Table 1 Summary water
Sulfate	1,300		_	analysis of barite mine,
TDS	2,000		_	Nevada 2012
pН	5.4	6.0 - 8.5	6.5 - 7.0	110 / 000 2012.

CapEx/OpEx balance and application objectives

Permanent membrane installation, particularly those of higher flows would usually be optimised to operate at higher MF flux rates (flow per unit filtration area). This is to minimise the capital cost of the installation by minimising the number of MF modules installed. This inevitably results in higher pumping costs by virtue of the elevated TMP. Furthermore. membrane cleaning burden will also be increase at higher flux operation both of which naturally creates a trade off with increased operating cost. For optimisation of operational MF flux, single module pilot tests can be run, the results of which can be accurately scaled up to reflect the performance of the final plant (Lilley 2005).

The plant described in the case study above was run at lower flux and would benefit from significantly reduced pumping costs and despite the high feed solids from the precipitated metals the elevated membrane cleaning burden did not compare to the higher energy costs and operating costs were about 75 % of the equivalent fixed plant. Table 2 summarises the operating costs of two typical alternative configurations.

In this way, we are able to tailor mem-

brane treatment designs to match individual application targets. The temporary installation above was run at reduced flux, partly to minimise chemical usage at that particular site but other temporary projects could attract much higher flux if the economic drivers dictate. It is important to note that filtrate quality is independent of flux for the PVDF MF membranes described above so overall plant performance will be assured irrespective of *modus operandi*.

Conclusions

Conventional water treatment chemistry can be used synergistiaclly with robust polymeric microfiltration membranes to treat mine waste streams to exceptional quality.

A detailed study of influent water characterises, matched to the relevant treated water standards and the economic targets is the key to a successful site installation and operation.

Selection of the optimum treatment chemistry can eliminate the need for multistage membrane processes

Membrane systems lend themselves to containerised as well as temporary mine site applications that require rapid deployment

Operating costs can be tailored to suit individual application needs and targets

Installation	Flowrate m ³ /h	Electrical o kWh/a (a	consumption t \$0.07/kW)	CIP \$/Year	OpEx \$/m ³		
Temporary	10.9	190000	13300	2840	0.17		
Fixed	10.0	255500	17885	2253	0.23		
			* Excluding membrane replacement costs				

Table 2 Typical operatingcosts* for temporary andfixed MF installations

Acknowledgments

Acknowledgement is extended to the staff of Linkan Engineering, Nevada, USA for sharing the site data and their dedicated site work during execution of the site deployment.

References

- Freeman H M (Ed) 1989, Standard Handbook of Hazardous Waste Treatment and Disposal, McGraw-Hill, New York, p 7.21-7.31
- Lilley T (2005) Membrane filters microfiltration and ultrafiltration. In: R Wakeman & S Tarleton (Eds), Solid liquid Separation, Scale-up of industrial equipment, Elesevier, Oxford, UK 140–195

- Liu C Mechanical and Chemical Stabilities of Polymeric Membranes (2007), AWWA Water Quality Technology Conference, November 4 – 8, (2007), Charlotte, NC, USA
- Lorch W (1981) Handbook of Water Purification, Mc-Graw-Hill, London
- NDEP, State of Nevada, Division of Environmental Protection, NDEP Profile I – Table of Parameters& Reference Values.
- Plasari E and Muhr H (2007) Development in precipitation engineering for process intensification in the environmental protection and other purification industrial activities, Chemical Engineering Transactions, p 65–70.

Resin Freeze Desalination Process for Acid Recovery

R. Malisa¹, J. P. Maree¹, E. Hardwick², F. S. Oosthuizen³

¹Department of Environmental, Water and Earth Sciences, Faculty of Science, Tshwane University of Technology, Private Bag X680, Pretoria, 0001, South Africa. ²Cwenga Technologies, Edenvale, 1609, South Africa ³Aqua-Simon UG, Rabenslücke 40, 24944 Flensburg, Germany

Abstract Acid streams rich in sulphate and metals such as acid mine drainage are normally neutralized with limestone or lime to produce gypsum and metal hydroxides or oxides as waste products. An innovative resin freeze desalination (RFD) process is described where metals are first removed with a cat ion exchange resin (Lewatit MonoPlus S108), followed by up-concentration of the acid using freeze desalination. It was found that complete iron removal was obtained with water containing (i) 0.7 g/L H₂SO₄ and 390 mg/L Fe²⁺ and (ii) 1.4 g/L H₂SO₄ and 1 056 mg/L Fe³⁺. Both iron species were eluted from the resin using 3 % H₂SO₄. The iron-free, resin treated water was concentrated up from 30 to 42 g/L H₂SO₄ using freeze desalination.

Keywords AMD, cat ion-exchange, freeze desalination, HybridICE, Lewatit monoPlus S108.

Introduction

Effluents from the chemical and mining industries require treatment to reclaim the water for reuse or for discharge into the environment (Adler and Rasher 2007). A general treatment method is to use limestone or lime for neutralization to produce neutral water and, if the water contains sulphate, gypsum sludge which is normally stockpiled (Maree & Van Tonder 2000). Neutralized water can be further treated through desalination using reverse osmosis (RO), electro-dialysis (ED; Amjad 1993; Schoeman and Steyn 2002) or ion-exchange. The brine or regenerant streams produced in these processes requires further treatment before discharge into the environment to meet environmental regulations. The following methods are currently used for brine disposal or treatment: Evaporation ponds, Distillation, Direct contact membrane distillation. Vacuum membrane distillation and Membrane distillation (Younos 2005; Lawson and Lloyd 1997). As these methods are either environmentally unacceptable or costly, the HybridICE technology was developed (Mtombeni et al. 2011).

The main objective of this study was the testing of the novel resin freeze desalination (RFD) process to recover sulphuric acid from acidic and metal rich streams. The RFD process is a combination of, freeze desalination with ion-exchange. It consists of the following steps: (i) Metal removal with an ion-exchange resin, (ii) Concentration of the dilute acid stream after the ion-exchange resin stage through freeze desalination, (iii) regeneration of the resin with the concentrated acid recovered through freeze desalination and, (iv) the remaining acid, which is concentrated further, being recycled to be used elsewhere without neutralization. The benefits of this approach are: (i) Resins are used for the selective removal of metals, (ii) acid is not destroyed through neutralization, but recovered (iii) low energy cost as the energy required to freeze water is seven times less than to evaporate the same volume of water (2500 kJ/kg for evaporation versus 333 kJ/kg for freezing (Shone 1987), (iv) no pre-treatment is required, and (v) reduced brine volume for disposal.

Methods

Synthetic acid mine drainage water was prepared, similar to a typical mine water. Water A contained 0.7 g/L H₂SO₄ and 400 mg/L of Fe (II) and Water B, 1.4 g/L H₂SO₄ and 1085mg/L of Fe (III). Lewatit MonoPlus S108 cat ion resin was used for iron removal from acid solutions. A laboratory scale, HybridICE[™] freeze desalination unit was used for freeze desalination.

The following procedures were followed:

- The resin bed of Lewatit MonoPlus S108, in a glass column (15mm diameter) was prepared in such a way that all air bubbles were eliminated.
- The resin bed was activated by passing three bed-volumes (BV) of 3 % sulphuric acid followed by three BVs of deionised water
- The acid water was fed into the cat ion-exchange column at a flow-rate of 5 mL/min.
- As the acid water passed through the column the metal ions were adsorbed onto the resin (H-R + MSO₄ → M-R + H₂SO₄; M = Fe⁺², Fe⁺³)
- The adsorption capacity of the resin was calculated.
- Upon saturation, the resin was regenerated by elution using 3 % H₂SO₄.
- Dilute H₂SO₄ was concentrated through freeze desalination using the HybridICE plant.
- The resin was regenerated with $3 \% H_2SO_4$.

Samples of eluate were collected regularly and filtered (Whatman No 1 glass fibre filter).

Acidity and pH determinations were carried out according to described procedures (APHA *et al.* 1985) and Fe (II) as described in Vogel (Vogel 1989). Total iron was assayed using atomic absorption spectrophotometry.

Metal removal

Table 1 and Figs. 1 and 2 show the results when Fe^{2+} and Fe^{3+} rich waters were passed through a resin column filled with 50mL of Lewatit MonoPlus S108 resin. Both Fe^{2+} and Fe^{3+} were removed down to less than 10 mg/L until break-through occurred. The saturation index was calculated to be 3.52 equivalents Fe/L resin for Fe^{2+} (Fig. 1) and 3.21 equivalents Fe/L resin for Fe^{3+} (Fig. 2). This corresponded with the product sheet which claimed > 2 equivalents Fe/L resin (LanXESS 2011). Figs. 3 and 4 show that the saturated resins were completely regenerated with 3 % H₂SO₄,

Table 2 and Fig. 5 show the relationship between amount of resin and iron removal for different contact times as determined during batch studies. In the case of a low resin content of 2.38 mL resin/L water, the iron Fe²⁺-absorption amounted to 2.52 equiv Fe/L resin at a contact time of 10 min, compared to 4.20 eq Fe/L resin at a contact time of 120 min. In a packed bed system during full-scale applications, 10 min contact time can be considered a realistic value. The design can be based on an adsorption capacity of 2.0 eq Fe/L resin, as recommended by the supplier. For counter current systems, where (i) the high metal concentration first encounters with the already loaded resin (to allow maximum utilization of

Parameter		Figu	re		
	Loadi	ng	Regeneration		
	1	2	3	4	
Iron species	Fe ²⁺	Fe ³⁺	Fe ²⁺	Fe ³⁺	
Concentration (mg/L) Feed rate (mL/min)	390 13.3	1056 5			
Resin bed volume (mL)	50	50	50	50	Table 1 Experimental condi-
$H_{2}SO_{4}(\%)$			3	3	
Iron adsorbed (g)	4.92	2.71			tions and results of resin
Iron desorbed (g)			2.99	1.54	loading and regeneration
Absorption capacity (equivalents Fe/mL resin)	3.52	3.21	1.94	1.65	results reported in Figs. 1 – 4.









Fig. 3 Regeneration of iron (II) loaded resin with H_2SO_4 (3 %).

Fig. 2 Iron (III) removal with resin (Bed volume = 50 mL; Fe(III)_{Feed} = 1 056 mg/L; Feed rate = 5.0 mL/min).



Fig. 4 Regeneration of iron (111) loaded resin with H_2SO_4 (3 %).

	Resin content (mL/L)								
	2.38	7.14	11.90	59.52	238.10				
Time (min)		Iron(II) i	n solution (mg	g/l)					
0	390	390	390	390	390				
10	222	111	223	56	56				
30	167	56	56	28	28				
120	111	28	56	28	28				
Time (min)		Fe adsor	rbed (eq/L resi	in)					
10	2.52	1.40	0.50	0.20	0.05	1			
30	3.35	1.68	1.00	0.22	0.05	CE			
120	4.20	1.81	1.00	0.22	0.05				

Table 2 Effect of resin concentration and contact time on metal removal.

the resin absorption capacity), and (ii) where the final water is contacted at the end of the contact period with the fresh resin, the design can be based on higher values such as the 4.0 eq Fe/L resin as determined for the longer contact period. In cases where excess amounts of resin were contacted with the 400 mg/L Fe²⁺ water, complete removal was achieved within 10 minutes.

Freeze crystallization

Figs. 6 and 7 show the acid concentrations in the brine and acid when cat ion-exchange resin treated water, containing $30 \text{ g/L} \text{ H}_2\text{SO}_4$,



Fig. 5 Effect of resin concentration on Fe²⁺ removal during batch reactions.

was concentrated through removal of water via ice crystallization. Fig. 6 shows the behaviour of acidity versus time and CF_{Flow} (Concentration Factor_{Flow}). The term Concentration Factor_{Flow} is defined as Concentration Factor_{Flow} = Volume Fed/Volume of reactor. It was noted that as CF_{Flow} increased from 1 to 1.9 (corresponding with Time from 0 to 18 h), the Acidity of the brine increased from 30 to 42 g/L (as $CaCO_3$), while the Acidity in the Ice increased from 0 to 5.5 g/L. When spots of "dry" ice were harvested the Acidity was found to be < 0.5 g/L (as CaCO₃). When selected ice samples were analysed they were found to contain <0.5 g/L acid. By further improvement to the ice separation system, full acid recovery from the brine stream is expected to be achieved.

Fig. 7 shows $CF_{Acidity}$ and CF_{Flow} versus CF_{Flow} . $CF_{Acidity}$ was defined as Acidity of brine with change in or CF_{Flow} (or Time). It was noted that $CF_{Acidity}$ was below CF_{Flow} . This was due to a fraction of the acid remaining in the Ice. Further improvements in ice/brine sepa-



Fig. 6 Behaviour of acidity of brine and ice during freeze desalination.

ration efficiency will result in the values of CF_{Acidity} becoming much closer to CF_{Flow} values.

Conclusions

- 1. Complete iron removal was obtained with waters containing (i) 0.7 g/L H_2SO_4 and 390 mg/L Fe^{2+} and (ii) 1.4 g/L H_2SO_4 and 1 056 mg/L Fe^{3+} .
- **2.** Both iron species were eluted from the resin using $3 \% H_2SO_4$.
- 3. The iron-free, resin treated water was concentrated from 30 to $42 \text{ g/L H}_2\text{SO}_4$ using freeze desalination.

Acknowledgements

This work was made possible with the financial support of the following institutions: The National Research Foundation's Technology & Human Resources for Industry Programme (THRIP), Rand Water and the Tshwane University of Technology.

The contributions of the following people are gratefully acknowledged: Prof. Fritz Carlsson for editing the manuscript. Jackson Makgati and Nomvuselelo Zikalala for assistance with laboratory work.

References

Adler R, and Rascher J (2007) A strategy for the management of acid mine drainage from gold mines in Gauteng. CSIR Report: NRE/PW/ER/2007/0053/C, CSIR, Pretoria.

Amjad Z (1993) Reverse osmosis membrane technol-



Fig. 7 Behaviour of up- concentration of acid during freeze desalination.

ogy, water chemistry and industrial applications. Van Nostrand Reinhold, New York, USA, 76–103.

- APHA, AWWA and WEF (1985) Standard Methods for the Examination of Water and Wastewater, 12th Ed., 1985. American Public Health Assoc., New York.
- LanXESS (2011) Product Information: Lewatit Mono-Plus S 108 H, 12 May.
- Lawson KW and Lloyd DR (1997) Membrane distillation. Journal of Membrane Science, 124: 1–25.
- Maree JP and Van Tonder GP (2000) Limestone neutralisation of iron (II) rich acid water.(Paper presented at the Biennial Conference of the Water Institute of Southern Africa, 28 May- 01 June, Sun City, South Africa).
- Mericq, JP., Laborie, S. and Cabassud, C (2009).Vacuum membrane distillation for an integrated seawater desalination process. Desalination and Water Treatment, 9(1–3): 287–296.
- Mtombeni T, Maree JP, Zvinowanda C, Asante J, Oosthuizen FS, Jessen H and Louw WJ (2011) Harnessing refrigeration waste heat to achieve zero liquid dis-

charge by the integrated HybridICE Technology. Paper presented at the 9th International Conference on Clean Technology for the Mining Industry, Paper No 8, p. 19.

- Schoeman JJ and Steyn A (2002) Treatment of a high nitrate concentration ground water with reverse osmosis in a rural area in South Africa. Paper presented at the Biennial Conference of the Water Institute of Southern Africa, May 19–23, Durban, South Africa.
- Shone RDC (1987) The freeze desalination of mine waters. Journal of the South African Institute of Mining and Metallurgy, 87(4): 107–112.
- Vogel AI (1989) Vogel's Textbook of Quantitative Inorganic Analysis, 5th Edition, John Wiley and Sons, New York, p.368.
- Younos T (2005) Environmental issues of desalination. Journal of Contemporary Water Research and Education, 132(1): 11–18.

Metals Removal from Mine Effluents – Understanding the Chelant is Key

Lucas R. Moore, Jean Robert Durand, Forrest Strickland

Kemira Minerals and Metals, 387 Technology Circle, Suite 300, Atlanta, GA, USA

Abstract Though dissolved metals can be a contaminant in mine effluents, the discharge criteria may vary from site to site. Removal of metallic contaminants can be difficult due to complex variations in coordination properties. Chelation is a useful tool that can be engineered to be more specific to a series of metals. A chelant treatment package was developed for the successful removal of copper from a mine effluent where the discharge criterion is being decreased to 25 μ g/L on the upcoming permit renewal. This evaluation explores a wide range of process variations such as pH, temperature, treatment dosage, and removal kinetics.

Keywords metals removal, water treatment, copper chelation

Introduction

Mine effluents are of significant environmental concern when considering the potential impact of inorganic contamination on the aquatic biota (Jiménez-Rodríguez 2009; Peleka 2007; Young 1981). Copper is one of the contaminants of concern due to its bioaccumulative effect, negative effects on the olfactory systems in aquatic biota, and level of toxicity (ATSDR 2012; Hara 2011; US EPA 2012). The fate of copper in aqueous systems depends on a number of factors including dissolved oxygen/oxidizing agents, coordinating ions, and pH.

A common technique for inorganic contaminant removal is by chemical precipitation. This is achieved by either chemically altering the solvent matrix to decrease/diminish the solubility of the substance or by conversion of the substance to an insoluble form (Britannica 2012). An understanding of the metal/ligand stability is critical when designing a metal contaminant treatment system. It is important to understand the strength or 'desire' of a ligand to coordinate to a metal and the stability of the resulting complex to allow for optimal precipitation. This is a very useful tool, and it is possible to coordinate many different kinds of ligands to metals, but the key to a successful application is getting them to remain ligated and become labile only when desired.

One way of maintaining coordination is through chelation. Chelation is the ability of a ligand, in this case a sequestering agent, to coordinate to a single metal ion through two or more ligation sites. Generally speaking, a chelating ligand has a much stronger coordination strength than a monodentate ligand with one ligation site (Clapp et al. 2006; Huheey et al. 1993; Greenwood and Earnshaw 2001; Fig. 1). This strength is mainly due to the proximity of the chelating ligand to the metal while labile. Consider ethylenediamine (B); even if one portion becomes labile, it can only get a few hundred picometers away from the metal, while amine (A) can come and leave. However, the level of chelation depends not only on the ligand, but also the oxidation state and charge of the metal, the presence of other



Fig. 1 Examples of coordination. A) Monodentate, B) Bidentate, C) Tridentate

Flement	Ba(II)	C ₂ (II)	Mg(II)	Fe(II)	Ni(II)	Cu(II)	Zn(II)	Co(II)	Hg(II)	Cd(II)	R	C	Si
Liement	$Da(\Pi)$		mg(n)	10(11)	$\mathbf{n}(\mathbf{n})$		Ln(n)	C0(II)	ng(n)	Cu(II)	Ъ	C	51
Atomic Radii (pm)	134	99	66	74	69	72	74	72	110	97	23	16	44
Open Sites	2	2	2	6	4	4	2	4	2	2	N/A	N/A	N/A

Table 1 Crystal ionic radii (pm)

ligands, and the available ligation sites on the metal.

The ring size, formed during chelation, can also play a significant role in the stability of a metal complex. Generally, a 5 membered ring is more stable than a 6 membered, which is more stable than a 7 membered. Of course, this can change according to the size of the metal, vacant coordination sites, and other ligands coordinated to the metal (Wiki 2013; Weast 1988; Webelements 2013; Table 1).

The major difference, contributing to the stability of a 5-membered ring over a 6-membered ring is mainly the bite angle or steric strain caused by chelating to the metal. (Hancock 1992; Fig. 2) A 5-membered ring has a much larger bite, thus can more easily "bite" many metals. In order for a 6-membered chelate ring to be more stable, a metal similar in size to a carbon must be used. For example: a Cu-N bond is about 2.3 angstroms, which would suggest a copper atom would be most stable in a 5-membered chelate ring, while Mg-O bond is 1.75, which would make a stable 6 membered chelate ring. This trend is also seen



Fig. 2 Bite angle comparisons between a 5 and 6 membered complex

when a 4-membered ring is considered. The larger atoms, like calcium, form a very stable complex with 4-membered rings, which is observed in carboxylates that are often found in calcium scale inhibitors and many dispersants. In complexes that form larger than 6-membered rings, the metal size is no longer the dominating factor in the stability of a chelate ring. The stability of such large chelate rings depends on the ability of both coordinating ligands to find the metal. Applying rigidity to the backbone of the chelant could assist in forming such 7 member ringed complexes.

Another way of maintaining coordination is by applying the Hard/Soft Acid/Base theory. This theory is a method of predicting the affinity of a ligand towards a specific metal, and in conjuncture with chelation, can aid in making the "perfect" complex. Hard acids are alkali metals, alkaline earth metals, and lighter transition metals in higher oxidation states (*e.g.* Ti, Cr, Al, Zn, Mn, B, Fe³⁺). Ligations of hard acids are preferred with hard bases, which are small and difficult to polarize, meaning electrons are donated from the ligand to the metal. Hard bases are ligands that contain the lighter elements with electron donating abilities (*e.g.* N, O, F, PO₄, SO₄, RC=OO-). (Fig. 3A)

Soft acids are the heavier transition metals and those of lower oxidation states (*e.g.* Rh, Ir, Pd, Pt, Ag, Au, Hg, Ni, Cu). As hard acids prefer hard bases, soft acids coordinate preferentially with soft bases. Soft ligands are large and easily polarized, meaning electrons from both the metal and ligand readily engage in bonding. Most often the ligand will donate σ electrons to the metal's empty d orbitals and the metal will back donate electrons into an empty π orbital on the ligand. (*e.g.* ex. phosphines, carbenes, thioethers, conjugated organics, mercaptans). (Fig. 3B)

25

160



Fig. 3 A) σ-donation of electrons from a hard base to a hard acid B) Interactions between a soft base and a soft acid.

0.625 0 20 40 60 80 100 120 140 Copper Remaining (µg/L)

Results and Discussion Copper Removal

A chelant, KemMet 1140, was designed with a superior ability to remove metal ions from aqueous systems. KemMet 1140 applies a bidentate coordination of sulfur containing substituents that provide the hard base requirements and the ring size that makes it a perfect candidate for complexing to copper. Altering the backbone of the system allows for low solubility once the complexation occurs. This chelant was applied towards water that was obtained from a mine site located in the United States and was stored in a cooling unit at 1 °C prior to use (Table 2). In this case the objective was to reduce the total copper at the existing operational conditions (pH and temperature) with minimal impact on production. Copper, which was present at an average concentration of 172 μ g/L, was released during the processing of the ore while in an acidic environment.

KemMet 1140 is efficient over a wide range

IC Analysis	Concentration	ICP Analysis	Concentration
Fluoride (mg/L)	2	Copper (µg/L)	172
Chloride (mg/L)	10	Arsenic (µg/L)	40
Sulfate (mg/L)	850	Selenium (µg/L)	283
Bromide (mg/L)	ND	Cadmium (µg/L)	1
Nitrate (mg/L)	ND	Sodium (mg/L)	120
Phosphate (mg/L)	ND	Magnesium (mg/L)	6
Conditions		Aluminum (mg/L)	170
pH	3	Calcium (mg/L)	27
Turbidity (NTU)	4800	Manganese (mg/L)	260
Total dissolved solids (ppm)	970	Iron (mg/L)	6
Hardness (as CaCO3)	94	Nickel (µg/L)	73
Conductivity (µS/cm)	1500	Molybdenum (µg/L)	9
Total suspended solids	2	Barium (µg/L)	230

Table 2 Effluent (raw water) analysis

Fig. 4 KemMet 1140 dosage demand over the customer specified process conditions (Temperature 49 °C, pH 3–4)

of pH. It can be either continuously fed or applied via a batch treatment process. It was evaluated in the above mentioned effluent towards the removal of copper under the customer-specified process conditions of 49 °C and pH 3 (Fig. 4). While the minimum dosage required to achieve the desired < 25 μ g/L discharge criterion was 1 mg/L total solution, 10 mg/L yielded copper levels less than the instrument detection limit of 5 μ g/L. Interestingly, the addition of a flocculant alone yielded a 27 % reduction in the copper concentrations, which could be due to the presence of a suspended copper salt.

Effects of Process Conditions

Understanding process limitations would make transferring this technology to treatment processes at other mine sites much easier. Therefore, a dosage of 25 mg/L KemMet 1140 was evaluated in the above mentioned raw waters under a broad range of temperatures and pH values to simulate seasonal variations and other potential site-specific process requirements (Fig. 5). The optimal conditions were found at a temperature of 4 °C, at which point the instrument detection limit was met for a pH range of 5–9. Only a slight decrease in performance was observed at pH 3. Increasing the temperature to 26 °C yielded a slight decrease in performance for those experiments carried out over the pH range of 5–7. An interesting increase in copper removal was observed as the pH was further increased to 9.

This trend continued as the temperature was increased to 49 °C. While operating at pH 3, a comparable level of copper reduction was achieved over the entire range of temperatures. The reduced performance at the elevated temperatures could have been due to the potentially increased rates of ligation-site oxidation of KemMet 1140.

The KemMet 1140 performance was consistent throughout the temperature range evaluated at pH 3, with a similar trend observed for those treatments carried out at pH 9, but there appeared to be a loss in performance at a pH range 5-7 at 49 °C. The reduced levels of copper at pH 9 can be explained by the precipitation of cupric hydroxide, though this does not explain the loss in performance at elevated temperatures at a pH of 5 to 7. To evaluate this inhibition in performance, the samples were analyzed for residual chelant (KemMet 1140) in both the samples treated with 0.625 mg/L KemMet 1140 at 26 °C and 49 °C. It was concluded that at 26 °C, a residual concentration of 180 µg/L remained in the effluent. The 49 °C treatment yielded nearly 100 % of the chelant as soluble, residual material in the effluent. One potential explanation would be an oxidizing effect on the nucleophilic sites as a competing reaction for the copper chelation, which can be evaluated by applying bleach to the water prior to treating, in efforts to increase the oxidizing conditions at a lower temperature (Fig. 6). This would also prove that it is not an effect of temperature as a means of decomposition, but rather the energy required to increase the rate of oxidation. During this evaluation, KemMet 1140 was greatly hindered at 26 °C, as the efficiency was decreased from 96 % removal to 40 % removal.

Even though the discharge criteria were met over the complete range of pH and tem-



Fig. 5 Evaluation of KemMet 1140 over a broad range of process conditions



Fig. 6 Effect of oxygen-rich environment on the efficiency of the removal of copper by KemMet 1140

perature, clear sensitivities were observed during the KemMet 1140 evaluation when pH and temperature were varied. To further evaluate the treatment efficiency and requirements, the rate of removal was measured as a function of temperature (Fig. 7). At 4 °C, > 99 % of the copper was removed within the first minute and was maintained insoluble for the entire 10 minute contact time. The efficiency was slightly reduced as temperature was increased to 26 °C, which yielded 96 % removal of the copper within the first minute. Copper concentrations continued to decrease over time until 5.38 µg/L was reached after 10 minutes. Though the discharge criteria were met at 49 °C, only 86 % of the copper was removed within the first minute, which began to degrade and release copper over the remaining reaction time.

Competing lons

Understanding what the treatment is doing to the water is important prior to moving into field evaluations, as there could be competing ions that could lead to requiring increased dosages. In addition, it is also crucial to study what was being left behind (Table 3). During this evaluation, sodium appeared to be the only ion that increased, approximately 20 %, from the raw water analysis to the post-treatment analysis. When evaluating for competing ions, the analysis of the post-treatment water was compared to water treated with flocculant only. This would allow an accurate understanding of the KemMet 1140 performance instead of what was just being removed through the flocculation process. KemMet 1140 appears to have the strongest affinity for copper, but zinc and cobalt were also removed through the chelation/precipitation process.

Experimental

Procedure

A sample of 500 mL of raw water (untreated effluent) and a stir bar was added to a 600 mL beaker, which was then placed on a Thermo Scientific stir plate for agitation. The pH was adjusted to the desired range using nitric acid or 10 % sodium hydroxide. Once the desired pH was reached and controlled, the temperature was adjusted to the experiment-specific tem-



Fig. 7 Effect of temperature on the efficiency of KemMet 1140 on the removal of copper (pH 3–4, 1 mg/L dosage)

perature using an iced water bath or a hot plate. Once the temperature was stabilized, the Kem-Met 1140 was added at the experiment-specific dosage using a $10 - 100 \mu$ L precision pipette equipped with disposable pipette tips. The water was allowed to agitate on high (400 rpm) for 2 minutes. This agitation should provide a vortex that extends 50 % down the solution. At the end of the specific time, 2 mL of 0.05 % of a flocculant (Superfloc A130HMW) was added and allowed to agitate for 1 minute on high. Then the agitation was decreased to the point that the vortex only extended 15 % down the solution volume and allowed to agitate for 5 minutes, at which time the precipitate was allowed to settle for 10 minutes. The solution was then filtered through a 0.45 µm Millipore filter. The filtrate was then submitted for ICP.

-		Raw	Post-treatm	nent	
	Turbid	ity 4800	1		
	TDS	970	970		
	TSS (mg	g/L) 2	17		
	Sulfate (n	ng/L) 850	700		
ICP Analysis	4 Raw	Post-flocculen	t Post-treatment	Treatment efficiency (%)	
Mg (mg/L)	6	6	6	0	
Ca (mg/L)	27	27	27	0	
Fe (µg/L)	5500	770	1100	-30	Table
Co (µ g/L)	34	23	11	52	
Ni (μ g/L)	73	22	27	-22	peting
Cu (µ g/L)	170	170	10	94	min);
Zn (µ g/L)	300	430	150	64	near

Table 3. Evaluation of competing ions (pH 3–4, 49 °C, 2 min); highlighted cells appear to be competing ions

Wolkersdorfer, Brown & Figueroa (Editors)

Instruments

In this study, a Thermo Scientific ICP-AES system model iCAP 6500 equipped with a charge injection device detector and a CETAC ASX-520 autosampler was used for determination of copper concentration following the EPA method 200.8. Low detection limits (5 µg/L for copper) were achieved by pre-concentration of 100 mL aqueous samples. Quantitative elemental analysis of trace elements was conducted on a Bruker S4 Explorer wavelengthdispersive x-ray fluorescence spectrometer.

Conclusions

That properly designing a chelant can provide somewhat metal selective coordination and can yield a desired level of solubility. It is evident by the required discharge criteria being met under the customer-specified processing conditions of pH \approx 3 and operating temperature of approximately 49 °C on lab scale evaluations. The required ratio of $\approx 3/1$ active Kem-Met/Copper ion was the minimum dosage to meet the discharge criteria in the lab. Due to potential increase in rate of ligand oxidation at elevated temperatures, the optimal process temperature for the application of the Kem-Met 1140 is 4 °C, but the discharge criteria can be met at temperatures as high as 49 °C. This was supported by the kinetics data, which also suggests a decrease in removal rate with an increase in temperature. The larger radii ions (e.q. Ca, Ba) were not a competing ion for this chelation. However, those ions with an atomic radii \approx 72 pm, similar to that of copper, posed as a competing ion for chelation.

References

- ATSDR (Agency for Toxic Substances and Disease Registry) Division of Toxicology, ToxFAQs for Copper. www.atsdr.cdc.gov/toxfaqs/tf.asp?id=205&tid=37 (accessed June 2012)
- Clapp LA, Siddons CJ, VanDerveer DG, Reibenspies JH, Jones SB and Hancock RD (2006) The amide oxygen donor. Metal ion coordinating properties of the ligand nitrilotriacetamide. A thermodynamic and crystallographic study. Dalton Trans, 16, p 2001–

2007.

- Edocs, Judit, www.westerhuis-restauratie.nl/pdf/chelating-agents.pdf. (Accessed June 2012)
- Encyclopedia Britannica. www.britannica.com/ EBchecked/topic/108784/chemical-precipitation, (accessed June 2012)
- Greenwood NN, Earnshaw, A. (2001) Chemistry of the Elements. 2nd edit, Ch 19, Coordination and organometallic compounds, Butterworth-Heinemann, Boston, MA, USA
- Hancock, R. D. J. (1992) Chelate ring size and metal ion selection, Chemical Education 69, 615–621
- Hara, T. J.; Law, Y. M. C.; Macdonald, L. S. (2011) Effects of Mercury and Copper on the Olfactory Response in Rainbow Trout, Salmo gairdneri, Journal of the Fisheries research Board of Canada, 33, p 1568–1573.
- Huheey JE, Keiter EA, Keiter RL (1993) Inorganic Chemistry: Principles of Structure and Reactivity. 4th edit, ch 9, Acid – Base Chemistry, Harper Collins College Publ, NYC, NY, USA
- Jiménez-Rodríguez AM, Durán-Barrantes MM, Borja R, Sánchez E (2009) Heavy metals removal from acid mine drainage water using biogenic hydrogen sulphide and effluent from anaerobic treatment: Effect of pH. J Hazard Mater 165:759–765
- Peleka EN, Matis KA, Blöcher C, Nenov V, Mavrov V (2007) The recovery of copper from a copper mine effluent in a hybrid flotation/microfiltration cell. Int J Environ Pollut 30:273–286
- US EPA, United States Environmental Protection Agency. Basic information about copper in drinking water. water.epa.gov/drink/contaminants/basicinformation/copper.cfm (accessed June 2012)
- Weast, R. C.; Astle, M. J. (1981) Crystal Ionic Radii of the Elements. In Handbook of Chemistry and Physics;, 62nd ed; CRC Press: Florida, pp F-175.
- Webelements (2013), www.webelements.com/cobalt/ atom_sizes.html (Accessed 2013)
- Wikipedia, http://en.wikipedia.org/wiki/Atomic_radius (accessed 2013)
- Young JL, Bohling RA (1981) Water treatment at Homestake's Bulldog Mountain operation. Mining Engineering, 33, p 1689–1691.

A high surface area media treatment trial of a circum-neutral, net alkaline coal mine discharge in the South Derbyshire Coal Field (UK) using hydrous ferric oxide

Arabella M. L. Moorhouse, Lee M. Wyatt, Ian A. Watson, Steve Hill

The Coal Authority, 200 Lichfield Lane, Mansfield, Nottinghamshire NG18 4RG, UK; abbymoorhouse@coal.gov.uk

Abstract In 2010, a trial using high surface area media, in the form of a SCOOFI (Surface Catalysed Oxidation of Ferrous Iron) system was undertaken for 12 months to assess the effectiveness of the medium for removing iron from a net-alkaline, circum-neutral mine water in Leicestershire. Three different configurations were investigated, which achieved mean iron area-adjusted removal rates up to 139 g/m²/d; higher than the 10 g/m²/d quoted in the literature for conventional schemes. Although the media successfully removed some iron, the ochre quickly clogged the system and the unstable nature of the precipitate resulted in problems when maintaining the scheme.

Keywords Coal mine water, net-alkaline, high surface area media, iron removal

Introduction

The South Derbyshire Coalfield (covers areas in the English-Midland counties of Derbyshire and Leicestershire) has been subject to rising mine water over the past twenty years, since mining ceased c. 1990, with the situation being monitored by the Coal Authority in a series of boreholes across the region. The Authority, a non-departmental government body responsible for the abandoned coal mine legacy within the UK, has a long term strategy to control these rising waters from Cadley Hill (c. 7 km to the NW), the lowest point of the coalfield. However, recent evidence obtained by the Authority suggests that the risks of contamination to the regional groundwater aquifer by the rising mine water are lower than previously considered. Hence, this dewatering strategy is currently in abeyance whilst further options are currently under review.

Saltersford Valley Picnic Area is a nature reserve located in the southern region of the South Derbyshire Coalfield, approximately 1 km NW of Measham, Leicestershire. Subsidence associated with sub-surface coal mining resulted in the Saltersford Brook flooding farmland producing a series of small permanent lakes, known locally as 'flashes', which form the nucleus of the nature reserve. The site was purchased by Leicestershire County Council in 1990 and was transformed into a recreational area, suitable for use by the local population in addition to enhancing conditions for wildlife. The site was designated as a Local Nature Reserve by Natural England in 2004, and includes woodland, grassland, wetland and freshwater lake habitats.

Mine water breached the surface at Saltersford from the abandoned Nether Leys Pit shaft in early 2010. The discharge quickly discoloured the lake, concerning both local residents and politicians, and was reported by the local press; prompt action was therefore required to minimise the visual impact of the discharging mine water to the area. The discharge is currently not included on the Environment Agency (EA) priority list, as the principal local water course of the Saltersford Brook, is presently not impacted by the discharge. However, as the Saltersford Brook flows directly into the River Mease, which is designated as a Special Area of Conservation (SAC) site, future protection of the water course may be required. The discharge may transiently dry up as a result of de-watering associated with a proposed nearby opencast site, and ultimately, if a pump and treat scheme is implemented near Cadley Hill. In these rather unusual circumstances, the Authority considered that a temporary mine water treatment method would be more appropriate for this location in preference to schemes (*i.e.* aeration cascades, settling lagoons and aerobic wetlands), typically constructed and operated by the Authority. The limited amount of land available for any treatment scheme combined with the need for a prompt, yet temporary response, made this site a prime location for trialling an alternative mine water treatment technique such as the use of high surface area media or a SCOOFI (Surface Catalysed Oxidation of Ferrous Iron) system.

SCOOFI Mine Water Treatment Schemes

The number of SCOOFI mine water treatment schemes in the UK have essentially been limited to small-scale field trials, (e.g. Younger 2000; Jarvis and Younger 2001) with an exception being a full scale trial installed at an ironstone mine at Skinningrove, Cleveland, c. 2000, which is no longer operational. SCOOFI media are suitable for net-alkaline waters with iron concentrations less than 50 mg/L, in locations where space is limited (PIRAMID Guidelines 2003), therefore the initial water chemistry of the mine water discharge at Saltersford was considered suitable for treatment with a SCOOFI reactor. A number of texts describe SCOOFI reactors in detail (e.g. Younger et al. 2002; PIRAMID Guidelines 2003); however, in essence a SCOOFI reactor is a porous plastic media with a very high surface area ratio. They work on the principal that as oxygenated water flows through the media, iron will gradually precipitate onto the surface of the media, steadily resulting in a thin layer of ferric hydroxide (ochre). Once the ochre has coated the porous material, the rate at which iron is removed from the water increases, as the rate of ochre catalysed iron oxidation is faster than iron oxidation in open water (Younger et al. 2002). As this process is continuous, iron will continue to be removed from the water until such quantities of ochre have accumulated that the water flow becomes restricted and the SCOOFI media become blocked. Once this occurs the plastic media must be extracted and the ochre removed. The occasional cleaning requirements of SCOOFI reactors mean that the plastic media need to be contained in such a way that they can be easily removed from the water channel. Two different techniques have been applied at Saltersford to date; a) by inserting the SCOOFI media into meshed bags and b) by stringing individual media along a cord to form a chain

Results and Discussion Flow and Chemistry of Mine Water

The flow and chemistry of the mine water discharge at Saltersford was relatively stable for the first six months of the trial, which coincided with the drought of Spring 2012. However, the iron and flow rate of the discharge has changed considerably since June 2012 as a result of the very wet summer (Table 1); the mine water monitoring boreholes in the South Derbyshire Coalfield demonstrated a rapid water level rise in June 2012, with an increase of 1.8 m recorded over a period of 8 weeks within 1 km of site. The mine water is net-alkaline, with a mean alkalinity of 457 mg/L expressed as CaCO₃ (laboratory results), a typical pH of 6.4 (on site), and mean sulphate and chloride concentrations of ≈ 2060 mg/L and 64 mg/L respectively; these parameters have remained comparatively constant throughout the trial period. The infrastructure installed at Saltersford was designed to accommodate a flow of 4 L/s with a maximum iron concentration of 35 mg/L; the increase in flow, and corresponding deterioration in the chemistry of the untreated discharge have therefore had a negative impact on the trial. In the first six months of the trial (December 2011 - May 2012), the average flow was 1.5 L/s and the

Sample	Flow (L/s)	рН	Ferrous Iron (mg/L)	Total Iron (mg/L)	-
Raw Water (n=64)	1.53	6.38	26.5	26.7	
(n=9)	3.75	6.38	35	35.5	
(n=24)	4.44	6.36	42.7	42.3	
SCOOFI Inlet (n=64)	1.53	6.55	25	25.2	Table 1. Sum
(n=9)	3.75	6.51	33.2	33.9	mean flow rat
(n=24)	4.44	6.58	40.5	40.3	chemistry of th
Treated Water (n=60)	1.53	6.55	18.6	19.5	Pit Discharge
(n=9) (n=24)	3.75 4 44	6.51 6.62	30.2 38.2	30.5 37.8	sult
	Sample Raw Water (n=64) (n=24) SCOOFI Inlet (n=64) (n=24) Treated Water (n=60) (n=9) (n=24)	Sample Flow (L/s) Raw Water (n=64) 1.53 (n=9) 3.75 (n=24) 4.44 SCOOFI Inlet (n=64) 1.53 (n=9) 3.75 (n=24) 4.44 Treated Water (n=60) 1.53 (n=9) 3.75 (n=9) 3.75 (n=9) 3.75 (n=9) 3.75 (n=9) 3.75 (n=9) 3.75 (n=24) 4.44	Sample Flow (L/s) pH Raw Water (n=64) 1.53 6.38 (n=9) 3.75 6.38 (n=24) 4.44 6.36 SCOOFI Inlet (n=64) 1.53 6.55 (n=24) 4.44 6.58 Treated Water (n=60) 1.53 6.55 (n=9) 3.75 6.51 (n=9) 3.75 6.51 (n=24) 4.44 6.68 Treated Water (n=60) 1.53 6.55 (n=24) 4.44 6.61	SampleFlow (L/s)pHFerrous Iron (mg/L)Raw Water $(n=64)$ 1.536.3826.5 $(n=9)$ 3.756.3835 $(n=24)$ 4.446.3642.7SCOOFI Inlet $(n=64)$ 1.536.5525 $(n=9)$ 3.756.5133.2 $(n=24)$ 4.446.5840.5Treated Water $(n=60)$ 1.536.5518.6 $(n=9)$ 3.756.5130.2 $(n=9)$ 3.756.5130.2 $(n=24)$ 4.446.6238.2	SampleFlow (L/s)pHFerrous Iron (mg/L)Total Iron (mg/L)Raw Water $(n=64)$ 1.536.3826.526.7 $(n=9)$ 3.756.383535.5 $(n=24)$ 4.446.3642.742.3SCOOFI Inlet $(n=64)$ 1.536.552525.2 $(n=64)$ 1.536.552525.2 $(n=64)$ 1.536.5518.619.5 $(n=60)$ 1.536.5518.619.5 $(n=60)$ 3.756.5130.230.5 $(n=9)$ 3.756.5130.230.5 $(n=24)$ 4.446.6238.237.8

mean raw total iron concentration was 26 mg/L (Table 1). For the last five months of the trial (September 2012 – January 2013) however, the system has been routinely dealing with flows of 4.4 L/s, which exceed the original design capacity and raw total iron concentrations of 42 mg/L that are in the upper region of the suggested acceptable SCOOFI treatment levels (PIRAMID Guidelines 2003).

Design of Treatment System

The scheme constructed at Saltersford (Fig. 1) consists of an aeration cascade comprised of a series of four steps, a small settling pond area and two parallel channels (0.5 m × 0.4 m \times 12 m; volume 2.5 m³) which house the Veolia Cascade Filterpak YTH1170 high surface area (200 m^2/m^3) units. Within the channels a series of baffle plates are installed to alternate

the flow of water both up and down through the SCOOFI media. Two different configurations of SCOOFI media have been used in this trial to facilitate easy handling and maintenance of the scheme; nylon mesh bags and SCOOFI chains. The results of the trial discussed here are divided into three sections, a) Bagged Media, b) Bags vs. Chains and c) Media Chains. For one week in March 2012 (20/03/12 -27/03/12), the system was emptied of media to ascertain the effectiveness of the scheme infrastructure to remove iron. During this period it was established that the small cascade and settling pond removes on average 2 mg/L of iron with a small amount of ochre also precipitating in the channels. The following discussion will therefore focus on the water chemistry of the inlet and outlet of the SCOOFI media channels.



Fig. 1. The Saltersford SCOOFI Reactor System showing the aeration cascade and settling pond to the left and media channels to the right; several SCOOFI media chains are visible in the bottom right hand corner of the settling pond.

Wolkersdorfer, Brown & Figueroa (Editors)

Bagged Media Trial

In this first trial, the SCOOFI media were contained within nylon mesh $(2 \text{ mm} \times 2 \text{ mm})$ bags 500 mm \times 380 mm in size. Over the first two weeks of the trial, the amount of iron removed by the media gradually increased as ochre steadily precipitated in the system (Fig. 2). During the period of peak performance, the system removed a mean of 7 mg/L of iron reducing the average total iron concentration from 25 mg/L to 18 mg/L. A similar pattern was observed for the ferrous iron, with a mean of 7 mg/L of ferrous iron also being removed by the media; based on a mean flow during this period of 1.4 L/s, this equates to an average area-adjusted iron removal rate of 119 $g/m^2/d$ for the media contained within the meshed bags.

During this short trial it was discovered that the iron quickly and preferentially precipitated on the mesh bags, congesting the system and unbalancing the flow of water; after only two months, the system blocked up, overflowed and had to be cleaned out. From a maintenance perspective, this rapid clogging of the system is impractical; furthermore, data were required to assess the performance of the media alone. Therefore, an alternative method of grouping the media together was necessary.

Bags vs. Chains

In order to investigate the performance of the media, it was decided to string a number of individual SCOOFI units together in a chain thereby making the mesh bags redundant. This second trial lasted for three months (April 2012 – June 2012) and compared the bagged media with the media chains to ascertain the impact of the mesh bags on the iron removal observed in the first trial.

The results shown in Figs. 2 and 3 ostensibly suggest that the bagged media were more successful at removing iron compared to the media chains, as on average the bagged media removed a mean 4.6 mg/L of iron whereas the media chains removed 3.4 mg/L of iron. However, these results are affected by an uneven distribution in the flow between the two channels during this trial. In a repeat from the first trial, ochre rapidly precipitated on the meshed bags, obstructing the channel and directing the majority of the flow through the media chains channel. Unfortunately flow data was not recorded from the two discharge channels during the trial, however, the channel containing the media chains was typically observed to have higher flows in contrast to the bagged media channel. Consequently the media chains were treating a higher loading compared to the bagged



Fig. 2. Total iron concentrations of the SCOOFI channel inlet and outlet waters for the three media configurations tested at Saltersford from December 2011 to January 2013.

Note: the total iron concentrations of the SCOOFI channel inlet and outlet waters during the Media Chains trial show that the media removed ≈ 3 mg/L of iron (e.g. October and November 2012), however as the system becomes clogged with ochre (due to being overwhelmed) iron is discharged from the scheme (e.g. December 2012). media, and therefore removing a greater amount of iron. The overall mean flow rate during this period was 2.4 L/s, and the raw iron concentration increased to 29.5 mg/L. Based on a limited number of direct observations, it is estimated that the channel containing the media chains typically contained 60 -70 % of the flow, whereas the bagged media channel had a maximum of 30 - 40 %. Based on these figures it is estimated that the areaadjusted removal rate for the media chains was, on average, in the range of 111 -129 g/m²/d, whereas the removal rate for the bagged media was in the range of 50 -99 g/m²/d. These results demonstrate that the media chains are more effective at removing iron compared to the meshed bags, probably due to the even flow distribution through the media chains, which, in contrast to the mesh bags, remained unimpeded by ochre.

The lower removal rate calculated for the bagged media in this second trial may be due to a number of reasons. Firstly, the flow rate being treated by the bagged media was lower compared to the first trial (<1 L/s) and secondly, the bagged media partially blocking the channel have a negative impact on the hydraulic efficiency of the channel resulting in shortcutting in the system. The meshed bags were removed at the end this trial and replaced with chains of SCOOFI media.

Media Chains

The flow rates and raw iron concentrations have varied throughout this third trial with peak flows (6.1 L/s) occurring in July – September (the average flow during this trial was 4.4 L/s) and a mean raw total iron concentration of 42 mg/L (Fig. 2); the scheme has therefore been subject to flows and iron concentrations that exceed the original design parameters. Throughout this final trial the scheme has removed a mean iron concentration of 2.4 mg/L; however, there have been periods when the channels have become overfull of ochre, resulting in iron being released from the system as ochre particulates. If the periods of iron release are discounted then the amount of iron removed by the media when they are not blocked, increases to 3.2 mg/L, with a maximum amount of 9.2 mg/L removed; typically the total iron concentration discharging from the scheme is 38 mg/L. Despite this trial being adversely affected by periods of very high flow rates which have occasionally swamped the scheme combined with periods of iron release when then scheme has become clogged with ochre, a mean area-adjusted iron removal rate of 139 g/m²/d has been calculated for the SCOOFI Media chains. This result indicates that the media chains are an effective form of treatment for the removal of iron.



Fig. 3. Total iron concentrations of the SCOOFI channel inlet and outlet waters during the Bags vs. Chain Media trial. Although the graph suggests that the bagged media were more efficient at removing iron, the media chains were treating a greater loading of iron during this period due to higher flow rates.

Note: for clarity, the axes differ from those used in Fig. 2 to illustrate the detail.

Conclusions and Recommendations

The scheme at Saltersford has been adversely affected by the increase in water flow rates and raw iron concentrations, which has resulted in the scheme being overwhelmed and unable to prevent the lake at Saltersford from being discoloured by the iron. However, the SCOOFI trial at Saltersford has provided some relevant results in the use of high surface area media. The media chain trial has produced some inarea-adjusted dicative removal rates $(139 \text{ g/m}^2/\text{d})$ that far exceed those typically quoted by Hedin et al. (1994; i.e. 10 g/m²/d), which suggest that high surface area media could potentially be used in areas where there is insufficient space for settlement ponds. However the trial has also raised some important maintenance issues which need to be addressed before the system can be used elsewhere. Firstly, the ochre which precipitates onto the media at Saltersford is very unstable. Although the flow of water in the scheme is not sufficient to flush out the ochre. as soon as the media are disturbed, the ochre readily detaches from the units and flows out of the channels. Therefore, although a thin layer of ochre initially forms on the media, the majority of the precipitate is present as an unstable amorphous mass which is very difficult to remove and contain in a controlled manner, especially during maintenance. Secondly, the channels at Saltersford become congested with ochre very rapidly, and have been found to be difficult to maintain and clear out. This has been exacerbated by the very high flow rates and increasing raw iron concentrations observed during the trial, which has necessitated in the requirement for regular monitoring and maintenance to endeavour to prevent the system from overflowing and flooding the public footpath. These two maintenance issues need to be addressed to make this type of technology more efficient and cost effective for future deployment.

The nature of the ochre which collects on the media would necessitate the need for an aerobic reed bed or possibly a Vertical Flow Reactor (VFR) to follow a SCOOFI system. This would facilitate the collection of any ochre disturbed during maintenance of the system in addition to 'polishing' (Batty and Younger 2002) the water; this trial has not provided any information to suggest that the media alone could treat iron down to the current Environmental Quality Standard (EQS) concentration of 1 mg/L. This technology, therefore, would not be suitable for very small areas. However, the use of SCOOFI media could reduce the size of settling ponds and the Authority plan to undertake further trials to investigate this possibility further.

Acknowledgements

The authors thank those people at Integrated Water Services for all of their efforts maintaining the trial at Saltersford and for their patience stringing the SCOOFI media together.

References

- Batty LC, Younger PL (2002) Critical role of Macrophytes in achieving low iron concentrations in mine water treatment wetlands. Environmental Science and Technology 36:3997–4002
- Hedin RS, Nairn RW, Kleinmann RLP (1994) Passive treatment of coal mine drainage. USBM IC 9389, US Dept of the Interior, Washington DC, 35 pp
- Jarvis AP, Younger PL (2001) Passive treatment of ferruginous mine waters using high surface area media. Water Research 35:3643–3648
- PIRAMID Consortium. (2003) Engineering Guidelines for the Passive Remediation of Acidic and/or Metalliferous Mine Drainage and Similar Wastewaters. European Commission 5th Framework RTD Project no. EVK1-CT-1999-000021 "Passive in-situ remediation of acidic mine/industrial drainage (PIRAMID). University of Newcastle Upon Tyne, UK, 166 pp.
- Younger PL (2000) The adoption and adaptation of passive treatment technologies for mine waters in the United Kingdom. Mine Water and the Environment 19:84–97.
- Younger PL, Banwart SA, Hedin RS (2002) Mine Water Hydrology, Pollution, Remediation – Vol 5 Environmental Pollution. Kluwer Academic Press, Dordrecht, 442 pp

Carbon dioxide impacts both passive treatment system effectiveness and carbon footprint

Robert W. NAIRN¹

¹Center for Restoration of Ecosystems and Watersheds, School of Civil Engineering and Environmental Science, University of Oklahoma, 202 West Boyd Street, Norman, Oklahoma, 73019, USA, nairn@ou.edu

Abstract Artesian discharges of net-alkaline, ferruginous waters from abandoned underground lead-zinc mines were examined in field mesocosms and a full-scale passive treatment system. Influent waters were calculated to contain ≈ 290 mg/L dissolved CO₂ (*p*CO₂ of 0.16 atm). Degassing of CO₂ improved iron and trace metal removal performance. Despite proton acidity produced by oxidative iron removal, pH values increased to >6.5, thus enhancing the rate of iron removal. Degassing resulted in return of $\approx 84,000$ kg of CO₂ to the atmosphere on an annual basis, while maximum biological productivity would result in carbon sequestration of $\approx 4,500$ kg a⁻¹ in the full-scale system.

Keywords passive treatment, carbon dioxide, exsolution, sequestration, carbon footprint

Introduction

Over the past three decades, hundreds of passive treatment systems have been designed and constructed for coal and metal mining impacted waters (e.g. Hedin et al. 1994, Younger et al. 2002). Properly operating passive systems are often viewed as sustainable "green" alternatives to energy- and resource-intensive active chemical treatment technologies. Longterm operation in gravity-driven passive systems typically requires no direct fossil fuel consumption and process units which include algae or macrophytic vegetation contribute to temporal carbon sequestration through photosynthetic primary production. These ecologically engineered ecosystems are considered to have a low to neutral carbon footprint, while providing direct benefits to society (e.q. water quality improvement and contaminant retention) and the natural environment (e.g. habitat provision and receiving stream ecological recovery).

In addition to problematic metals, sulfate and acidity concentrations, many mine water discharges also contain elevated concentrations of dissolved carbon dioxide (CO₂) depending on geological and environmental conditions. In treatment design scenarios, CO₂ concentrations may be examined for their contribution to acidity as carbonic acid (H_2CO_3) , however that role is typically viewed as temporary because CO₂-rich mine waters readily degas when exposed to atmospheric conditions (e.g. Kirby et al. 2009). Dissolved CO₂ may also be considered for its implications on effective treatment, either due to the fact elevated concentrations constrain the performance of some alkaline additions due to carbonate solid formation, or, in anoxic limestone drain applications closed to the atmosphere, the role they play in enhancing equilibrium alkalinity concentrations (e.g. Cravotta 2007). In each case, the role of elevated CO_2 concentrations in mine water treatment is typically assessed from a water quality perspective, and not from a more holistic systems point of view.

In this study, the role of dissolved CO_2 in passive treatment system performance for circum-neutral pH, net-alkaline mine waters was analyzed using a simple ecosystems-driven carbon-balance approach. Influences of CO_2 on water quality improvement mechanisms were the driving force for the field studies. Compared to traditional active treatment technologies, the system may certainly be considered a more sustainable "green" technology, however, initial evaluation of the contributions to atmospheric CO₂ by the passive treatment system questions the low to neutral carbon footprint of at least some of these technologies.

Methods

Field mesocosm experiments were conducted at a mine drainage discharge in the Tar Creek Superfund Site, part of the historic Tri-State Lead-Zinc Mining District. Water quality at the discharge has been well-documented (Nairn et al. 2009, Nairn et al. 2010a; Nairn et al. 2010b; Table 1). Eighteen field mesocosms (40-L plastic tubs) were filled with untreated mine water and were incubated in standing water near the discharge to maintain ambient temperature conditions throughout the 24-hr experiment. Six treatments were examined to evaluate the effects of passive and active oxygenation/CO₂ degassing on heterogeneous and homogenous iron retention and trace metal sorption. Treatments included: i) Closed, ii) Closed + Fe, iii) Open, iv) Open + Fe, v) Open Aerated and vi) Open Aerated + Fe. All "Closed" treatments included a properly fitted plastic lid, fitted with a sampling line (so water samples could be drawn without exposing the water surface) and a stoppered hole allowing placement of a water quality data sonde for in situ measurements. "Open" systems remained uncovered. Each "Aerated" treatment was mechanically aerated with two standard aquarium aeration stones and aquarium pumps. In all "+Fe" treatments, approximately 50 cm³ of iron solids collected on-site were added to the already water-filled tubs.

Design and construction of the full-scale Mayer Ranch passive treatment system for this discharge was reported by Nairn et al. (2009) and initial evaluation documented by Nairn et al. (2010a, 2010b, 2011, 2012). The system was designed for 1000 L/minute of flow and consists of ten distinct process units including two parallel treatment trains (Fig. 1). Waters from three discharges flow into an initial oxidation pond (1), followed by parallel surface-flow aerobic wetlands/ponds (2N and 2S), vertical-flow bioreactors (3N and 3S), re-aeration ponds (4N and 4S), horizontal-flow limestone beds (5N and 5S), and are recombined in a single polishing pond/wetland (6). Each process unit is designed to carry out specific functions as described in Table 2 (Nairn et al. 2009). Construction was completed in late 2008 and the full system has been sampled regularly (n=28 sampling events)

Temperature, pH, dissolved oxygen, oxidation-reduction potential, total dissolved solids, conductivity, and specific conductance were determined in situ with a YSI 600QS multiparameter datasonde and YSI 650MDS display. Total alkalinity and turbidity were measured immediately upon sample collection via titration with appropriate normality sulfuric acid using a Hach digital titrator (Method 8203) and via a Hach 2100P turbidimeter, respectively. Samples were collected in 250-mL HDPE bottles and preserved with trace metal grade HNO₃ to pH <1 for metals analyses at the Center for Restoration of Ecosystems and Watersheds (CREW) laboratories at the University of Oklahoma. Preserved samples were first nitric acid digested in a CEM MARSXpress Diges-

Constituent	Mean	Constituent	Mean	_
pH	5.95	Fe (mg/L)	177	
Temperature (°C)	18	Zn (mg/L)	8.3	
Salinity (ppK)	1.9	Pb (mg/L)	0.07	Table 1 Selected water qual-
Total alkalinity (mg/L CaCO ₃)	393	Cd (mg/L)	0.02	ity data for artesian dis-
Calculated dissolved CO ₂ (mg/L)	283	As (mg/L)	0.06	charges used in full system
Calculated pCO ₂ (atm)	0.16	Ni (mg/L)	0.95	design.

Process unit	Targeted parameter	Function
Oxidation pond	Fe	Oxidation, hydrolysis and settling of iron oxyhydroxide solids; Trace metal sorption
Surface-flow wetlands/ponds	Fe	Solids settling
Vertical-flow bioreactors	Zn, Pb, and Cd	Retention of trace metal sulfides via reducing mechanisms
Re-aeration ponds	Oxygen demand and odor	Wind- and solar-powered re-aeration; Oxygen demand and ${ m H}_2S$ stripping; Addition of ${ m O}_2$
Horizontal-flow limestone beds	Zn, Mn and hardness	Final polishing of Zn as ZnCO3 and of Mn as MnO2; Hardness addition to offset bioavailability of remaining trace metals
Polishing pond/wetland	Residual solids	Solids settling: Photosynthetic oxygenation; Ecological buffering

Table 2 Summary of process units, primary targeted water quality parameters and design functionfor passive treatment system.



Fig. 1 Mayer Ranch passive treatment system, Tar Creek Superfund Site, Oklahoma, USA.

tion System following EPA Method 3015 (EPA 2006). Digested samples were then analyzed with a Varian Vista-PRO simultaneous axial Inductively Coupled Plasma-Optical Emission Spectrometer following EPA Method 6010b (EPA 2006) for 15 analytes (Al, As, Ca, Cd, Co, Cr, Cu, Fe, Pb, Mg, Mn, Ni, K, Na, and Zn). Dissolved carbon dioxide concentrations and partial pressures were calculated from field measurements of pH, temperature, salinity and total alkalinity using appropriate reference equations from Harned and Owen (1958), Millero (1995), Stumm and Morgan (1996) and Weiss (1974).

Results

In the mesocosm experiment, degassing of CO₂ in the "Open Aerated" treatments led to rapid pH increases to ≈ pH 8 despite concomitant proton production by iron hydrolysis (Fig. 2). In "Closed" and "Open" treatments, pH remained suppressed and only slightly greater than 6. Total alkalinity showed a dramatic initial decrease (in the first ten hours) as proton acidity produced by iron hydrolysis was neutralized. Note that pH increased or remained constant as alkalinity decreased, again indicative of the important role of CO₂ degassing. The greatest iron removal was seen in the "Open Aerated" treatment which showed consistent and dramatic concentration decreases to < 10 mg/L in 24 hours. "Open Aerated" and "Open Aerated + Fe" data were best fit by exponential models of $[Fe] = 150e^{-0.144t}$ (r² = 0.91) and $[Fe] = 159e^{-0.149t}$ (r² = 0.94), respectively, the slopes of which were not significantly different (p < 0.05). "Open" treatments demonstrated slightly lower final iron concentration changes than closed treatments. Trace metals concentrations did not demonstrate significant decreases in "Closed" or "Open" treatments (data not shown). In "Open Aerated" treatments, zinc concentrations demonstrated steady decreases to less than 2 mg/L, again with no dif-



Fig. 2 Selected water quality changes in 24-hr mesocosm experiment.

ference between "Open Aerated" and "Open Aerated + Fe" treatments. Nickel concentrations demonstrated similar decreases but only from ≈ 1 to ≈ 0.75 mg/L. Arsenic, cadmium and lead concentrations decreased in a similar manner, although arsenic and lead concentrations were below analytical detection limits by six hours and 12 hours, respectively. Cadmium concentrations decreased steadily to 12 hours, after which they became asymptotic. Trace metal sorptive capabilities of iron solids are long well-documented (e.g. Dzombak and Morel 1990, Kairies et al. 2005, Neely 2010). The critical effects of CO₂ degassing in effective mine water treatment was demonstrated by this short-term mesocosm experiment.

IMWA 2013

The full-scale passive treatment system has been operational for over four years. From

a water quality improvement perspective, the system has performed as designed, maintaining a net al.kaline nature throughout the system as target metals were removed from solution. Due in part to degassing of elevated CO_2 concentrations in the artesian discharges, pH increased from less than 6 to >7 at final discharge. Table 3 shows typical changes in selected measured and calculated constituents for a single sampling event.

Iron was predominately retained in the oxidation pond and surface flow wetlands. Arsenic, lead, and cadmium concentrations also demonstrated significant decreases in these units via sorption to iron solids. Degassing of CO₂, and subsequent increases in pH, directly influenced iron, and thus trace metal, removal in these initial process units. Zinc and nickel

	System influent	System effluent		System influent	System effluent
pH	5.96	7.36	Fe (mg/L)	183	0.096
Temperature (°C)	17.87	28.02	Zn (mg/L)	8.1	0.005
Salinity (ppK)	1.89	1.80	Pb (mg/L)	0.058	<pql< td=""></pql<>
Total alkalinity (mg/L CaCO ₃)	374	288	Cd (mg/L)	0.025	<pql< td=""></pql<>
Dissolved CO ₂ (mg/L)	262	6.56	As (mg/L)	0.062	<pql< td=""></pql<>
pCO ₂ (atm)	0.14	0.005	Ni (mg/L)	0.968	0.040

Table 3 Typical water quality performance of full-scale passive treatment system. Data are from August 2009 sampling event. PQL is practical quantification limit.

were primarily removed in the vertical flow bioreactors.

Dissolved CO_2 concentrations dramatically decreased with flow through the passive treatment system. For the data presented in Table 3 for a typical mid-summer day (representing the most extreme water temperature changes with flow through the system as well as a period of peak biomass production and thus photosynthetic rates), the system received approximately 213 kg d⁻¹ of dissolved CO_2 from the artesian mine water sources and discharged slightly more than 5 kg d⁻¹ in the final effluent, resulting in a loss of 208 kg of CO_2 on this summer day.

Few authors haves systematically examined the carbon footprint of passive treatment systems, although some initial efforts have been made (e.g. Gusek et al. 2011, Jordahl et al. 2009). On an annual basis, the studied system is estimated to have lost approximately 84,000 kg a^{-1} of dissolved CO₂ from the water column. An assumption of peak primary production rates for the vegetated units of the system results in a potential carbon utilization of approximately 4,500 kg a⁻¹. Therefore, it may be projected that the system loses the great majority of CO_2 (around 79,500 kg a^{-1}) to the atmosphere. These estimated CO₂ emissions are equivalent to approximately 17 passenger vehicles for one year or 34,000 L of gasoline (EPA 2013).

Conclusions

Dissolved carbon dioxide is a common constituent in many mine waters and plays an important role in many passive treatment processes. Degassing of elevated concentrations of CO_2 can lead to increased pH, thus having a positive impact on oxidative iron removal rates, which may also lead to trace metal removals via sorption. Despite this critical contribution to contaminant removals, the role of CO_2 is often neglected or misunderstood. In the mesocosm and full-scale passive treatment system studies described herein, CO_2 degassing from net alkaline mine waters played a critical and influential role in several water quality improvement processes (*e.g.* oxidative iron removal, subsequent trace metal sorption, pH increase, etc.) and contributed considerably to overall system performance. Enhancement of the rates of water column aeration and CO_2 degassing in the primary oxidation pond, perhaps through solar- and wind-powered devices, is a potential line of additional research necessitating further inquiry and could decrease passive treatment system sizing requirements.

This initial analysis focused on carbon dynamics during passive treatment system operation. It neglects to include carbon inputs during system construction, tradeoffs between passive treatment system operation and other alternatives (*e.g.* either no action or active chemical treatment) and does not delve into individual process unit carbon balances. However, it does indicate that comprehensive analysis of "green" technologies requires an understanding of mine water geochemistry and should be performed using a whole ecosystem approach.

Acknowledgements

The author thanks the many student, staff and faculty members of the University of Oklahoma Center for Restoration of Ecosystems and Watersheds who contributed to this study. Funding for passive treatment system design and construction was provided by the U.S. Environmental Protection Agency and U.S. Geological Survey. Private landowners provided access for this research.

References

- Cravotta C (2007) Passive aerobic treatment of net-alkaline, iron-laden drainage from a flooded underground anthracite mine, Pennsylvania, USA. Mine Water and the Environment 26: 128-149
- Dzombak DA, Morel FMM (1990) Surface Complexation Modeling Hydrous Ferric Oxide. John Wiley & Sons Inc. New York, USA, 393 pp.
- Environmental Protection Agency (2006) Test Methods for Evaluating Solid Wastes, Physical and Chem-

ical Methods. USEPA SW-846, Office of Solid Waste, Washington, D.C. (www.epa.gov/epaoswer/ hazwaste/test/sw846.htm)

- Environmental Protection Agency (2013) Greenhouse Gas Equivalencies Calculator, www.epa.gov/ cleanenergy/energy-resources/calculator.html
- Gusek J, Josselyn L, Agster W, Lofholm S, Millsap D. (2011) Process selection and design of a passive treatment system for the Empire Mine State Historic Park, California. 28th National Conference of the American Society of Mining and Reclamation, Bismarck, ND, USA, p 232-253
- Harned HS, Owen BB (1958) The Physical Chemistry of Electrolyte Solutions. 3rd ed. Van Nostrand Reinhold, New York, USA
- Hedin RS, Nairn RW, Kleinmann RLP (1994) Passive Treatment of Coal Mine Drainage. US Bureau of Mines Information Circular 9389, 37 pp
- Jordahl J, Frank P, Kealy MJ, Bays J (2009) Going beyond carbon footprint: Elements of sustainability for treatment wetlands and design implications, WEFTEC 2009, Session 31-40, p 1991-2005
- Kairies C, Capo R., Watzlaf G (2005). Chemical and physical properties of iron hydroxide precipitates associated with passively treated coal mine drainage in the Bituminous Region of Pennsylvania and Maryland. Applied Geochemistry 20:1445-1460
- Kirby CS, Dennis A, Kahler A (2009) Aeration to degas CO2, increase pH, and increase iron oxidation rates for efficient treatment of n*et al*.kaline mine drainage. Applied Geochemistry 24: 1175-1184.
- Millero FJ, (1995) Thermodynamics of the carbon dioxide system in the oceans. Geochim. Cosmochim. Acta 59, 661-677
- Nairn RW (2012) Design, Construction and Evaluation of a Passive Treatment System for Contaminated Mine Waters, Draft Final Report submitted to US Environmental Protection Agency, 566 pp
- Nairn RW, Beisel T, Thomas RC, LaBar JA, Strevett KA, Fuller D, Strosnider WH, Andrews WJ, Bays J, Knox RC (2009) Challenges in design and construction of

a large multi-cell passive treatment system for ferruginous lead-zinc mine waters. 26th National Conference of the American Society of Mining and Reclamation, Billings, MT, USA, p 871-892

- Nairn RW, LaBar JA, Strevett KA, Strosnider WH, Morris D, Neely CA, Garrido A, Santamaria B, Oxenford L, Kauk K, Carter S, Furneaux B (2010a) A large, multicell, ecologically engineered passive treatment system for ferruginous lead-zinc mine waters. Mine Water and Innovative Thinking, Proceedings International Mine Water Association, Sydney, Nova Scotia, Canada, p 255-258
- Nairn RW, LaBar JA, Strevett KA, Strosnider WH, Morris D, Garrido AE, Neely CA, Kauk K (2010b) Initial evaluation of a large multi-cell passive treatment system for net-alkaline ferruginous lead-zinc mine waters. 27th National Conference of the American Society of Mining and Reclamation, Pittsburgh, PA, USA, p. 635-649
- Nairn RW, LaBar JA, Strevett KA, (2011) Passive treatment opportunities in a drastically disturbed watershed: Reversing the Irreversible? 28th National Conference of the American Society of Mining and Reclamation, Bismarck, ND, USA, p 450-468
- Neely CA (2010) Characterization and Possible Sustainable Sorbent Use of Iron Oxides from Abandoned Mine Drainage Discharges, MS thesis, University of Oklahoma, 150 pp
- Stumm W, Morgan JJ (1996) Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters. 3rd edition, Wiley-Interscience, New York, U.S.A. 1022 pp
- Weiss RF (1974) Carbon dioxide in water and seawater: the solubility of a non-ideal gas. Marine Chemistry 3:203-215
- Younger P, Banwart SA, Hedin RS (2002) Mine Water: Hydrology, Pollution, Remediation. Kluwer Academic Publishers, Boston, USA, 442 pp

Successful Passive Treatment of Iron-Rich Lead-Zinc Mine Waters and an Effective Method to Address Nuisance Constituents

Robert W. NAIRN

Center for Restoration of Ecosystems and Watersheds, School of Civil Engineering and Environmental Science, University of Oklahoma, 202 West Boyd Street, Norman, Oklahoma, 73019, USA, nairn@ou.edu

Extended Abstract Data from hundreds of passive treatment systems demonstrate successful improvement of abandoned mine water quality by decreasing ecotoxic metals concentrations, and increasing alkalinity concentrations and pH. However, certain biologically-based process units may produce excessive concentrations of atypical, non-mine drainage related constituents. These predominately anaerobic units (*e.g.* vertical flow bioreactors) are designed to promote reductive microbial mechanisms. Therefore, even if functioning properly from a mine water quality improvement perspective, effluent waters may initially contain excessive amounts of non-target contaminants, *e.g.* biochemical oxygen demand (BOD), sulfide, and nutrients, have low dissolved oxygen concentrations and oxidation-reduction potential, and cause nuisance odor problems. Compounding a general lack of understanding of these issues, these non-mine drainage water quality constituents are not typically included in most monitoring schemes and system performance evaluations.

At the study site, artesian discharges of net-alkaline, ferruginous waters from abandoned underground lead-zinc mines cause considerable surface water degradation. A passive treatment system (≈ 2 ha total surface area), completed in 2008, was designed to receive 1000 L/min of mine water flowing from abandoned boreholes (pH 5.95±0.06, total alkalinity 393±18 mg/L CaCO₃, total acidity 364±19 mg/L CaCO₃, Fe 192±10 mg/L, Zn 11±0.7 mg/L, Cd 17±4 µg/L, Pb 60±13 µg/L and As 64±6 µg/L). The system includes an initial oxidation pond followed by parallel treatment trains of aerobic wetlands, vertical flow bioreactors, re-aeration ponds, and horizontal-flow limestone beds, and a final polishing wetland/pond.

Mean final effluent waters had pH >7, were n*et al*.kaline and contained < 1 mg/L total Fe and 0.2 mg/L total Zn, and had concentrations of Cd, Pb and As below detectable limits. However, the vertical flow bioreactors seasonally produced concentrations of nitrogen, phosphorus and sulfide that exceeded applicable water quality or aquatic toxicity criteria, and which presented nuisance odor problems. BOD values were not elevated. Summer nitrogen and phosphorus concentrations in the final effluent were 1.01 \pm 0.26 mg/L and 0.59 \pm 0.14 mg/L, respectively, well above U.S. Environmental Protection Agency (EPA) nutrient criteria. Summer sulfide concentrations in the final effluent were greater than the U.S. EPA freshwater criterion continuous concentration of 2 µg/L, with vertical flow bioreactors effluent concentrations of 15.8 \pm 9.22 mg/L.

The re-aeration ponds include renewable energy-driven (solar- and wind-powered) re-aeration devices, which demonstrated seasonally effective enhancement of re-oxygenation and mixing of the water column downstream of anaerobic process units. More robust monitoring schemes, including constituents beyond the typical mine water parameter suite, may be appropriate when anaerobic process units are included in passive treatment system designs.

Keywords vertical flow bioreactors, re-aeration, nuisance constituents, eutrophication, toxicity

Advances in using sewage sludge to remediate sulfidic mine tailings – An overview from pilot- and field-scale experiments, northern Sweden

Peter Nason

Luleå University of Technology, Department of Civil, Environmental and Natural Resources Engineering, SE-97187, Luleå, Sweden

Abstract Sewage sludge can and has been used effectively as an organic-rich cover for sulfidic mine waste remediation. However, the optimum use of the material as a layer in engineered covers remains unconfirmed. Results obtained from four different sewage sludge applications are presented and discussed in context to their success and for their applicability for being used at full-scale sulfidic-mine waste remediation projects. The experiments evaluated sewage sludge when used as a vegetation substrate on bare tailings, a water-saturated cover, a composite cover, and lastly when used as a sealing-layer barrier material, which was deemed the most successful technique.

Keywords Sewage sludge, geochemistry, remediation

Introduction

In Sweden, 59 Mt of mine waste are produced annually (Statistics-Sweden 2008b). The weathering of un-remediated sulfidic tailings may produce acid rock drainage (ARD). ARD mitigation in Sweden is largely directed towards constructing engineered dry covers to cap and reduce oxygen diffusion to the underlying sulfide tailings (Höglund *et al.* 2005).

Traditional cover materials have consisted of durable, unreactive natural materials such as glacial overburden or natural soil. Sourcing and excavating large volumes of these is often problematic and of further environmental concern. Replacing natural soils with an alternative such as an organic waste generated from another industry has become an inexpensive and attractive solution for the mining industry, providing the co-disposal of two separate wastes together. One such organic waste is sewage sludge (SS), a solid by-product material generated during the treatment of domestic waste-water.

Approximately 210 Kt of SS are produced annually (Statistics-Sweden 2008a) from more than 2100 waste water treatment plants in Sweden (Marklund 1997). It has been investigated as a vegetation substrate on the surface of tailing impoundments and waste rock dumps (Forsberg 2008), and has been proven to be a suitable substrate for supporting and sustaining long-term vegetation establishment (Pichtel *et al.* 1994). SS is not traditionally utilised as a sealing layer material for mine waste, but it may have the potential for such usage because of its favourable physical and geochemical suitability, such as a low hydraulic conductivity of 1×10^{-9} m/s (Mácsik *et al.* 2003). In addition, fresh SS contains a high organic matter content that may allow it to function as an organic reactive barrier (Peppas *et al.* 2000).

However, limitations surround the use of SS as it is chemically unstable. It may contain readily-leachable concentrations of metals (Cd, Cu, Ni, Pb, Zn; Eriksson 2001) which may migrate as soluble organo-metallic complexes (Andres and Francisco 2008). The release of nitrate may exceed vegetation requirements and leach into underlying sulfide-mine tailings (Cravotta 1998) where it may be a primary terminal electron acceptor to pyrite where groundwater is devoid of oxygen (Appelo and Postma 2005).



Fig. 1 Schematic diagram of the four different sewage sludge applications

The use of SS may therefore be problematic. This paper evaluates four different SS applications at pilot- and field-scales in northern Sweden. The experiments were conducted over the course of 0 to 8 years at 2 mine sites run by the Swedish mining company New Boliden AB. The results are summarized in this paper. It is the aim of this paper to identify the optimum use for SS so that it may be utilised by the mining companies on successful sulfide-tailings remediation projects in the future.

Study Sites and Experimental Set-up Pilot-scale Experiment: Sewage Sludge Sealing Layer

The Georange Environmental Test Site is located at the Kristineberg Mine in northern



Fig. 2 Experiment set-up and location of the pilot-scale test cells

Sweden (Fig. 2). A SS sealing layer was evaluated to understand if it was able to prevent oxygen diffusion and ARD formation to underlying tailings. Data from pore gas, leachate and sediment geochemistry were derived over an 8 year time-span. The engineered dry cover arrangement was applied above a 1.0 m thick fresh unoxidized tailings layer sourced from the Kristineberg Pb-Zn-Cu mine (Fig. 1: A). It consisted of a 0.25-0.30 m thick compacted anaerobically-digested SS sealing layer and an overlying 1.5 m thick protective layer consisting of locally-derived glacial till. For reference, the geochemistry was compared to a neighbouring cell consisting of 1.4 m thick unoxidized tailings identical in origin and experimental set-up.

Field-scale experiment: Sewage sludge vegetation substrate above engineered dry composite cover and water saturated cover

Field trials were conducted at a formally remediated sulfide-tailings facility, Impoundment 1 (Fig. 3), at the Kristineberg Mine. After 50 years of natural weathering, sulfide oxidation and ARD formation, the impoundment was remediated in 1996 by applying an engineered composite dry cover (1.5 m protective layer of glacial till and 0.3 m clay-rich till sealing layer) to the formerly raised tailings dam area, and by applying a simple 1 m thick water-saturated till cover in the west of the impoundment. In August 2009, 10.8 Kt of anaerobically-digested SS sourced from Stockholm Municipality was applied onto the dry covered area of the impoundment, and 1.2 Kt onto the water saturated cover areas to a depth of 0.3 m. It was applied to provide a substrate and nutrients to areas of the impoundment that had had poor vegetation establishment. A profile of the two cover applications is illustrated in Fig. 1: B/C.

Groundwater monitoring took place a few years after remediation in 1998–2006 and from June 2009-October 2011 after the SS application. Samples were collected from five installed groundwater wells from: the uncontaminated inflowing groundwater (Well P); the



Fig. 3 Map of Impoundment 1 showing location and cover types with sewage sludge application. Line A-B indicates dominant groundwater flow direction

water-saturated areas of the impoundment (Well F and G); the dry-covered areas of the impoundment (Well Q); and the outflow at the impoundment toe (Well L). Solid SS samples were collected before application, and after 2 years. The objective of the study was to identify if sludge-borne metals and nitrate were released to the underlying groundwater system, and if so, to delineate their magnitude, duration and fate.

Sewage sludge vegetation substrate directly on tailings

Field trails were conducted on a large-scale unremediated sulfide-tailings facility, the Gillervattnet Impoundment, at the Boliden Mine. Fresh tailings were applied up until 2008. Three plots were sampled for solid inorganic geochemistry, and pore-water analysis: an uncovered reference tailings plot oxidized for 2 years; an uncovered reference tailings plot oxidized for 1 year and covered with SS for 1 year; a tailings plot covered with SS immediately after application 2 years ago. The SS in both applications was sourced from the Stockholm Municipality. It was applied to a depth of 0.2 m in both applications (Fig. 1: D). The three applications can be visualized in Fig. 4. It was the objective of this study to evaluate if the SS altered the underlying tailings geochemistry, if it was effective at allowing successful vegetation establishment and if it prevented sulfide oxidation.

Results

Sewage Sludge Sealing Layer

The SS sealing layer was effective at reducing oxygen diffusion to the underlying tailings. It was calculated that a mass transfer of $0.54 \text{ mol}^{-1}\text{m}^{-2}\text{a}^{-1}$ oxygen occurred during the period 2004–2005 (Nason *et al.* 2013), conforming to the limitations set out for a conventional sealing layer in Sweden of <1 mol⁻¹m⁻²a⁻¹ (Carlsson 2002). Measured oxygen, carbon dioxide and methane indicated



Fig. 4 Three field-scale plots at the Gillervattnet Impoundment: Uncovered tailings oxidized for 2 years; 1year application of sewage sludge; 2-year application of sewage sludge

Wolkersdorfer, Brown & Figueroa (Editors)

that the SS may have functioned as an organic reactive barrier, consuming oxygen due to aerobic degradation of the organic matter, and producing methanagenesis and sulphate reduction.

It was additionally advantageous in that it created a reductive, alkaline environment in the underlying sulfidic-mine tailings, which promoted the precipitation of metals, improving the quality of the effluent drainage. The geochemical processes are illustrated by the schematic diagram in Fig. 5. However, up to -85 % depletion of the organic fraction of the SS occurred, accounting to a total volume loss of -20 % from the sealing layer. This is far less than surface applications of SS, though it should be considered a possible limiting factor when using SS as a sealing layer material in the long-term (>100 years). Nevertheless, in comparison the uncovered sulfide-bearing mine tailings received extensive sulfide oxidation characterised by the onset of ARD and a 0.35m deep acidic oxidation front formation.

Sewage sludge vegetation substrate above an engineered dry composite cover

Within the first year after SS application substantial vegetation establishment had occurred, and was a host to a vole population and an attractive bird-population such as grey wagtails, lapwings and rough-legged buzzards. The visual improvement of the SS application can be seen in Fig. 6. However, geochemically, the SS mass volume decreased in the two years after the application by -16.25 %. The mass lost was attributed to organic matter depletion (-22 %) and the leaching of sulfate, calcium and the metals, Cu, Ni, Pb and Zn. Nitrification of the SS also released excessive nitrate into the underlying cover materials. Fortunately, the results indicate that the function of the original engineered dry cover underlying the SS application focused the sludge-borne leachate laterally, where it was concentrated at the impoundment toe, without reaching or reacting with the tailings groundwater system.

Sewage sludge vegetation substrate above an engineered water saturated cover

Similarly to the dry covered area, plant establishment occurred within 1 year of application, and the SS mass volume decreased in the two years since the application by -17.76 %. Copper, Pb and Zn were removed more so than from the dry covered area. This was due to a rapid mobilization of the metals by the interaction of the raised groundwater table with the SS. Consequently, unhindered due to the lack of a sealing layer, the sludge-borne constituents migrated into the underlying tailings groundwater system with concentrations of the metals Cu (188 µg/L), Ni (263 µg/L), Pb (95 µg/L) and Zn (2060 µg/L) peaking two years after the SS application occurred, up from 2009 pre-SS concentrations of Cu (0 μ g/L), Ni (3.8 μ g/L), Pb $(0.4 \mu g/L)$ and Zn (1610 $\mu g/L$). The plume readily migrated laterally underneath the entire



Fig. 5 Schematic diagram of the dominant geochemical processes governing in the sewage sludge sealing layer experiment
impoundment to the toe due to speciation linked with organo-complexes. It was accompanied by a nitrate pulse of 67 mg/L. Using SO_4^2 -/Fe²⁺ molar ratios, pyrite oxidation was indicated in the tailings as the plume travelled laterally, caused by the introduction of nitrate as a primary terminal electron acceptor for pyrite, and as indicated by a decrease in pH and an increase in Fe concentrations. The plume was released by the SS over a 2-year period and ceased when vegetation establishment immobilized and retained the nitrate and metals, as has been prevalent in similar studies conducted in Sweden (Forsberg 2008). Concentrations subsided to within \pm 10 % of pre-SS concentrations by 2011 in the area underlying the SS application in the water-saturated area. Modelling of the plume has indicated it will have exited the impoundment within 6 years after the SS application.

Sewage sludge vegetation substrate directly onto tailings

The unoxidized tailings plot had a 0.05 m deep oxidized zone characterized by active sulfide oxidation, indicated by a reduced pH (2.75) and elevated Cd and Pb pore water concentrations. In the two-year SS application, successful plant establishment (Fig. 4) had occurred. However, upon visual inspection, the plant roots from the application penetrated into the underlying tailings, creating oxygen and water pathways, and a 0.04 m oxidation zone. Concentrations of Cu, Fe and Zn, significantly increased in the underlying pore-water, up to two magnitudes higher than the reference, in the immediate 0.1 m of tailings. The pH was maintained at circum-neutral. Iron precipitated in the top 0.2 m of the underlying tailings yet the Cu and Zn did not, and continued to exhibit elevated porewater concentrations up to 0.8 m in depth. It is likely that these metals were sludge-borne. In the 1 year sludge applied cover, no plant establishment had occurred, but cracks in the SS existed, causing a 0.02 m oxidation front in the underlying tailings. A similar pattern in the pore-water geochemistry to the 2-year application existed but to a lesser degree.

Optimum approaches to sewage sludge use in sulfide-mine tailings remediation

The best practices for the mining industry are ranked and summarized as follows:

- 1. The use of SS as a sealing layer offers a medium-to-long term-solution to the abatement of ARD, due to the successful mitigation the material has at decreasing oxygen diffusion to the underlying tailings. The primary limitation of SS in this application type regards the life-time of the cover due to the degradation of organic matter.
- 2. Using SS as a vegetation substrate onto an engineered dry composite cover is a successful remedial approach for promoting vegetation establishment. A temporary nitrate and metal-laden sludge-borne leachate may be released over a 2 year period. Though avoiding direct contact with tailings, it must be collected and treated



Fig. 6 Impoundment 1: Before sewage sludge application; after sludge application of the dry covered area; after sludge application on the water-saturated area

before entering peripheral environments.

- **3.** Using SS on water-saturated cover types should be avoided. Though temporary, the nitrate and metal-laden sludge-borne leachate rapidly enters the tailings groundwater system, creating further oxidation of pyrite, and creating a contamination plume of elevated nitrate, Cu, Fe, Ni, Pb and Zn. Its residence time is dependent on the dominant hydrogeological regime.
- **4.** Using SS directly onto fresh tailings should be avoided. Though vegetation is established rapidly, and it is aesthetically pleasing, cracking via drying and root penetration, promotes sulfide oxidation, and in addition the SS releases elevated sludge-borne metals (Cu, Fe, Zn) to the underlying tailings. This application merely slows the inevitable formation of ARD.

Acknowledgements

This study was funded by Georange, and has been conducted within the framework of the Centre of Advanced Mining and Metallurgy (CAMM) at Luleå University of Technology. The authors express gratitude to New Boliden AB for providing assistance and access to the site at the Kristineberg and Boliden Mine sites and to Bert-Sive of Bergteamet who provided further field assistance. Finally, thanks goes to Milan Vnuk for help preparing the figures.

References

- Andres NF, Francisco MS (2008) Effects of sewage sludge application on heavy metal leaching from mine tailings impoundments. Bioresource Technology 99: 7521–7530
- Appelo CAJ, Postma D (2005) Geochemistry, Groundwater and Pollution, 2nd Edition A.A. Balkema Publishers
- Carlsson E (2002) Soil-cover remediation of sulphiderich tailings. Technical Report, SBLO50: EC2002

- Cravotta CA (1998) Effect of sewage sludge on formation of acidic ground water at a reclaimed coal mine. Ground Water 36: 9–19
- Eriksson J (2001) Concentrations of 61 trace elements in sewage sludge, farmyard manure, mineral fertiliser, precipitation and in soil and crops: 5159–69
- Forsberg SL (2008) Reclamation of Copper Mine Tailings Using Sewage Sludge. Doctoral Thesis, 88 pp
- Höglund LO, Herbert RB, Lövgren L, Öhlander B, Neretnieks I, Moreno L, Malmström M, Elander P, Linvall
- M, Lindström B (2005) MiMi Performance Assessment – Main Report: MiMi Report 2003:3. In:
- Höglund, LO and Herbert RB (Eds.), MiMi Print, Luleå, Stockholm
- Mácsik J, Rogbeck Y, Svedberg B, Uhlander O, Mossakowska A (2003) Fly ash and sewage sludge as liner material – Preparation for a pilot test with flyash stabilized sewage sludge as landfill liner. Report 837. (In Swedish)
- Marklund S (1997) Dewatering of Wastewater Sludge by Natural Air Drying. Licentiate Thesis, 7 pp.
- Nason P, Alakangas L, Öhlander B (2013) Using sewage sludge as a sealing layer to remediate sulphidic mine tailings: a pilot-scale experiment, northern Sweden. Environmental Earth Sciences, DOI: 10.1007/s12665-013-2369-0 (Article in Press)
- Peppas A, Komnitsas K, Halikia I (2000) Use of organic covers for acid mine drainage control. Minerals Engineering 13: 563–574
- Pichtel JR, Dick WA, Sutton P (1994) Comparison of Amendments and Management-Practices for Long-Term Reclamation of Abandoned Mine Lands. Journal of Environmental Quality 23: 766–772
- Statistics Sweden (2008a) Discharges to Water and Sewage Sludge Production in 2006. Published in Collaboration with the Swedish Environmental Protection Agency http://www.scb.se/templates/Publikation_232141.Asp
- Statistics Sweden (2008b) www.scb.se Published in Collaboration with the Swedish Environmental Protection Agency

Influence of temperature in sulphate-reducing anaerobic bacteria (SRB) development and metal removal efficiency

Nora H. Paños, Luis V. Gutiérrez, Ana A. Senese

San Juan National University, Av. Libertador Gral San Martín 1109 (O), 5400 San Juan, República Argentina; npanos@unsj.edu.ar

Abstract Treatment processes to remove metals and sulphate, neutralizing the acidity of acidic mining drainage (AMD) involve phenomena as sulphate-reducing anaerobic bacteria (SRB) development and biosorption. Processes have found widely varying efficiencies ranging from 40 and 90 %. We carry out a test plan to determine the effect of temperature: 6 °C, 13°C and 25 °C. At 25 °Cthe black precipitate formation begins during the first hours reaching a metal removal efficiency of 90.44%, while at6 °Cin general there was no evidence of SRB development, even at 30 days of incubation, without significant changes in pH and Eh.

Keywords temperature, bacteria, sulphate, biosorption, efficiency

Introduction

Passive systems to mitigate acid mine drainage (AMD) depends essentially of sulphate-reducing anaerobic bacteria (SRB) development to neutralize the acid drainage, producing SH₂. which reacts with metals producing metals sulphides. Other mechanisms that immobilize metals in treatment systems such as biosorption and co-precipitation may simultaneously take place in such systems.

As any other microorganisms sulphate-reducing bacteria are living beings with a high specific surface and sensibility to the physicchemical conditions of the micro-environment around their membrane cell. So, they have a very high capacity to give a response (positive or negative) to each external stimulus. The main mechanism of biosorption is ionic-interchange which is also affected by factors as pH.

Systems to mitigate AMD at pilot or full scale have found widely varying efficiencies (Karathanasis *et al.* 2010). Several variables impact the efficiency including $SO_4^=$ concentration, temperature, AMD particular composition, residence time, pH, redox potential (Eh) and carbon source.

Laboratory tests plans have been carried out to obtain quantified answers to the prior questions (Paños *et al.* 2012). Only the complete knowledge of the phenomena involved in AMD treatment systems and the conditions affecting them, could allow predicting, designing and optimizing such systems. A test plan was carried out to analyze the influence of temperature at two levels of $SO_4^=$ and organic nutrients availability, in SRB development and the other mechanisms of iron removal.

Methods

Synthetic media were prepared by mixing the three following solutions:

Solution I Only tap water corresponding to tests indicated in Table 1 as $SO_4^{=}$: 0 or tap water with 3 g of MgSO₄.7H₂O per litter and is indicated in Table 1 as added $SO_4^{=}$: 3.

Solution II Organic nutrients compounds coming from dry leaves of the blackberry tree (high availability in our region). To liberate tha maximum contained labile compounds, dry leaves were mixed with water in a relation 7.5:100 (W:V) and kept at 20–25 °C during 48 hours before to separate the solution from solids. Solution Ii was added in quantities of 1 or 5 mL each 100 mL of Solution I. **Solution III** 5 g of $FeSO_{4.7}H_2O$ in 100 mL of SO_4H_2 acid 0.5 % (V:V). Iron was used as a marker to analyze SRB development. 1 mL of Solution III each 100 mL of Solution I was added to all the tests.

Once the media of each test was prepared with the corresponding composition, pH was adjusted to the indicated values around 7 in Table 1 (pHin) also measuring Eh (Ehin). Flasks were filled, closed and film-sealed to ensure an anaerobic medium. Tests were prepared by triplicate incubating one of them at 6 °C in a refrigerator, other at ambient temperature with a media of 13 °C and the other at 25 °C.

Observations were made every day to determine the time (days) required for the begining of SRB development given by the begining of the black precipitate formation. At 35 days all the flasks were open. At the moment of open each flask the final pH and Eh were measured (pHout and Ehout) and a sample was filtered to analyze iron and determine iron removal efficiency. In tests with possitive SRB development, the pHout measured at the moment of flasks opening is in the order or more acidic than pHin due to the dissolved SH₂. Nevertheless, when the SH₂ excess come off (some hours latter the flasks opening) pHout is stable and higher than pHin.

Results

Table 1 shows the results of tests prepared with two sulphate concentrations and two organic compounds concentrations, incubing each group at three temperatures: 6, 13 and 25 °C.

Even in tests with negative SRB development a yellow-brown precipitate was formed and the solution lost the typical brown colour given by the organic compounds coming from dry leaves. The iron removal efficiency may be as high as 78.06 % indicating other mechanisms as biosortion and co-precipitation are responsable of the iron remosion. It may be see in Fig. 1 showing tests incubated at 6 °C. In tests IV and X, prepared with higher organic compounds concentration, any very slow SRB growth is observed, pHout decreased by the dissolved SH₂ and the organic matter remain suspended probably due to the gas disolved.

Fig. 2 is a picture of the tests incubated at 25 °C. In tests III SRB development was negative due to the very low sulphate and organic matter availability. In the others SRB development was possitive and the time required for the begining of the black precipitate formation notably decreased with higher sulphate and organic matter availability, as it is shown in the results of Table 1.



Fig. 1 Tests incubated at 6 °C, I and VII with negative SRB development in 35 days, IV and X with a very slowly growth starting from 30 and 25 respectively.



Fig. 2 Tests incubated at 25 °C, III with negative SRB development in 35 days and XII with a fast SRB development in less than 1 day, depending on sulphate and organic nutrients availability.

Discussion

In tests with negative SRB development, pHin respect to pHout is kept constant or in the same order and Ehin didn't decrease to reach the required for the development of SRB showing that there was not any significant bacterial development. In tests with positive SRB development; pHout was increased respect to pHin and Eh was decreased to the order or below the order required for SRB development (-180 mV). To reach such Eh order others bacterial populations must have developed before. Obviously, their development is also temperature dependent.

By comparing the black precipitate formation time of tests X, XI and XII: 25 days, 5 days and less than 1 day respectively, with the same medium composition but incubated at 6 °C, 13 °C and 25 °C respectively, it is put in evidence the very high influence of temperature, either in SRB development velocity, as in the growth velocity of the prior necessary microbial populations.

Furthermore, sulphate concentration and organic compounds availability are important factors. At a constant temperature, for example 25 °C, the results comparison between tests III and IX (both with 1 mL of organic solution each 100 mL of Solution I) shows whereas SRB development was absolutely negative even at 35 days of incubation in test III, in test IX there

Test	Added ^(a)	Organic	$pH_{in} \\$	Eh _{in}	pH_{out}	Eh _{out}	Time SRB	Efficiency	Observations
N°	SO4	Sol. (b)					Growth ^(c) (days)	(%)	
				Incuba	tion tem	perature:	6 ℃		
Ι	0	1	6.994	-120.8	6.774	-46.5	(-)	78.06	Without SRB growth
IV	0	5	6.996	-110.2	6.855	-179.3	30	67.44	Any SRB low growth
VII	3	1	7.085	-121.2	6.797	-107.9	(-)	-	Without SRB growth
Х	3	5	7.075	-11.04	6.774	-190	25	70.21	Any SRB low growth
Incubation Temperature: 13 °C									
II	0	1	6.994	-120.8	6.758	-137.6	(-)	-	Without SRB growth
V	0	5	6.996	-110.2	8.382	-191.2	6	72.00	Positive SRB growth
VIII	3	1	7.085	-121.2	6.868	-161.9	(-)	-	Without SRB growth
XI	3	5	7.075	-114.0	8.237	-213.0	5	79.73	Positive SRB growth
				Incuba	tion tem	perature: 2	25 °C		
III	0	1	6.994	-120.8	6.715	-126.3	(-)	-	Without SRB growth
VI	0	5	6.996	-110.2	7.803	-202.1	2	89.30	Positive SRB growth
IX	3	1	7.085	-121.2	7.700	-171.1	19	76.04	Low nutrients conc.
XII	3	5	7.075	-114.0	8.120	-216.7	< 1	90.44	Fast SRB growth

 $^{(a)}:MgSO_{4}.7H_{2}O$ (g/L) added to Solution I

(b) : Organic solution (solution II) added each 100 mL of Solution I

^(c) : Times (days) required for the begining of the black precipitate formation

(-): Negative SRB development even at 35 days of incubation

- : Data non obtained

Table 1 Results of tests prepared with two sulphate concentrations and two organic compounds con-
centrations, incubing each group at three temperatures: 6, 13 and 25 °C.

was evidence of growth in 19 days. By comparing tests VI and XII (both with 5 mL of organic solution each 100 mL of Solution I) the addition of sulphate in test XII (moreover the added as FeSO₄₋₇H₂O in Solution III), allows the bacterial growth in a time less than a day, while in test III without the extra-addition, 2 days are required. Equivalent analysis could be done for tests incubated at other temperatures. The influence of organic compounds availability is shown by comparing the results of tests III and VI as well as IX and XII.

Even in tests with negative SRB development during 35 days, the efficiency (% of removed iron) was relatively high, over 67-70 % due to iron biosorption by bio-molecules and micro-particles coming from dry leaves. As it is shown in Fig. 2, the organic material sorbing iron is deposited in the flask button turning translucent the medium solution.

Comparing tests I and X incubated at 6 °C, (see Table 1 and Fig. 2), in test X at 25 days of incubation SRB development began, while in test I, there was not any evidence of bacterial growth at 35 days. Nevertheless, the efficiency reached in test X (70.21 %) is lower than test I efficiency (78.06 %). It is suggesting SRB development and the associated production of SH₂ and CO₂ are making difficult or less efficient the mechanism of biosorption, mainly an ionic-interchange mechanism, and co-precipitation. An equivalent analysis may be done by comparing the results of test I and IX, taking furthermore into account test IX was incubated at 25 °C and a clear SRB development was obtained.

Conclusions

Temperature is a factor of very high influence in SRB development. In cold climes or during winter season, it should not be expected SRB development in passive processes for acidic mining drainage (AMD) treatment, unless steps were taken in the system design.

Biosorption is a mechanism that can be efficient in metals removal near neutral pH when SRB development is negative. Nevertheless, when SRB development is positive, it generate conditions that difficult in some extension the mechanism of biosorption.

Acknowledgements

The authors thank San Juan National University for supporting this work.

References

- Karathanasis AD, Edwards JD (2010) Influent water quality affects perfomance of passive treatment systems for acidic mine drainage. Mine Water Environ 29:135–143.
- Paños NH, Gutierrez LV, Senese AA (2012) Approaches to predetermine the variables affecting the efficiency for the design of mining effluents and acidic drainage treatment systems.International Mine Water Association. Proceedings of the Anual Conference 2012: 265–273.

Passive Co-Treatment of Acid Mine Drainage and Municipal Wastewater: Removal of Less Commonly Addressed Metals at Cerro Rico de Potosí, Bolivia

R. A. M. Peer¹, W. H. J. Strosnider¹, B. K. Winfrey², R. W. Nairn³

¹Saint Francis University, Loretto, PA, USA; ²University of Oklahoma, Norman, OK, USA; ³University of Maryland, College Park, MD, USA

Extended Abstract Acid Mine Drainage (AMD) and Municipal Wastewater (MWW) are common effluents both in the developing and the developed world; their treatment is necessary to ensure clean water supplies across the globe. The feasibility of a passive co-treatment system was tested with a laboratory-scale three-stage batch reactor system.

Keywords Aluminum, Iron, Zinc, Manganese, Copper, Cadmium, Nickel, Lead, Acid mine drainage, Sewage

Zn-rich AMD from an abandoned adit on Cerro Rico de Potosí and raw MWW from Potosí, Bolivia were combined at a 5:1 ratio and introduced to the system. Four replicate systems consisting of three unit processes each: a clarifier unit, an anoxic limestone drain, and an oxidation pond, were used to assess the functionality of passive co-treatment. The unit processes were constructed using 1-L cubitainers. Commonly used in AMD experimentation, cubitainers are collapsible low-density polyethylene containers. The contaminant streams were mixed within 8 hours of collection and samples were taken within five minutes of mixing (ActMix) due to rapid reactivity of waters. The chemical composition of the theoretical influent mix (TheoMix) was also calculated with the AMD to MWW ratio. All unit processes were exposed to ambient conditions, maintaining water temperature between 8.2 and 10.3 °C throughout the system. Physiochemical data were recorded and samples were taken prior to transfer of water from one unit process to the next. The residence times in unit processes were 24 h, 24 h, and 48 h, for the sedimentation pond, limestone, and oxidation pond, respectively.

The AMD influent had pH 3.58, acidity 1080 mg/L as CaCO₃ equivalent, and 12, 68, 17,

550, 0.44, 0.13, 0.13 and 0.090 mg/L of dissolved Al, Fe, Mn, Zn, Cd, Cu, Ni, and Pb, respectively, among other metals/metalloids. The MWW contained 5.6 and 38 mg/L of nitrate and phosphate, respectively. The system efficiently reduced metal concentrations for common metal/metalloid contaminants as well as less commonly addressed contaminant metals/metalloids. Dissolved concentrations of common metals such as Al, Fe, Mn, and Zn decreased throughout the system by 99.7 %, 99.9 %, 4.5 %, and 33.9 %, respectively. Dissolved concentrations of less commonly addressed metals such as Ag, Cd, Ce, Cr, Cu, Gd, Ni, and Pb also decreased notably throughout the system. Among the metals removed, dissolved concentrations of Cr and Gd were decreased below detection limits in the first and second unit processes. Less commonly addressed contaminant metals were removed mostly in the clarifier unit. Notably, Ni, Pb, and Cu contaminants were removed 25.5 %, 45.9 %, and 18.3 %, respectively, primarily by the first unit process (Fig. 1). However, Cd was removed primarily in the last two unit processes, with an overall removal of 78.5 % (Fig. 1).

During the limestone incubation, concentrations of some contaminants increased. For example, Ag is removed in the clarification



Fig. 1 Mean concentration of the four metals of concern from initial mixing through each unit process in the system (n=4). Error bars represent the 95 % confidence interval constructed with the

t-statistic. "ActMix" and "TheoMix" do not have error bars as they were a single measurement/calculation. Measurements shown for Actual Mix (Act Mix), Theoretical Mix (Theo Mix), Sed (sedimentation unit), Lime (limestone unit), Ox (oxidation unit).

unit process, but the concentration was increased in the limestone unit process. Ca, B, Ba, K, Li, Mg, Na, and Sr concentrations also increased in the second unit process, likely due to limestone impurity dissolution. Potosí is in one of the most highly mineralized regions in the world, making the existence of impurities in local limestone unsurprising. Three rare earth metals were also tracked throughout the system. Concentrations of Nd and Pr were increasing in all three unit processes. However, La was removed from solution in all three unit processes.

The results from the experiment suggest that passive co-treatment of AMD and MWW could be a valid treatment method for streams with wide ranges of contaminants. Results from the study could be applied as a feasible solution to chronic water quality issues due to the common co-occurrence of the two contaminant streams throughout the developed and developing world. Due to lack of funding and resources in the developing world, inexpensive, non-energy-intensive, and low-maintenance solutions are essential for remediation of contaminated streams. In the developed world, passive co-treatment could result in cost and energy savings from the renewal of less efficient treatment systems currently in use. Elements of the experimental system (e.g. removal of phosphate with metal oxides) could be utilized to improve the performance of existing conventional AMD or MWW treatment systems. To further the knowledge of passive co-treatment, the construction of a pilot-scale system is necessary. A pilot system could provide further information on operational and maintenance costs, sustainability requirements, and the longevity of a full-scale treatment system.

Integrated synthesis of nanosized semiconductors in a bioremediation system for the treatment of AMD using biologically produced sulfide

João Pinto da Costa¹, Ana Violeta Girão², João P. Lourenço³, Olinda C. Monteiro⁴, Tito Trindade², Maria Clara Costa^{1,*}

¹ Centro de Ciências do Mar, CCMar, Faculdade de Ciências e de Tecnologia, Campus de Gambelas, 8005– 139 Faro, Portugal. ² Centro de Investigação em Materiais Cerâmicos e Compósitos, CICECO, Campus Universitário de Santiago, 3810–193 Aveiro, Portugal. ³ Centro de Investigação em Química do Algarve, CIQA, Faculdade de Ciências e de Tecnologia, Campus de Gambelas, 8005–139 Faro, Portugal ⁴Centro de Química e Bioquímica, CQB, Faculdade de Ciências Universidade de Lisboa, Campo Grande 1749–016, Lisboa, Portugal.

*Corresponding author: mcorada@ualg.pt

Abstract The use of sulfate-reducing bacteria in bioremediation processes for the treatment of effluents with high-content of sulfate and metal generates an excess of sulfide. The elimination of this excess sulfide is a problem that needs to be addressed. Metal nano-sulfides, such as CuS and ZnS, have attracted much attention due to their excellent potential in catalysis, optical and electronic functionalities. In the present work, we set out to produce sulfide nanoparticles by combining a well-established bioremediation system into the synthesis process, thus allowing for an integrated environmentally friendly solution for some challenges facing the metallurgical and extractive industries.

Keywords nanoparticles, metal sulfides, bioremediation.

Introduction

Semiconductor nanocrystals possess unique optical and electronic properties, which bestow them with a huge potential in a wide range of applications (Sweeney et al. 2004). Of these, zinc sulfide (ZnS), copper sulfide (CuS) and iron sulfide (FeS) are of special interest. ZnS is photoconductive, luminescent and a piezoelectric material, making this compound suitable to be applied in solar cells, light emitting diodes, probes for the determination of proteins and photodegradation of organic compounds (Stanic et al. 1997; Yanagida et al. 1990; Zhu et al. 2004). CuS nanomaterials have a wide range of applications, which include catalysts (Liu and Xue 2009), nano-switches (Sakamoto et al. 2003), optical filters (Chen et al. 2009), solar radiation absorber (Li et al. 2009), among others. Iron sulfides are recognized as advanced inorganic materials with high potential in many applications, such as

high-density batteries, chalcogenide glasses and solar energy materials (Chin et al. 2005). The synthesis of all these nanomaterials has been described using a wide variety of methods, including the use of surfactants, organic solvent micro-emulsions, controlled doublejet precipitation, hydrothermal synthesis, liquid-solid phase synthesis, chemical vapor deposition, high gravity or gas phase decomposition, among others (Bessergenev et al. 1995; Biswas et al. 2007; Chen et al. 2004; Close et al. 1999; Ding et al. 2007; Thurston and Wilcoxon 1999; Xu and Zhang 2008). In general, these methods rely on the use of high temperatures, as well as high pressures, radiation and sometimes hazardous chemicals.

During sulfide-mining operations, sulfidic rock comes into contact with the surface or groundwater. Under oxidizing conditions, pyrite-containing rock produces sulfuric acid and dissolved iron. In turn, these acidic waters

then dissolve other metals contained in the rock, resulting in a low-pH, metal-bearing water known as acid mine drainage (AMD) or acid rock drainage (ARD; Doshi 2006). As a result, in some of those areas several mine lakes are very acidic (pH < 3) and contain high concentration of sulfate (up to 3.5 g/L) and metals, particularly iron, zinc and copper (Martins et al. 2008). Passive treatments, such as bioremediation using sulfate-reducing bacteria (SRB) have proven to be a good solution (Garcia et al. 2001; Huisman et al. 2006). Previously, work has been carried out in our group and a bioremediation system for AMD has been successfully developed (Martins et al. 2010). The selective precipitation of metals from multi-metal containing systems, such as wastewaters and soils, has been previously studied, using either chemical sulfide sources or biogenic sulfide (Fang et al. 2012; Sahinkaya et al. 2009; Sampaio et al. 2009; Tokuda et al. 2008). However, when reported, the particles obtained were always in the micron range (>1 μm). Previously, we have proven that the production of zinc sulfide nanoparticles (<25 nm) using SRB growth media containing biologically produced sulfide, at room temperature and atmospheric pressure, avoiding the use of additional and expensive chemicals, is a possibility (da Costa et al. 2012). Moreover, it has been demonstrated that the use of growth media of different complexities, as well as the filtration or not of these same media, yielded nanoparticles (NP's) with no considerable differences amongst one another. Using this previously acquired knowledge, we set out to, in the present work, selectively synthesize metallic (Cu²⁺, Fe²⁺ and Zn²⁺) sulfide nanoparticles. This was achieved using artificial metallic solutions as a source of the metal ions and real AMD in the feeding of the continuous bioremediation system, used as the source of sulfide, thus demonstrating the feasibility of this method of synthesis.

Materials and Methods

The bioremediation system used was the one

previously described by (Martins *et al.* 2010) and the synthesis principle has been described by (da Costa et al. 2012). After reaching continuous operation, the excess sulfide produced by the SRB in the bioremediation system was used as the sulfide source for the precipitation of the metals. The metal-containing solutions were prepared using distilled water and a combination of Cu²⁺ (CuSO₄.5H₂O, >99 %, Riedelde-Haën), Zn²⁺ (ZnSO₄.7H₂O, >99.5 %, Panreac) and Fe²⁺ (FeSO₄.7H₂O, >99 %, Panreac). These salts were added so that an approximate final concentration of 100 mg.L⁻¹ of each metal ion was obtained. The initial pH was corrected to 2.1, using a 6M solution of HNO₃ (Panreac). Sulfide concentration was measured immediately after sampling using a UV-visible spectrophotometer (DR2800 spectrometer, Hach-Lange) by the Methylene Blue Method (665 nm, Hach-Lange). The pH values were measured using a pH Meter (GLP 21, Crison) and corrected to 5.0 and 6.5 after the first and second precipitation steps, respectively, using a 2M NaOH solution, which was added drop-by-drop. Metal concentrations, before and after precipitation, were determined by flame atomic absorption spectroscopy using a Shimadzu AA-680 model spectrometer. XRD analyses were done using a PANalytical X'Pert Powder diffractometer with an X'Celerator detector, at 45 kV and 40 mA, with a step size (21) of 0.016. Transmission Electron Microscopy (TEM) coupled to EDX was carried out using a FEG-TEM Hitachi H9000 microscope operating at 300 kV. The samples were prepared by placing a drop, containing the precipitates dispersed in ultra-pure distilled water, on a copper grid coated with amorphous carbon film.

Results and Discussion

A solution containing 96 mg.L⁻¹ of copper, 103.7 mg.L⁻¹ of zinc and 104.04 mg.L⁻¹ of iron, at pH 2.1, was used. Fig. 1A shows the removal percentage, as well as each metal concentration after every precipitation step. Also shown are the removal efficiencies of all metals for the overall process. As observed, the first precipitation step seems to be very selective in the removal of copper, resulting in the precipitation of only minor amounts of zinc and iron. At the end of the second precipitation step (Fig. 1A), the remainder copper still in solution is, in essence, completely removed in all samples, never exceeding a concentration of 5 mg.L⁻¹. At this step, there is also an undesired high removal of iron (77 %), and, at the last precipitation step, at which the removal of iron is desired, this is achieved in almost its entirety (>93 % of the iron in solution after the second precipitation step). Overall, the process re-

moved 93 to 97 % of all the metals present. The final pH, after all precipitation steps, ranged between 7.2 – 7.5. Having successfully removed the metals from the solutions, the precipitates obtained at each step were analyzed by X-ray diffraction (XRD) and the results obtained are shown in Fig. 1B. In the diffractogram of the first precipitate, the peaks corresponding to covellite (CuS, JCPD #00-001-1281) are clearly present, as well as in the other precipitates; however, in the second precipitate, peaks consistent to those corresponding to sphalerite (ZnS) are also present (JCPD #00-003-0579).



Fig. 1 In A, metal (Cu, Zn and Fe) removal percentages as well as the overall removal percentage for each metal at the end of the each precipitation step. In B, the concentrations of each metal at the end of each precipitation step. In both A and B, error bars are shown. In C, the X-ray diffractograms of the precipitates obtained at each step. Due to the high profusion of peaks, the identified phases are not indicated for simplification purposes. These, however, included covellite (CuS; JCPD #00-001-1281), sphalerite (ZnS; JCPD #00-003-0579) and iron (III) hydroxide (JCPD #00-038-0032).

These also contribute to the diffractogram of the precipitate obtained at the third precipitation step, in which peaks corresponding to iron (III) hydroxide are visible (JCPD #00-038-0032). Overall, these results corroborate those illustrated in Figs. 1A and 1B, further indicating that the precipitation process that herein described is very selective for copper and less discriminatory when precipitating zinc and iron. Also, in the case of the latter metal, it should be noted that the corresponding crystallites identified were hydroxides, not sulfide. This may be due to the fact that the addition of the NaOH for the correction of the pH may culminate in the formation of the iron hydroxide.

The elemental and morphological characterization was done by TEM-EDX. In Fig. 2, the TEM images obtained for each precipitate synthesized at each precipitation step are shown (Fig. 2A - 2C). The corresponding EDX spectra are shown in Figs. 2D - 2F. The precipitates all seem to show spheroid morphology, with sizes ranging between 2O - 3O nm, though some needle-like structures are identifiable in the precipitate obtained at the third step. The EDX results are consistent with the removal efficiency data, shown in Fig. 1. The main precipitated phase, in the first precipitation step, is CuS, with traces of both Fe and Zn.

This highlights the high selectivity of this method for precipitating CuS, with minimal co-precipitation of Zn and Fe species. At the second precipitation step, ZnS is the main phase present, followed by FeS and, to a smaller extent, CuS. The former is the main phase present in the precipitate obtained at the final step. However, ZnS is also present, as well as some amounts of Cu. Nonetheless, it should be noted that the presence of copper in other precipitates other than the one ob-



Fig. 2 TEM images of the precipitates obtained at steps 1, 2 and 3 (A, B and C, respectively). Also shown are the corresponding EDX analyses (2D - 2F). The elements identified are shown. Due to the composition of the grid (Cu) and the high relative presence of this element, insets are shown, evidencing the presence or absence of Fe as well as of Zn in the precipitates obtained at the second and third steps.

tained initially should be carefully discussed, as the TEM grid used is composed of copper. Consequently, this element appears prominent in the analyses made for the precipitates obtained at the end of both the second and third steps. Additionally, Cl was also found, which is not surprising, considering that the water used for the preparation of the growth media is tap water. Interestingly, traces of Si were also identified in the last sample, which may result from either cross-contamination with other samples (in which SiO₂ was used) or from the fact that this sample was kept in a glass vial.

Conclusions and Future Perspectives

In summary, by integrating a previously described bioremediation system and a synthesis process for obtaining nano-sized metal sulfides, we were able to selectively precipitate CuS nanoparticles and ZnS particles, though the latter with a smaller degree of selectivity. The precipitation of FeS was not achieved, with the Fe precipitates consisting, mostly, of hydroxides (Fig. 1B). The authors speculate that this limitation, however, may be circumvented by using, for example, on-line systems for the accurate control of pH. Moreover, the implementation of a completely oxygen-free environment may contribute for obtaining Fe precipitates in the form of sulfides, thus resulting in a final highly selective recovery process of metal sulfides. Finally, the use of real metalcontaining wastewaters, such as Acid Mine Drainage, may be a possibility, further contributing to an integrated green process, resulting in the simultaneous remediation of contaminated waters and concomitant metal sulfide nanocrystals production.

Acknowledgements

Funding by Fundação para a Ciência e a Tecnologia (FCT) through a PhD grant (SFRH/BD/43784/2008) and through project PTDC/AAG-TEC/2721/2012 is acknowledged. A. V. Girão also thanks FCT for the Post-Doc grant (SFRH/BPD/66407/2009).

References

- Bessergenev V, Ivanova EN, Kovalevskaya YA, Gromilov SA, Kirichenko VN, Zemskova SM, Vasilieva IG, Ayupov BM, Shwarz NL (1995) Optical and Structural Proper Ties of Zns and Zns-Mn Films Prepared by Cvd Method. Mater Res Bull 30(11): 1393-1400.
- Biswas S, Kar S, Chaudhuri S (2007) Thioglycolic acid (TGA) assisted hydrothermal synthesis of SnS nanorods and nanosheets. Appl Surf Sci 253(23): 9259-9266.
- Chen JF, Li YL, Wang YH, Yun J, Cao DP (2004) Preparation and characterization of zinc sulfide nanoparticles under high-gravity environment. Mater Res Bull 39(2): 185-194.
- Chen LF, Yu W, Li Y (2009) Synthesis and characterization of tubular CuS with flower-like wall from a low temperature hydrothermal route. Powder Technol 191(1-2): 52-54.
- Chin PP, Ding J, Yi JB, Liu BH (2005) Synthesis of FeS2 and FeS nanoparticles by high-energy mechanical milling and mechanochemical processing. J Alloy Compd 390(1-2): 255-260.
- Close MR, Petersen JL, Kugler EL (1999) Synthesis and characterization of nanoscale molybdenum sulfide catalysts by controlled gas phase decomposition of Mo(CO)(6) and H2S. Inorg Chem 38(7): 1535-1542.
- da Costa JP, Girao AV, Lourenco JP, Monteiro OC, Trindade T, Costa MC (2012) Synthesis of nanocrystalline ZnS using biologically generated sulfide. Hydrometallurgy 117: 57-63.
- Ding Y, Liu X, Guo R (2007) Synthesis of hollow PbS nanospheres in pluronic F127/cyclohexane/H2O microemulsions. Colloid Surface A 296(1-3): 8-18.
- Doshi SM (2006) Bioremediation of Acid Mine Drainage Using Sulfate-Reducing Bacteria. U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response and Office of Superfund Remediation and Technology Innovation 65.
- Fang D, Zhang R, Liu X, Zhou L (2012) Selective recovery of soil-borne metal contaminants through integrated solubilization by biogenic sulfuric acid and precipitation by biogenic sulfide. Journal of Hazardous Materials 219–220(0): 119-126.
- Garcia C, Moreno DA, Ballester A, Blazquez ML, Gonzalez F (2001) Bioremediation of an industrial acid mine water by metal-tolerant sulphate-reducing bacteria. Minerals Engineering 14(9): 997-1008.

- Huisman JL, Schouten G, Schultz C (2006) Biologically produced sulphide for purification of process streams, effluent treatment and recovery of metals in the metal and mining industry. Hydrometallurgy 83(1-4): 106-113.
- Li F, Kong T, Bi WT, Li DC, Li Z, Huang XT (2009) Synthesis and optical properties of CuS nanoplate-based architectures by a solvothermal method. Appl Surf Sci 255(12): 6285-6289.
- Liu J, Xue DF (2009) Solvothermal synthesis of CuS semiconductor hollow spheres based on a bubble template route. J Cryst Growth 311(3): 500-503.
- Martins M, Santos ES, Pires C, Barros RJ, Costa MC (2010) Production of irrigation water from bioremediation of acid mine drainage: comparing the performance of two representative systems. J Clean Prod 18(3): 248-253.
- Martins MSF, Santos ES, Barros RJJ, Costa MCSD (2008) Treatment of Acid Mine Drainage with Sulphate-reducing Bacteria Using a Two-stage Bioremediation Process. Mine Water and the Environment Proceedings: 297-300
- Sahinkaya E, Gungor M, Bayrakdar A, Yucesoy Z, Uyanik S (2009) Separate recovery of copper and zinc from acid mine drainage using biogenic sulfide. Journal of Hazardous Materials 171(1-3): 901-906.
- Sakamoto T, Sunamura H, Kawaura H, Hasegawa T, Nakayama T, Aono M (2003) Nanometer-scale switches using copper sulfide. Appl Phys Lett 82(18): 3032-3034.
- Sampaio RMM, Timmers RA, Xu Y, Keesman KJ, Lens PNL (2009) Selective precipitation of Cu from Zn in

a pS controlled continuously stirred tank reactor. Journal of Hazardous Materials 165(1-3): 256-265.

- Stanic V, Etsell TH, Pierre AC, Mikula RJ (1997) Sol-gel processing of ZnS. Mater Lett 31(1-2): 35-38.
- Sweeney RY, Mao CB, Gao XX, Burt JL, Belcher AM, Georgiou G, Iverson BL (2004) Bacterial biosynthesis of cadmium sulfide nanocrystals. Chem Biol 11(11): 1553-1559.
- Thurston TR, Wilcoxon JP (1999) Photooxidation of organic chemicals catalyzed by nanoscale MoS2. Journal of Physical Chemistry B 103(1): 11-17.
- Tokuda H, Kuchar D, Mihara N, Kubota M, Matsuda H, Fukuta T (2008) Study on reaction kinetics and selective precipitation of Cu, Zn, Ni and Sn with H(2)S in single-metal and multi-metal systems. Chemosphere 73(9): 1448-1452.
- Xu ZY, Zhang YC (2008) In air liquid-solid phase synthesis of metal sulfide nanoparticles from metal acetates and thiourea. Mater Chem Phys 112(2): 333-336.
- Yanagida S, Yoshiya M, Shiragami T, Pac CJ, Mori H, Fujita H (1990) Semiconductor Photocatalysis .9. Quantitative Photoreduction of Aliphatic-Ketones to Alcohols Using Defect-Free Zns Quantum Crystallites. J Phys Chem-Us 94(7): 3104-3111.
- Zhu CQ, Zhao DH, Chen JL, Li YX, Wang Y, Wang L, Zhou YY, Zhuo SJ, Wu YQ (2004) Application of L-cysteinecapped nano-ZnS as a fluorescence probe for the determination of proteins. Anal Bioanal Chem 378(3): 811-5.

Removing barium from saline waters in coal mines of the Upper Silesia (Poland)

Pluta Irena

Central Mining Institute, Department of Water Protection, Plac Gwarków 1 40-166 Katowice, Poland, i.pluta@gig.katowice.pl

Abstract Natural mine waters in the Upper Silesian Coal Basin (Poland) frequently exhibit high salinity and contain barium. Waters with this element discharged from coal mines cause contamination of water transportation systems, surface waters and their sediments. Therefore, purification of mine waters from barium is an important mining and ecological task in the Upper Silesia. This paper presents various methods applied in coal mines since the 1990s aimed at reduction of barium content in mine waters. Majority of these methods is an example of the most favorable elimination of contamination at the point of origin, *i.e.* in mine workings (pollution "at the source").

Keywords Barium, Purification, Sulphates, Mine waters

Introduction

Mine waters with chemical composition ranging from fresh waters to brines occur naturally in the Carboniferous formations of the Upper Silesian Coal Basin (USCB). Majority of them exhibit high concentration of chlorides, sodium, potassium, calcium, magnesium, sulphates and micro-components, especially barium. Some of these components reach the highest concentration reported for the undergroundwaters in the world (Różkowski et al. 2004; Pluta 2005). Among them barium is particularly harmful in the water environment. Its concentration in waters flowing into mines exceed more than thousand (1000) times the highest permissible limit determined for waste waters- mine waters pumping from mines in Poland (Pluta and Pałys 1999; Pluta 2005; Ordinance of the Minister of Environment 2006). Waters discharged from coal mines of the Upper Silesia in Poland containing barium cause contamination of mine pipes in mine workings (Fig. 1a), especially the environmentally important pipeline of the Olza Collector (Fig. 1b), of settling ponds, of surface waters and their sediments (e.g. Bojakowska and Sokołowska 1998; Pluta 2005). Its causes technical problems, *e.g.* the pollution ("overgrown" of pumps, pipe, pipelines) of water transport systems. Therefore, purification of coal mine waters from barium is an important mining and ecological task in the Upper Silesia (Poland). This problem is particularly serious for coal mines situated in the south-western part of the USCB (Pluta and Pałys 1999; Pluta 2011).

The simplest, and the most effective method of removal of barium from waters is its precipitation in the form of practically insoluble deposits, mainly sulphate, according to the following reaction:

$$Ba^{2+} + SO_4^{2-} \longleftrightarrow BaSO_4 \tag{1}$$

The sources of ion sulphate (VI) in mines are different sulphur compounds contained in the Upper Carboniferous strata or in covering deposits, as well as substances used in mining operations. The most important process of sulphates generation is the oxidation of sulphides. As the effect of dissolving, leaching and oxidation, sulphates infiltrate into mine waters.



Fig. 1 Boring pipe from coal mine (a: left) and of the pipeline of the Olza Collector (b: right)

Since the 1990s various attempts to develop simple and economically sound methods to reduce the impact of barium on the aquatic environment have been undertaken. Particular attention was drawn to the use of mining activities. This paper explains all the used processes that reduce barium in coal mine waters of the USCB.

Removing barium from mine waters by sulphate minerals

In the Upper Silesian Coal Basin sea sediments of the Miocene and the Triassic occur. Some of them contain evaporated sulphate minerals, especially containing calcium: gypsum (CaSO₄. 2H₂O) and anhydrite (CaSO₄). Their dissolving enriches the mine waters with sulphates. Mine waters can also dissolve sulphate minerals contained in the Upper Carboniferous deposits. Gypsum, anhydrite occur in different lithostratigraphic series (Kuhl 1955). Besides them hydrated sulphate minerals: epsomite (MgSO₄.2H₂O), jarosite ((Na,K)Fe₃ (SO₄)₂(OH)₆. melanterite (FeSO₄.7H₂O) in the form of crusts and powder aggregates, mainly in fracture zones exist in the Upper Carboniferous coalbearing deposits.

Removing barium from mine waters by sulphite minerals

Sulphates can also penetrate into mine waters as a consequence of the oxidation processes of sulphide minerals, and organic matter containing different sulphur organic components. The disulfides occur in the Upper Carboniferous deposits as pyrite and marcasite (FeS₂). Under certain circumstances these substances can become the source of sulphates for the mine waters in contact with the coal-bearing strata. Sometimes this process is observed in water flowing through cavities made by extraction, gobs, old mine workings. This process was noticed for the first time in the "Silesia" coal mine (Pluta *et al.* 1994) and later in other coal mines in the south-western part of Upper Silesian Coal Basin (Pluta 2004).

Removing of barium by mine activities in mine workings

It is much preferred to carry out the mine waters treatment "at source" (reduction "at source"). Therefore, the substance causing mine waters contamination, especially barium, should be reduced or removed in the underground mine workings, i.e. at the point of origin of contamination rather then on the surface. The special chemical or biological methods of mine waters treatment are difficult, and above all expensive. The best method is the initiation of these processes in places where natural mine waters enter mine workings, removing of harmful substances in situ in the water-bearing layer or limitation of their amount during flow through a "protective barrier", "purifying barrier". Since 1990s attention was drawn to the possibility of purify mine waters from barium by means of the mining methods and technologies applied in mine workings.

The process of coal extraction is regulated by various laws and legal regulations particularity in the area of mine safety. Therefore, it is necessary to carry out many operations, among them such as: filling of underground cavities caused by the extraction, performance of roadside packs, construction of water and stopping gas dams. In these works different substances are used. Some of them contain sulphates and sulphides which can cause precipitation, oxidation or sorption of barium comprised in natural mine waters.

As it is mentioned above, barium can be removed from waters by its precipitation with of sulphates derived from sulphate minerals (products) – gypsum and anhydrite. These substances are used in some mining technologies. Gypsum and anhydrite are used in coal mines as an sealing mixture for fire protection. Anhydrite is also used for the protection of mine working places against overpressure of the Carboniferous rocks. These technologies were used in the "Morcinek" and "Jastrzębie" mines (Pluta and Ślaski 1993; Pluta 2001a).

Since the mid-1980s, the fine-grained industrial wastes have been utilized in coal mines. They have been used in different mining technologies, among others for self-consolidating filling, for filling (sealing) of longwalls and roadways, for performing of plugs and dams as well as roadside packs. Wastes from power plants contain mainly fly ashes and the flue gas desulphurisation products. These wastes contain sulphates: anhydrite (CaSO₄) and gypsum (CaSO₄· $2H_2O$) as well as hannabachite (CaSO3:½H2O). From these wastes in underground mine workings sulphates penetrate into mine waters. Systematic investigations of sulphates in the mine waters draining off from storage of wastes, have shown that their concentrations can reach 4150 mg/dm³. Their amounts depend on the mining technologies, type of wastes, type of coal used for combustion and the hydrogeological conditions in the mine workings (Pluta *et al.* 2002, 2006; Pluta 2011).

The post-extraction cavities, gobs and old mine workings also are filled also with mining wastes. The wastes are mainly Carboniferous barren rocks, separated from the extracted coal in coal cleaning preparation. In these processes the fine-grained wastes derived from flotation and washing processes, as well as sediments from drainage roads are used. In these wastes, as in wastes from power plants sulphates occur. They originate from the oxidation processes of sulphur minerals contained in the Upper Carboniferous coal-bearing deposits. Generally their amounts are lower than in the case of the described above wastes originating in power plants. For example into the water of the "Borynia" mine about 500 mg of sulphates are released into 1 dm³ of mine water from the flotation tailings. Sulphates contained in waters leaching from the places of power and mining wastes using in different technologies cause precipitation of barium from natural mine waters flowing into mine workings. These favourable effect of the reduction of the barium content in mine waters were observed for example during the storage of fly ashes in the "Pniówek" coal mine (Pluta and Waleczek 1996). Such a situation takes place in coal mines of the south-western part of the USCB where the natural mine waters contain barium. In the "Borynia" coal mine the technologies of placing of wastes have been optimized in order to maximize quantities of sulphates needed to be released into natural mine waters containing barium (Pluta and Piotrowski 2002).

Removing barium by sodium sulphate

Since the beginning of the XXI century natural processes of dissolution of sulphate minerals and desulphurisation products of the Carboniferous rocks and mining activities with industrial wastes rich in sulphur, as described above, were not enough to reduce the whole amount of barium present in natural mine wa-



Fig. 2 Feedres of sodium sulphate: in mine working (left) and on the surface (right)

ters. Therefore, since that time sodium sulphate (VI) has been used to purify saline waters from barium (Pluta 2001b). This substance is added into mine water in special feeders built in mine workings, sometimes also on the surface (Fig. 2). About three thousand tons of sodium sulphate are dissolved in mine water each year. This process results in removing barium from mine waters and at the same time keeps the water transportation systems free of this harmful component.

Summary and conclusions

Natural mine waters containing barium flow into mine workings of the Upper Silesian Coal Basin and the rivers of the Upper Silesia in Poland. This element cause contamination of mine workings, mine waters transportation systems, surface waters and their sediments, and its concentration in mine waters flowing from coal mines exceed the maximum permissible value in Polish Water Law (Ordinance of Minister of Environment 2006). Therefore, the content of barium should be reduced. For its removal or substantial decrease sulphates (VI) can be used. In coal mines of the Upper Silesia in Poland the natural processes, mining methods and technologies can be used. Sulphates (VI) ions can be obtained from waters with either the evaporated minerals or oxidation products of various sulphur compounds occuring in Carboniferous formation. Sources of sulphates include: gypsum, anhydrite and industrial wastes such as: fly ashes, slags and flotation tailings. Gypsum and anhydrite are used in coal mine workings as components of an isolating mixture for fire protection. Anhydrite is also used for the protection of the wall of work places against overpressure. Industrial wastes: fly ash, slags from electric plants and flotation tailings from coal mines are stored in the mine workings, especially in gobs as fire and methane protection agents. Development of clean-burning-coal technologies produces wastes with high concentration of sulphur. Since the beginning of the XXI century the purification of mine waters by sodium sulphate has been used.

Majority of the methods described above are examples of the most favorable reduction of pollution "at the source" of its arising, *i.e.* underground, and they do not need any capital outlays.

Use of mining methods and technologies and application of wastes from the power and coal mines in purification of mine waters is unique on the world scale, therefore the project was awarded at the IMWA international congress held in Sevilla in 1999.

References

Bojakowska J, Sokołowska G (1998) Influence of mining and metallurgy on pollutants in sediments of Oder river (in Polish). Przegląd Geologiczny, No 7:603-608 Kuhl J (1955) Petrografic classification of rocks in Carboniferous formations of the Upper Silesian Coal Basin (in Polish). Prace GIG, Seria A, Komunikat No 171:32

Ordinance of Minister of Environment 2006 in Poland (w sprawie warunków jakie należy spełniać przy wprowadzaniu ścieków do wód lub do ziemi oraz w sprawie substancji szczególnie szkodliwych dla środowiska wodnego, Dz. U. 2006, Nr 137, poz. 984 z późniejszymi zmianami).

Pluta I (2001a) Barium and radium discharged from coal mine in the Upper Silesia, Poland. Environmental Geology, 40 (3):345-348.

Pluta I (2001b) Purification of mine waters from barium and radium by sodium sulphate (in Polish). In: Proceedings "Waters southern part of the USCBcontamination and purification" Ustroń, SI.

Pluta I (2004) Acid mine waters in coal mines of the south-western part of the Upper Silesian Coal Basin (in Polish). Przegląd Górniczy, No 2:20-23

Pluta I (2005) Mine waters of the Upper Silesian Coal Basin – origin, pollutants and purification (in Polish). CMI, Katowice, 169 pp

- Pluta I (2011) Hydrogeochemistry of Carboniferous formation in coal mines of the southwestern part USCB (in Polish), CMI Katowice, 171 pp
- Pluta I, Ślaski R (1993) Using studies of origin mine waters and fire protection gypsum-anhydrite wells in radium purification mine waters of the Morcinek coal mine (in Polish). In: Proceedings "Ekologiczne aspekty górnictwa podziemnego złóż minerałów użytecznych", CMI, Katowice, p 206-210

- Pluta I, Waleczek E (1996) Purification of brines in the Pniówek Coal Mine from barium and radium (in Polish). In: Proceedings VI "Problemy Geologii w Ekologii i Górnictwie Podziemnym". Ustroń CMI, Katowice, p 309-318
- Pluta I, Pałys J (1999) Barium in mine waters of the Upper Silesian Coal Basin (in Polish), Przegląd Górniczy No 4:16-22

Pluta I, Piotrowski Z (2002) Storage of wastes in mine workings of the Borynia Coal Mine for limitation of barium and radium in mine waters (in Polish). Przegląd Górniczy No 1:12-14

Pluta I, Zuber A, Pytlak M (1994) Possibility of used gobs in purification of mine waters. In: Proceedings V "Problemy geologii w ekologii i górnictwie podziemnym", Szczyrk, p 347-353.

Pluta I, Mazurkiewicz M, Łukaszczyk Z (2002) Utilization of wastes in coal mines using in water protection (in Polish). Miesięcznik WUG Bezpieczeństwo Pracy i Ochrona Środowiska w Górnictwie, No 10:28-32

Pluta I, Łukaszczyk Z, Badurski R (2006) Purification from barium and radium of mine waters in the Jastrzębskiej Spółki Węglowej S.A. (in Polish). Miesięcznik WUG Bezpieczeństwo Pracy i Ochrona Środowiska w Górnictwie, No 12:14-18

Różkowski A *et al.* (2004) Hydrochemical environment of Carboniferous coal-bearing formations of the Upper Silesian Coal Basin (in Polish), SU, Katowice 2004, p 174

Remediation of environmental impact of acidic dam of mines through membrane process

Renato Ramos¹, Osmar Cunha¹, Fabio Rodrigues², Walter Scassiotti², Mauricio Ribeiro², Aerts Peter³

¹The Dow Chemical Company, Av. Nações Unidas. 14.171, São Paulo, Brazil, renato.ramos@dow.com, ocunha@dow.com ²Brazilian Nuclear Industries, Caixa Postal 961, Poços de Caldas, Brazil, fabiorodrigues@inb.gov.br, scassiotti@inb.gov.br, mauricio@inb.gov.br

³Dow Benelux BV, 439 Building (PTC-1)/122, Terneuzen, Netherlands, paerts@dow.com

Abstract Mining industry is assuming sustainable position looking for higher efficiencies. Water is the most sensible resources being discussed in the mineral market once its dependence is quite high due to consumption in mining process. The challenge is to convert waste residual matter into resource and the application of new technologies can be an important tool in this development. Conventional treatment methods for such sites with no production or process improvement prove to be too expensive to be economically attractive. This paper details an industrial scale application using nanofiltration membranes on acid mine drainage water from waste rock piles dam. This source from legacy uranium mine (Brazilian Nuclear Industries) located in Caldas, Brazil has been treated and discharged in order to comply with the local legislation.

Keywords manganese, uranium, nanofiltration, acid mine drainage (AMD)

Introduction

Acid Mine Drainage (AMD) stream is the result of exposure of sulfide containing material with oxygen and water. The production of AMD usually occurs in iron sulfide-aggregated rocks and typically it is characterized by low pH and high concentrations of (semi)-metals as well as other potentially toxic elements (1). Although this is a natural process, the mining industry is the major producer of AMD waters. Waters draining active mines, abandoned mines and mine wastes are often net acidic. Such waters typically pose an additional risk to the environment because they often contain high concentrations of metals (iron, aluminum and manganese, and other metals and metalloids, incl. arsenic).

Acid mine drainage (AMD) may form in underground chambers of deep mines, when a mine is in active production this is generally of minor importance because the water tables are kept artificially low by pumping. However, when mines are closed and abandoned, and the pumps are turned off, the rise of the water table can lead to contaminated groundwater being discharged, sometimes in a catastrophic event such as the one that happened at the Wheal Jane mine in 1992 when a range of contaminants entered the environment (Younger *et al.* 2004; Neal *et al.* 2004).

Abatement of acid rock drainage (ARD) is of increasing scientific and technical interest because of stringent regulations regarding environmental pollution. Acidity and dissolved (semi)-metals released from different sources of mine waste including underground and open pit mines, mine waste rock deposits, and tailings heaps and ponds result in a deterioration of soil and water quality (Sand *et al.* 2006).

Nanofiltration is a separation technique that considers membrane with a reported pore diameter in the range of half a nanometer to a few nanometers. These membranes are charged when in contact with aqueous solutions and as such, separation takes place based on charge and size. As a consequence, species with an effective diameter of one nanometer or greater will be removed. Multivalent ions are removed to a greater extent that single charged ions. Under the circumstances where removal of multivalent ions rather than monovalent ions is important, nanofiltration offers a more cost-effective option than other membrane technologies, as reverse osmosis, because the equipment can be operated at significantly lower pressures to obtain the same permeation rates.

Description of the Study Site

The Pocos de Caldas mining site is located in the Minas Gerais state, in the southern region of Brazil (latitude 21°45'S and longitude 46°35'W), 180 km northwest from São Paulo city and 360 km southwest from Rio de Janeiro the two major cities in the country. It occupies an area of about 15 km². The location map is presented in Fig. 1, where the city of Poços de Caldas (200,000 inhabitants) is located 20 km north from the mining site. The two major water sources which receive the releases of the mining and milling operation are the Antas River that flows in the direction of Poços de Caldas city and the Soberbo river which flows in the direction of the city of Caldas. Average annual precipitation is 1800 mm/a. The mine covers an area of 2.0 km². The mineralized zone was located at about 200 m below surface and the mine area was divided into three different ore bodies (A, B and C) for the purpose of mining operations (Fernandes et al. 2008). Bacia Nestor Figueiredo (BNF) is the place where the treat AMD came from indicated in the Fig. 2.

Chemical composition of the rocks is shown in Table 1. Attention must be called to the high contents of sulfur, occurring as pyrite that varies from 5637 to 18,961 ppm. The occurrence of pyrite in the rock has an important bearing in the generation of acid drainage as



Fig. 1 INB mining location.



Fig. 2 Bacia Nestor Figueiredo

discussed previously in this text (Fernandes *et al.* 2008).

The Poços de Caldas Project was intended to produce 500 t U_3O_8/a and 275 t/a of calcium molybdate as a by-product. The operations gave rise to two main sources of contaminants to the environment; the waste rock piles (WRP)

Element	Body A	Body B	Body E
SiO ₂ (%)	55 ± 0.53	53 ± 2.85	55 ± 2.64
Al ₂ O ₃ (%)	21.7 ± 0.64	20 ± 2.96	23 ± 1.14
Fe-tot (%)	2.6 ± 0.60	4.88 ± 3.68	2.61 ± 1.06
F (mg/kg)	1,488 ± 172	4178 ± 2,957	2,013 ± 803
Th (mg/kg)	60 ± 46	96 ± 89	318 ± 962
U (mg/kg)	89 ± 57	538 ± 958	279 ± 619
Zn (mg/kg)	253 ± 47	570 ± 646	592 ± 1,360
S (mg/kg)	8,616 ± 2,544	18,961 ± 18,025	5,637 ± 5,321
Zr (mg/kg)	1,708 ± 873	4,334 ± 7,115	1,009 ± 828

Table 1 Average composition and Standard Devi-ation of rocks from the three ore bodies of Pocosde Caldas mine (from : Waber et al. 1991).

and the tailing dam. After 15 years (1982–1997) the uranium mining and milling operations have ceased while the chemical plant in charge of the liquid effluent treatment is still active. Recently, due to the exhaustion of the capacity of the tailing dam to receive additional wastes, the precipitate from the chemical treatment has been deposited in the mine open pit. The effluent from the tailing dam is treated with BaCl₂ to remove radium isotopes from the solution. Regarding the tailing dam, it has already been mentioned that the direct release of untreated effluents into the receiving waterbodies will result in unacceptable doses to members of the public (Fernandes *et al.* 2008).

Results and Discussion

From January 2012 to June 2012 a nanofiltration pilot plant has been the focus of a study in a Uranium site placed in Poços de Caldas, Brazill called Industrias Nucleares do Brasil (Brazilian Nuclear Industries). The aim of the application was to remove MnSO₄ from an acid mine drainage water source that was stored in a dam named Bacia Nestor Figueiredo (BNF) and whose volume capacity was 750 m³. Currently INB faces a process of site clean-up and it must limit the manganese content of the dam according the local legislation (CONAMA 430/11) that limits to < 1 mg/Lfor environmental disposal. Currently, in order to achieve the current value, INB spends tons of Ca(OH)₂ on a daily basis in a lime precipitation process. The precipitate is pumped to open pit and supernatant is released to the environment. The cost of managing waste water after a non-scheduled environmental release is usually very high from a financial, ecological and social aspect. As a result, mining firms worldwide are focused on the early planning and implementation of water-management plans. In order to look for an alternative technology, the following process has been considered at INB:

Number of Units:1/Configuration:1 stage/Vessels: Codeline 8"/Elements per Vessel:1 Type of Element: Polyamide Thin Film/Manufacturer: Dow-Filmtec/Model:XUS 229323

Feed water: Acid mine Drainage at 1500 $\mu\text{S/cm}$ @ 25 °C.

A cartridge polishing filter to remove fine particulate not removed by previous filters

Typical RO Feed: SDI < 3/RO Recovery: 9 % (avg/element)/Feed Capacity Per Unit: 10 m³/h

Pre-Treatment

The water coming from BNF is driven to a leadlag multimedia filtration system (Fig. 3). The multimedia filtration has been chosen for colloidal removal so that the Silt Density Index (SDI_{15}) before Nanofiltration membrane reaches less than 5 (100 % of time).

The cylindrical multimedia filters used for this purpose were made of carbon steel and hard rubber inner coating. The vessels (height × diameter: $1.5 \text{ m} \times 0.9 \text{ m}$) were partly filled with layers of : 150 mm of pebble (4.5 mm particle size); 400 mm of sand (0.6 mm – 1.2 mm particle size) and 300 mm of anthracite (0.8 mm – 1.0 mm particle size). The average flow rate was 11 m³/h.m² and pressure operation was 21 psi. Each filter was equipped with backwash system and two manometers. The backwash was performed every time the differential pressure has exceeded 3.6 psi.

Pre-filtered stream was passed through a $5\,\mu m$ (effective) cartridge filter prior to the



Fig. 3 Multimedia filters



Fig. 4 NF containerized unit



Fig. 5 Nanofiltration System

Nanofiltration tests to remove particulate coming from the multimedia filters, which could rapidly foul the membranes. In any industrial application feed pre-treatment could be replaced for an Ultrafiltration to minimize even more the particulate fouling.

Nanofiltration unit (NF)

In order to provide a compact solution it has been established a containerized system with the Nanofiltration membrane and associated automation as showed on Fig.4

That system has considered only one element in the vessel in order to be adequate to small water consumption during the tests but with possibility to leverage the acquired knowledge to larger systems (Fig. 5). The system is able to consider anti scaling in the RO feed stream and also to be prepared to run clean-in-place (CIP) procedure. Several signals were able to be monitored on-line as permeate flow, reject flow and feed pressure. Also analogical data as cartridge filter pressures, dosing pumps flow, and RO differential pressure has been measured.

The system has a centrifugal pump whose feed pressure has been set at 4.5 bar. A pressure control valve in front of the pump was triggered to a pressure transmitter that kept the pressure constant. Another control valve in the concentrate side had the function to keep the recovery of the system $r = \frac{\text{PermeateRow}}{\text{FeedHow}}$. A differ-

ential pressure between the feed and the concentrate was monitored continuously so that the 10 % increasing of that difference would alarm for a cleaning procedure (clean in place - CIP).

Nanofiltration membranes

In this particular case it has been used a membrane named XUS-229323 that has high sulfate removal capacity at brackish water. That membrane has showed excellent performance during the tests. It is a thin film composite (TFC) membrane whose area is 37 m² and manufactured by The Dow™ Chemical Company through its subsidiary FILMTEC™.

Recovery

As the considered system had one element, the concept of the project has been to work around 9-12 % recovery by the element. Considering larger systems where usually number of membranes in the vessels is between five and seven it is possible to leverage similar recoveries for each element inside the vessels so that the expected recovery for a larger system would be around 70 %. This would mean only a reject flow around 30 % of the feed flow.

Key contaminant removal

The results from the diary analysis showed that membrane acted in efficient level, considering the removing results were higher than

Species	Average Removal ± RSD/%
Manganese	98.8 ± 0.7 (<i>n</i> =45)
Fluoride	98.1 ± 0.8 (<i>n</i> = 55)
Sulfate	$95.1 \pm 0.5 (n = 48)$
Zinc	98.1 ± 0.1 (<i>n</i> =3)
Calcium	97.9 ± 1.9 (<i>n</i> =8)
Aluminium	99.1 ± 0.5 (<i>n</i> =8)
Uranium	87.0 ± 5.0 (<i>n</i> =45)

Table 2 Average removal of higher concentrationelements using nanofiltration system; RSD: Rela-tive Standard Deviation and n = number of samples

95 % for contaminant key elements, except for Uranium that showed 87 % removal. The table 2 presents the average removal results for analyzed elements. The best results were the aluminum, manganese (Fig. 6) and fluoride (Fig. 7) removals. The membrane performance for sulfate removal was significant, taking into account the great concentration in the feed – around 1,000 mg/L (Fig. 7).

The results obtained for contaminants removal showed the feasibility of nanofiltration technology with XUS-229323 membrane as the contaminants concentration was reduced to acceptable levels for environmental disposal, especially for manganese and fluoride. In addition, the membrane was able to remove a wide range of elements, including rare earth elements.

Fouling tendency

One of the main concerns, when ARD is treated, is the lifetime of the membranes. During the tests, a very close and efficient operational monitoring occurred so that the correct cleaning was performed at the right time. Based on that, it was decided to autopsy the membranes after the test period. Additionally ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry) have been applied in a membrane extract in order to identify what element would have more probability to cause scaling. The ICP-OES results are presented in table 4.

Aluminum and iron were the most important metals whose precipitation has been significant but in levels that did not intrude membrane performance.

Cleaning Procedures

A protocol of different cleanings has been applied during the test period what leaded to ten CIPs during 2000 hours of operation. It has been defined that oxalic acid cleaning followed by caustic soda cleaning have presented better results in terms of differential pressure recovery. Because the water source was surface water, eventually biocide (DBNPA) cleaning has been considered in shock treatment (by CIP) in order to avoid biofouling growth.

Scaling tendency

We took the opportunity to test 3 different Dow anti scalants (Acumer 4300, 3100 and 1100). One of the results is that that Acumer



Fig 6 Manganese feed, permeate and reject



Fig 7 Sulfate feed, permeate and reject

Elements	U	Mn	SO ₄ ²⁻	Fe	Са	Mg	Р	Al	Ti	Ni	Zn	Ba	Cr
mg/L	4.8	2.8	127	13	6.1	2.9	1.2	47	0.4	0.2	3.3	0.13	0.27

	Parameters	Ca(OH) ₂ Consumption	рН	Flow Rate	Ca(OH) ₂ consumption
#	Systems	kg/m ³		m³/h	kg/h
1	Conventional Treatment	1.70	11.0	300	510
2	Nanofiltration Reject	1.77	11.1	90	159.3
3	Nanofiltration Permeate	0.04	6.5	210	8.4

4300 has presented lower trend to fouling in comparison to the others (Acumer 3100 and Acumer 1100). Acumer 4300 is a maleic multipolymeric antiscalant whose molecular weight is around 2000 g/mol and containing 54–56 % of solids content.

Operational Costs and membrane life

Despite of the good permeate quality which can be used in the industrial area or returned to environment according the legislation, the membrane process has showed a very favorable Operational Expense (OPEX) in comparison to the current remediation applied at INB. INB makes use of chemical precipitation using $Ca(OH)_2$ what is generating a significant amount of mud which is a complicated to be handled. Based on the pilot plant test performed at the site, it was possible to define the amount and cost of lime used in the conventional treatment versus the cost of Nanofiltration. The table 5 shows the consumption and pH for the different streams.

According the data, comparing lime consumption in a Nanofiltration system with lime consumption in a conventional physico chemical treatment, the amount of lime used is the same but treating significantly less water. Additionally, a Nanofiltration system occupies 70 % less area than an conventional physic chemical treatment.

Conclusions

- 1. The membrane considered on the site had a great performance and the nanofiltration system was able to reduce sulfate, manganese and fluoride in order to generate a permeate flow according the local regulation for disposal in the environment or reuse;
- **2.** A correct operational action and a proper pre-treatment design can drag out the time life of the membranes in tough waters as ARD;
- **3.** ACUMER 4300 has been proved as the best anti scalant for this particular water on site;
- **4.** Nanofiltration process has been found to present lower OPEX reducing the occupied area of precipitates;

References

- Fernandes H.M., Franklin M. R., Gomiero L.A. (2008) Critical analysis of the waste management performance of two uranium production units in Brazil part I: Poços de Caldas production centre, Journal of Environmental Management, Volume 87, Issue 1, April 2008, pp 59–72
- Younger P.L., Coulton R.H, Froggatt E.C. (2004) The contribution of science to risk-based decision-making: lessons from the development of full-scale treatment measures for acidic mine waters at Wheal Jane, UK Sci. Total Environ. (2004)

Mine water treatment options for meeting stringent selenium regulatory limits

Tom Rutkowski¹, Rachel Hanson², Kevin Conroy³

Golder Associates Inc., 44 Union Boulevard, Suite 300, Lakewood, CO 80228, USA ¹TRutkowski@golder.com, ²RHanson@golder.com, ³KConroy@golder.com

Abstract Selenium can be a constituent of concern in mine waters and is often present in neutral waters. Selenium is typically leached from waste rock piles as the selenate ion and mines can be faced with multiple, high-flow contaminated discharges. In recent years, biological treatment has emerged as an effective and relatively inexpensive method compared to physical and chemical methods. With some waters, biological treatment alone is sufficient to achieve stringent regulatory limits; however, in other cases, additional unit processes are required. Three treatment cases studies are included for treating moderate levels of influent selenium (50 – $500 \mu g/L$).

Keywords selenium, biological, water treatment

Introduction

Biological selenium treatment is well-established with dozens of pilot studies and multiple full-scale plants. However, biological treatment is not always capable of meeting stringent regulatory limits (i.e. 5 µg/L) currently being promulgated in North America. For mines with influent selenium concentrations in the range of 50 μ g/L – 500 μ g/L, additional unit processes may be necessary. This concentration range is termed moderate as other industries (i.e. oil and gas, power, agriculture) can generate higher concentrations. Selenium is typically present as the oxidized inorganic selenate species in mine waters. A block flow schematic is provided in Fig. 1 for compliance with stringent limits.

Biological treatment relies on the microbial oxidation of organic carbon to reduce selenium and is subject to the preferential reduction of competing electron acceptors including oxygen and nitrate. During anaerobic biological treatment, selenium is reduced to particulate, elemental selenium and organic carbon is oxidized to carbon dioxide, as shown in Equation 1.

$$SeO_4^{2-} + 2 CH_2O \rightarrow 2 CO_2 + 2 H_2O$$
 (1)

The process requires an electron donor, or substrate, which can be a variety of organic materials, including molasses, ethanol, or proprietary vendor products. The majority of the elemental selenium is retained within the microbial matrix and some can be released in the



bioreactor effluent. Bulk removal of selenium has been demonstrated with passive and active treatment. Active treatment technologies include packed bed reactors and fluidized bed reactors. Regardless of the bioreactor configuration, the underlying microbial reactions and removal mechanism is the same. After biological treatment, care must be taken to prevent re-oxidation and mobilization of particulate selenium. Depending on project considerations, a solids separation polishing step may be necessary to remove particulate selenium which is not retained within the bioreactor.

Currently, it is believed selenium reduction is carried out by a group of organisms, called denitrifiers, which also reduce nitrate. Denitrifiers will not reduce selenium if oxygen and nitrate are present. Presence of alternative electron acceptors, such as oxygen and nitrate, can increase demand for the substrate. Sulfate reducing bacteria (SRB) can also compete for substrate during biological treatment. Sulfate is a less favorable electron acceptor than selenium, and generally will not be reduced until selenium is treated; however, if excess substrate is present, sulfate reduction can proceed. Sulfate reduction can result in the production of hydrogen sulfide gas, which is a health and safety concern. Thus, substrate addition must be balanced to promote selenium reduction, which may include oxygen and nitrate reduction, while limiting sulfate reduction. The biological treatment process produces biomass which must be periodically removed and disposed of. The solids production for a bioreactor can be expressed as a ratio of the amount of biomass produced to the amount of substrate, or chemical oxygen demand (COD), consumed. In a recent fluidized bed reactor pilot study, the observed yield was 20 g TSS/100 g of COD (Munirathinam 2011). Advantages of biological treatment for mining applications include the ability to function with high influent total dissolved solids concentrations (TDS), relatively small chemical requirement, and low sludge production as compared to chemical treatment. Disadvantages of biological treatment are pH and temperature dependence, a long start-up period (*i.e.* systems can also take several weeks to start-up and achieve full treatment capacity and cannot be shut down for extended periods without repeating the lengthy start-up process), and an aeration requirement to add dissolved oxygen prior to discharge.

Selenium post-treatment is required when biological removal is insufficient to achieve stringent regulatory limits. The goal of post-treatment is to reduce total selenium concentrations with conventional treatment processes that can remove particulate selenium that is not retained in the bioreactor. The following processes can be applied for selenium post-treatment:

- Coagulation/Flocculation Coagulation is the process of inducing contacts between a chemical and colloidal particle to encourage a reaction to form microfloc particles. Flocculation is the process of encouraging contact between coagulated particles to form larger particles referred to as floc particles which settle more effectively.
- Clarification Coagulation/flocculation can be followed by clarification to settle and collect precipitated solids.
- Filtration Filtration can be employed, if necessary, to treat clarifier effluent for total selenium and TSS removal. Multimedia or media filtration, rather than membrane filtration, is preferred for cost purposes. Filtration testing is recommended for evaluation during pilot testing by testing with multiple pore size filters.

The processes may be combined depending on testing results. Proprietary sorption media may be an alternative to these conventional processes. Consideration of selenium oxidation and mobilization is important when designing post-treatment and polishing processes. If selenium post-treatment and nutrient/TSS polishing processes are both required, the post-treatment process will remove total selenium prior to aerobic treatment and mobilization of selenium should not be a concern. If bulk removal is sufficient to meet the selenium treatment goals and nutrient/TSS polishing is necessary, then the possibility of selenium mobilization in the aerobic treatment process should be considered. Three case studies are presented below for treatment of moderate selenium levels to stringent regulatory limits.

Golder Case Study 1 – Reverse Osmosis with Immobilized Cell Bioreactor Treatment

Golder designed and constructed an active treatment system that includes biological treatment to remove selenium at a closed mine site in South Dakota, U.S. The biological technology is the Immobilized Cell Bioreactor (ICB). The treatment system is designed to treat pH-neutral, waste rock leachate characterized by high TDS (approximately 5,000 to 15,000 mg/L), high hardness, and high sulfate concentrations. The average influent selenium concentrations are approximately 70 μ g/L, the discharge limit is 4.6 μ g/L, and the maximum design flow is 160 cubic meters per hour (m³/h). Influent selenium is present as selenate. The process flow includes the following processes.

Reverse Osmosis (RO) for TDS management and volume management during peak flows. The RO system includes influent water heating (including a boiler and heat exchanger), anti-scalant addition, and membrane cleaning; and,

 Active biological treatment to remove selenium from the RO reject stream. Treated biological effluent is recombined with RO permeate to meet the regulatory limit for TDS. Any excess bio-treated brine is discharged to the local municipal wastewater treatment system.

The biological treatment system achieves removal of selenium to residuals less than 10 μ g/L and the regulatory limit is achieved by blending with the RO permeate prior to stream discharge. The combination of RO and a microbial reduction treatment system is beneficial because it meets stringent regulatory limit while allowing the installation of a treatment system with a large range of treatment capacity in a 0.4 ha treatment facility.

Golder Case Study #2 – Biological Treatment with Selenium Post-Treatment

Bench testing was conducted for a mine water with high levels of nitrate and selenium over the course of four months with the ICB technology in continuous flow reactors. Influent and effluent selenium and nitrate concentrations are provided in Table 1. The average total and dissolved selenium concentrations for influent were 179 and 177 µg/L, respectively. Influent selenium was present as selenate. The average total and dissolved effluent selenium concentrations were 41 μ g/L and 24 μ g/L, respectively. The lowest observed effluent concentrations were 19 µg/L total selenium and 16 µg/L dissolved selenium. A graph of selenium concentrations and a bench test photo are provided in Attachment 1. Effluent concen-



Wolkersdorfer, Brown & Figueroa (Editors)

Description	Influent Se _{tot} (µg/L)	Biological Effluent Se _{tot} (μg/L)	Biological Treatment, Percent Removal	Influent Se _{filtered} (μg/L)	Biological Effluent Se _{filtered} (μg/L)	Biological Treatment, Percent Removal
Average	179	41.0	77%	177	24.5	86%
Minimum	NA	19.1	56%	NA	16.7	91%
Maximum	NA	78.6	89%	NA	36.1	80%

Table 1 Bench testing results for biological treatment

Iron Dose (mg/L)	$Se_{tot}(\mu g/L)$	$Se_{filtred}$ (µg/L)	% Removal
0	13.6	13.5	20.9
5	13.2	13.0	23.3
10	10.4	11.5	39.5
20	7.08	7.82	58.8
40	4.53	4.03	73.7
50	4.42	3.70	74.3

Table 2 Bench testing results for iron co-pre-cipitation

trations for total selenium were consistently higher than dissolved concentrations, likely due to the presence of volatile and particulate selenium. Selenate was effectively reduced to less than 1.0 µg/L, but low levels of selenite and selenocyanate remained in the treated effluent. An average influent nitrate concentration of 168 mg/L as N was reduced to an average of 1.0 mg/L in the effluent. Iron co-precipitation was also tested as potential polishing treatment (Table 2). Iron co-precipitation results indicated a dose of 40 mg/L iron was able to reduce dissolved selenium to less than 5 µg/L in the effluent.

Note: Only average values are shown for influent concentrations since testing was conducted on one bulk sample and influent values did not vary. All values are dissolved values. Effluent total selenium was somewhat higher than effluent dissolved values.

Based on the bench testing outcome, the recommended block flow schematic to achieve

an effluent concentration of 5 $\mu g/L$ is provide in Fig. 3.

Golder Case Study #3 – Passive Biological Treatment

Passive biological treatment of selenium typically consists of a gravity flow reactor containing solid organic media. The organic media slowly degrades and provides a carbon source to sustain the microbial reduction of selenate to elemental selenium. Examples of successfully-implemented organic media include hay, wood chips, sawdust, rice straw (Pahler 2007; Zhang 2008). The media can also contain an alkalinity buffer such as limestone. This is a passive technology as it operates without electricity or continuous chemical inputs and does not generate continuous treatment residuals. BCR effluent can contain elevated levels of biochemical oxygen demand and may require a polishing step in order to comply with regulatory standards. BCRs are typically used to treat



Influent	Pa Ana Biolo	Passive Anaerobic Biological BCR		Passive Aerobic Biological (engineered wetland)	Treat Efflue	ed ent → Fig. f	Fig. 4 Block flow schematic for passive treatment		
-	Description	Influent Se _{tot} (μg/L)	Biologica Effluent Se (μg/L)	l Biological _{tot} Treatment, Percent Removal	Influent Se _{filtered} (μg/L)	Biological Effluent Se _{filtered} (µg/L)	Biological Treatment, Percent Removal		
-	Average	22.3	1.0	94%	24.4	2.0	90%		
	Minimum	5.3	0.5	75%	5.9	0.4	46%		
	Maximum	41.6	1.5	98%	48.4	14.0	99%		

Table 3 Pilot testing results for passive BCR treatment – Test Conditio	n 1
--	-----

Description	Influent Se _{tot} (µg/L)	Biological Effluent Se _{tot} (µg/L)	Biological Treatment, Percent Removal	Influent Se _{filtered} (μg/L)	Biological Effluent Se _{filtered} (ug/L)	Biological Treatment, Percent Removal
Average	68.5	8.5	87%	66.0	7.3	88%
Minimum	61.5	1.1	69%	58.1	1.5	69%
Maximum	79.5	18.9	98%	76.8	18.4	98%

Table 4 Pilot testing results for passive BCR treatment – Test Condition 2

contaminants that precipitate or are biologically removed under reducing conditions, such as metals, nitrate, and sulfate. Full-scale BCRs have been constructed in the US, Canada, Europe, and South Africa.

A pilot study was conducted with a single 124 m³ pilot BCR to treat an average flow of $3 \text{ m}^3/\text{h}$. Influent was drawn from a dewatering trench in a gravel pit next to the Colorado River near Grand Junction, Colorado, US. The pilot operated, with varying detention times, over a thirteen-month period from September 2008 until October 2009. Influent selenium was predominantly present as the selenate species. Influent and effluent selenium concentrations are provided in Attachment 2. During the first eight months, influent selenium concentrations were less than 40 µg/L and effluent concentrations were less than 5 µg/L. This period is labeled Test Condition 1 in Attachment 2 and Table 3. During Test Condition 2 (Table 4), the influent source was altered to evaluate removal efficiencies with higher concentration water. With low influent selenium concentrations during Test Condition 1, effluent concentrations of total and dissolved selenium were below 5 μ g/L. During Test Condition 2 with moderate influent concentrations, effluent total and dissolved concentrations averaged 8.5 and 7.3 μ g/L, respectively. An additional unit process would be necessary under moderate influent concentrations to achieve the regulatory limit of 5 μ g/L. The BCR treatment process was effective throughout the winter months with ambient temperatures below freezing and influent water temperatures below 10 degrees Celsius.

Conclusions

Treatment of moderate selenium concentrations in mine waters to meet stringent regulatory limits remains a technical challenge. Biological treatment methods are capable of bulk selenium removal but are not always capable of meetings stringent limits due to residual particulate or reduced selenium species in bioreactor effluent. In these circumstances, pre-treatment with reverse osmosis or selenium post-treatment are necessary. These processes have been demonstrated at full-scale but add significant complexity and cost. Removal efficiencies and effluent concentrations are similar for active and passive biological treatment processes.

References

- Blumenstein EP, Volberding J, and Gusek, JJ (2008) Designing a biochemical reactor for selenium and thallium removal, from bench scale testing though pilot construction. Presented at the 2008 National Meeting of the American Society of Mining and Reclamation, Richmond, VA on 14–19 June.
- Munirathinam K, Srinivasan R, Tudini JJ, Sandy TA, Harrison TD (2011) Selenium treatment of mine water effluent in a fluidized bed reactor. Proceedings of the 2011 Water Environment Federation (WEFTEC) Conference.
- Pahler J, Walker R, Rutkowski T, and Gusek J. (2007) Passive removal of selenium from gravel pit seepage using selenium reducing bioreactors. Presented at

the 2007 Annual Meeting of the American Society for Mining and Reclamation, Gillette, WY.

- Pruden A, Pereyra LP, Hibel SR, Inman LY, Kashani N, Reardon KF, Reisman D. Microbiology of sulfate-reducing passive treatment systems. Proceedings of the 2006 International Conference on Acid Rock Drainage (ICARD), St. Louis, MO. Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502
- Sandy T, DiSante C (2010) Review of available technologies for the removal of selenium from water. Prepared for North American Metals Council. CH2MHill.
- Zhang Y, and Frankenberger Jr. WT (2003) Removal of selenate in simulated agricultural drainage water by a rice straw bioreactor channel system. Journal of Environmental Quality, 32: 1650–1657.

Electronic attachements can be found at: http://bit.ly/IMWA2013_570

Treatment of high total dissolved solids and acidity in Cerro de Pasco mining wastewater, Peru

Tom Rutkowski¹, Melissa Rhodes¹, Jessa Smith¹, Kevin Conroy¹, Mike Bratty²

¹Golder Associates Inc, 44 Union Blvd, Suite 300. Lakewood, CO, USA. trutkowski@golder.com ²Golder Associates Ltd. #400 – 4260 Still Creek Drive, Burnaby, British Columbia, Canada. mbratty@golder.com

Abstract The current wastewater treatment plant at the Cerro de Pasco mine in Peru is a low density sludge process and treats 630 m³/h with an influent pH of 2.5 and elevated metals concentrations. The project goals include increasing capacity to 1,375 m³/h, meeting new mine discharge regulations, and reducing unit operating costs. Technologies considered included high density sludge (HDS), sulfide treatment for recovery of copper, and neutralization with limestone. The sulfide and limestone processes are projected to reduce annual chemical costs by 15 % and 20 %, respectively.

Keywords HDS, Limestone, Sulfide, Mine Peru

Introduction

The Vulcan SAC-owned Cerro de Pasco mine produces lead, zinc and silver and is located in Chaupimarca district, Cerro province, about 295 km from Lima at an altitude of 4,300 m. The current wastewater treatment plant at the mine is a low density sludge lime neutralization plant that treats approximately 630 m³/h of influent water with a pH of 2.5 and elevated metals concentrations. The mine will need to increase the capacity of the plant to 1,375 m³/h to treat all acidic water at the site in order to comply with recent mine discharge regulations. There are end-of-pipe discharge requirements (LMP) for some parameters. The current annual lime cost is projected to increase fivefold due to the plant expansion. The future influent water has a pH of 2.0, 16.2 g/L of acidity as CaCO₃, and a TDS concentration of 19 g/L. The influent acidity includes 15.7 g/L of metal acidity. The current plant treats water from 5 sources; the future plant will treat higher flows from the current sources as well as two additional sources. The contaminants of concern (COCs) are those parameters that exceed the LMPs: As, Cd, Cu, Fe, Pb, Zn.

Treatment alternatives evaluation

A treatment alternatives evaluation was conducted in order to select a treatment technology that would meet treatment goals and reduce lime costs. Neutralization methods considered included low density sludge (LDS), high density sludge (HDS), and neutralization with limestone. Given the high influent copper concentrations, metal recovery options were also considered including sulfide treatment, ion exchange, and solvent extraction and elec-

	Existing plant	Future plant	
Flow rate, m ³ /hr	630	1,375	
Quicklime (CaO) dose, g/L	10.9	11.1	Table 1 Estimated lime costs
Quicklime (CaO) consumption, tonne/yr	49,080	121,740	for existing LDS plant and future LDS plant

trowinning. Sulfide treatment allows recovery of copper from the mine water as a marketable copper sulfide, generating revenue through copper concentrate sales to offset costs. The sulfide process is used in conjunction with a neutralization process (*e.g.* HDS) to treat for other metals and acidity.

A summary of the treatment alternatives is provided in Attachment 1. In Attachment 1, Table 1A, the existing LDS plant is considered the base case and cost difference with other neutralization methods are provided. Switching to HDS is estimated to save 23 % and switching to limestone/lime neutralization is estimated to save 20 % of the annual chemical cost. In Attachment 1, Table 1B, metal recovery alternatives are presented. The sulfide process is projected to reduce annual operation costs by 15 %. Ion exchange, which is predicted to result in 18 % savings, was not retained because the technology has not been demonstrated at full scale for copper recovery on a similar water matrix. Based on this evaluation. HDS. limestone pretreatment, and sulfide pretreatment were chosen to carry forward for bench testing.

Bench testing methods

The bench testing objective is to provide indications of treatment performance and design parameters and form a basis for the development of full-scale design criteria and operating conditions. The bench testing was comprised primarily of jar testing that can be used to quickly and easily evaluate contaminant removal over a range of treatment conditions with relatively small quantities of water. Lab grade hydrated lime (Ca(OH)₂) was used for all lime titrations and added as a 30 % by weight slurry. Lab grade limestone (CaCO₃) was used for all limestone titrations and added as a 20 % by weight slurry.

The seven water sources were mixed according to predicted flow contributions from each source; this will be referred to as the total blend. The second blend used only the Source 2 and 6 waters; this is referred to as the copper recovery blend. This was the blend evaluated for the possibility of copper recovery using sulfide. Six lime titrations (T1 - T6) were performed on the total blend to determine the optimum pH for metals removal. Five additional lime titrations (O1 - O5) were performed with aeration by inserting a coiled air diffuser wand into the bottom of the beaker. The goal was to see how aeration with similar lime dosing affected the end pH and metals removal. Six limestone titrations (LS1 - LS6) were performed on the total blend. Once a limestone dose was selected, two-stage neutralization was evaluated (R1 - R6). Limestone was added at a set dose of 10 g/L to six different samples and allowed to react, and then lime doses between 1 and 6 g/L were added, with no solids separation step in between the two stages.

The goal of the copper recovery blend titration tests was to evaluate the pretreatment conditions which are necessary to produce a marketable sulfide product in subsequent tests using sulfide reagent, sodium hydrosulfide (NaSH). The copper recovery blend contained high levels of iron, arsenic and other metals which needed to be removed in order to maximize the value of the copper sulfide product. Titration testing was performed using the copper recovery blend water in nine jar tests. The objective of this testing was to determine the pH that would maximize arsenic removal while minimizing copper loss, and to produce pretreated copper solution for subsequent testing.

HDS recycle testing, which involves successive batch HDS neutralization cycles, was performed to provide a comparison between HDS and conventional lime treatment on settling, filtration, and effluent quality. Tests were performed using the total blend water.

Results

Lime titrations

It was found that a pH of 8.1 at a lime dose of 10 g/L resulted in metal concentrations that me*et al.* l discharge requirements. A theoretical dose, based on metals removal, was calculated at 10.1 g/L. The actual required dose was equal to the theoretical, which indicates high lime utilization. This was the lowest pH that met al. l treatment targets, and is within the range of the current plant, which operates at a pH of around 8 using a lime dose of between 5 and 10 g/L, depending on the time of year. The titration curve is shown in Fig. 1. Informal testing showed that the titration curve hit a plateau (buffering zone) at roughly pH 8, between a lime dose of 9 and 10 g/L.

The samples which were provided supplemental air had a higher final pH than the samples which were simply mechanically mixed ("non-aerated"), with the same lime dose as shown in Fig. 1. The reaction time was with supplemental aeration was reduced to roughly an hour.

The analytical results for both the "aerated" and "non-aerated" samples are presented in Attachment 2. The lime dose, final pH after the 3 hour reaction time, and aeration are indicated in the field results section of the Attachment 2. Analytical samples for pH, dissolved metals, and sulfate were submitted to an outside laboratory on samples T-3 through T-6, and O-1 through O-5. T-1 and T-2 did not have a high enough pH value to warrant analytical sampling, as it was thought the metals removal would not be high enough at such a low pH. T-5 and T-6 both meet al. I the treatment targets; however, T-5 has a lower lime dose, so it was chosen as the optimum treatment condition for subsequent testing. Metal concentrations in T-3 and T-4 were several orders of magnitude greater than in T-5 and T-6. O-1 and O-2 exhibited unexpectedly low metal removal rates. However, because their final pH is far greater than is considered representative for the treatment plant, these samples were not carried forward for further discussion. Metals removal in samples O-3, O-4, and O-5 was fairly similar for both the aerated and nonaerated samples at the same general pH, although there were a few minor differences. Manganese removal was higher with aeration; this would be an expected result for manganese.

Limestone titrations

The selected dose was determined to be 10 g/L which results in a pH of 5.8. A theoretical dose, based on metals removal, was calculated at 10.3 g/L. The actual required dose was equal to



Wolkersdorfer, Brown & Figueroa (Editors)

the theoretical, which indicates high limestone utilization. There was a steep inflection point between pH 2.48 and 5.83, corresponding to lime doses of 5 g/L and 10 g/L, respectively. This pH range is where iron begins to precipitate, resulting in the rapid change in pH. The pH stops increasing after 10 g/L; it appears that the maximum possible pH through limestone addition is around 5.8. Fig. 2 shows the titration curve for the total blend with limestone addition.

Much lower lime doses were required if limestone was used for pre-neutralization; 10 g/L limestone and 3 g/L lime reached the same pH of around 8.1 as 10 g/L of lime only. This method also results in a lower reaction time. The limestone stage reached a pH within 0.3 of the final pH within 30 minutes. It was allowed to react for two hours to confirm the final pH, but this could be shortened considerably. The reaction time for the lime stage then ranged between 30 and 60 minutes as opposed to upwards of three hours without the limestone pre-neutralization. The reason for this is believed to be related to the carbon dioxide formed by limestone when it reacts with acid. The bubbles formed when the limestone reacts may be generating enough shear force to break up the gypsum particles before they can completely coat any unreacted limestone. The bubbles also create a lower bulk fluid viscosity, which can assist with mixing.

Copper recovery blend

There were a number of challenges encountered while conducting the titration testing on the copper recovery blend: high lime demand, high solids generation, and difficulty in selectively removing iron and arsenic without also removing copper. A theoretical dose, based on metals removal, was calculated at 119 g/L for the high strength, high copper solutions. A large dose of lime, 75 g/L, was required to neutralize the copper recovery blend to a pH of 4.66. The solids generation was commensurately high, and the solids produced a viscous slurry that was difficult to mix. The solids produced in the procedure were low density and settled poorly. After two hours settling time, there was no free liquid on the top of the solids, indicating that the solids were too thick to consolidate. The samples were filtered in an outside laboratory before analysis. Only the two samples that had a pH of less than 4 produced visible free water (decant). The solids produced in these tests were unusual because two different solid morphologies were observed: a red, less viscous material, and a thick, black material. The black material could be removed from the slurry using a strainer. At the pH range tested, significant copper removal occurred. The highest residual copper in a sample was 12 mg/L which is a 99.4 % removal from a starting point of 1,966 mg/L of copper. Three other samples had residual copper values of less than 1 mg/L. The low levels of copper remaining after pretreatment were unexpected, and further optimization work on the pretreatment process is required before the metal recovery step can be demonstrated to produce a marketable, clean copper sulfide product. For example, a lower pH should be tested in future, or more process alternatives may be tested to demonstrate economic metal recovery options.

High density sludge recycle testing

The large amount of solids generated in the later recycles resulted in the sample only undergoing hindered settling wherein liquid moves up through the spaces between particles, and the solids settle as a unit, maintaining their relative position to other particles. A clear solid-liquid interface develops as the particles settle. Compression settling occurs when the solids have reached a concentration where further settling can only take place through compression of the structure. The weight of the particles and the supernatant causes compression. Unhindered settling occurs when the solids particles drop out of solution at different rates. Heavier particles settle first, while lighter particles take more time to settle out. This can be observed as clear decant on top,
leading into a cloudy layer in which particles are still settling, and finally into the sludge layer, where particles have settled and are beginning to compact. Several tests were conducted to experiment with unhindered settling. A small amount of sludge was diluted with additional decant water, and more polymer was added and the mixture allowed to settle. The sludge settled more quickly, but the clarity of the overflow was compromised as expected. Overall more pin floc was seen in the decant with unhindered settling. However, the projected clarifier underflow concentration is not significantly affected by the dilution. Attachment 3 shows the interface height over time for select recycle batches. It can be seen that the interface height increased at first while the amount of solids generated was increasing, then began to decrease as the solids began to compact and densify. Most compression during each recycle had occurred by 50 minutes into the settling test, although 60 minutes of settling time was allowed for maximum compaction. Some samples were left overnight. Once compression had begun to occur, even the extended settling time did not result in a lower interface height. The HDS evaluation was performed to 13 recycles in an effort to confirm underflow densification.

Total suspended solids (TSS) values for the underflow are shown in Attachment 4. The underflow shows a rising trend with recycle number in thirteen consecutive batch recycle tests. The maximum density was approximately 21%, though higher density can be expected in continuous pilot or full scale trials. Analytical results from Recycle #10 decant are provided in Attachment 5. The recycles were run in a pH range of 8.0 – 8.5, recycle #10 reached a pH of 8.4. Metals removal remained high, similar to the removal rates seen in the initial lime titration. Both sulfate and manganese removal showed significant improvement over the single pass titrations run at a similar pH. Since the recycle tests resulted in more efficient sulfate and manganese removal for a given pH setpoint compared to simple titrations, then by the same token, the same sulfate and manganese removal can be expected at a lower pH with recycle compared to simple titrations.

Discussion

Most operating facilities treating acid rock drainage do not use limestone as a neutralizing agent, but limestone is commonly used to neutralize high strength acidic wastes such as autoclave barren solutions. Some of the advantages to using limestone instead of lime are: lower material costs, denser sludge, and lower sludge volumes. Typical disadvantages include the inability to raise the pH above 5.0-7.0, low utilization efficiencies due to armoring, and longer reaction times (EPA 1983, Hammarstroma et al. 2003). The practical limit of pH 5-7 is due to declining reaction kinetics. In order to achieve higher neutralization pH, a two-stage neutralization is typically used, with lime being added to a second reactor following the limestone reactor. Based on bench results for the Cerro de Pasco mine wastewater, the chemical cost savings of utilizing limestone and lime are 20 % if limestone is $\frac{1}{2}$ the cost of lime on a weight basis. If limestone is less expensive relative to lime, the cost savings increase. Depending on local availability, in some cases limestone may be quarried and milled at a substantial savings for high acidity wastewaters. Limestone-lime combination treatment can reportedly produce less and denser sludge than lime alone (EPA 1974). The EPA reported that the volume of sludge produced in limestone-lime treatment is roughly one-third the volume versus hydrated lime alone. The solids content can also be up to five times higher. Testing results indicated that limestone also produced a shorter reaction time than lime. Under bench test conditions using batch reactors, a reaction time of three hours was required to reach a stable pH with lime. In two stage tests the limestone reached its final pH of about 5.8 in thirty minutes, and the additional lime reaction time was thirty minutes, resulting in a combined reaction time of one hour. It is possible that the carbon

dioxide generated by the limestone reaction helped to improve mixing in the reactor and in preventing the formation of gypsum around unreacted lime. Based on research done on scale formation, gypsum preferentially precipitates onto the surface of bubbles (Amjad 1988). As the gypsum precipitates onto the carbon dioxide bubbles, it is prevented from forming on the surface of the lime or limestone particles, thereby decreasing reaction time of both the limestone and lime addition. Finally, the use of limestone has been discouraged for low strength wastewaters with higher starting pH due to armoring with metal hydroxides with waters that contain more than 50 mg/L of acidity or 5 mg/L of iron (Skousen et al. 1995).

Conclusion

The Cerro de Pasco mine wastewater is notable for its elevated acidity and TDS. Conventional lime treatment processes, such as LDS and HDS, are effective in achieving the treatment goals but require high annual chemical costs. Alternate neutralization methods using limestone or copper recovery through sulfide precipitation are two potential ways to decrease or offset operating costs. A copper recovery approach is believed to have potential application at the site, in that copper supplied may be sold to offset treatment costs. However, difficulty in separating arsenic to produce a marketable copper sulfide concentrate, and high sludge generation rates represent barriers to implementation of the technology. Limestone as a pre-neutralization step may offer benefits, including a net reduction in reagent cost and a reduction reagent armoring at low pH, resulting in better reaction rates.

References

Amjad, Z. (1988) Calcium Sulfate Dihydrate (Gypsum) Scale formation on heat exchanger surfaces: The influence of scale inhibitors. J. Colloid Interface Sci., 123, 523–3615.

- Consigny, A. and Kratochvil, D. (2011) Sulphide precipitation and ion exchange technologies for cost effective removal of selected metals in wastewater. In Proceedings of the Conference of Metallurgists (COM), Montreal.
- Hammarstroma, J.M., Sibrell, P.L. and Belkina, H.E. (2003) Characterization of limestone reacted with acid-mine drainage in a pulsed limestone bed treatment system at the Friendship Hill National Historical Site, Pennsylvania, USA. Applied Geochemistry 18, 1705–1721.
- MEND (Mine Environmental Neutral Drainage) (1994) Report 3.32.1: Acid mine drainage – Status of chemical treatment and sludge management practices. Canada: MEND.
- Nordstrom, K.D., Alpers, C.N., Ptacek, C.J. and Blowes, D.W. (2000) Negative pH and extremely acidic mine waters from Iron Mountain, California. Environ. Sci. Technol., 34, 254–258.
- Skousen, J., Politan, K., Hilton, T. and Meek, A. (1995) Acid mine drainage treatment systems: Chemicals and costs. In J.G. Skousen and P.F. Ziemkiewicz (Compilers), Acid mine drainage: Control and treatment (121–129 – Chapter 14). Morgantown, WV: West Virginia University and the National Mine Land Reclamation Center.
- EPA (United States Environmental Protection Agency) (1983) Design manual: Neutralization of acid mine drainage. Environmental Protection Agency.
- EPA (United States Environmental Protection Agency) (1974) Environmental protection technology series: Limestone and limestone-lime neutralization of acid mine drainage. Environmental Protection Agency.

Electronic attachements can be found at: http://bit.ly/IMWA2013_455

Selenium Removal from Effluents in Industrial Mineral Processes

Laura Sanders, Lucas R. Moore, Jean Robert Durand

Kemira Minerals and Metals, 387 Technology Circle, Suite 300, Atlanta, GA, USA

Abstract Selenium is a trace mineral that can lead to contamination in mine related aqueous waste streams. Although selenium is essential for life and necessary for cellular function in many organisms, at elevated concentrations, the elemental forms and aqueous oxyanions of selenium are considered toxic. The most common forms of selenium released during mining processes are the aqueous forms, selenite and selenate. An innovative chemical technology that can successfully reduce selenium to a level below the permitted discharge criterion of 5 µg/L was developed. An evaluation of dosage and process limitations, such as temperature, filtration methods, and treatment dosage were explored on water obtained from a mine site in North America that processes industrial minerals.

Keywords selenium removal, effluents, water treatment

Introduction

Selenium is a naturally occurring metalloid that is applied in global industries including electronics, vitamin and mineral supplements, plastics, fertilizers, anti-dandruff shampoos and many others. In small doses (0.1-0.5 mg/L), selenium is a micronutrient that is a part of everyday life for humans and animals, but it becomes toxic at higher levels (>3 mg/L dry weight). The National Primary Drinking Water Standard is 50 µg/L for selenium and the National Fresh Water Quality Standard is 5 µg/L for total selenium (EPA 2001; EPA 2011). In some regions, the selenium standards for discharge are even lower. In the US, there are several research groups and committees, who have presented evidence that the level should be as low as $2 \mu g/L$. Examples of these groups include the California Environmental Protection Agency (CEPA), the State Water Resources Control Board Committee (SWRCBC), and the University of California Committee (UCC; Hamilton et al. 1999).

Selenium enters local ecosystems through a number of different methods. For instance, the release of selenium to aquatic systems is generally a result of weathering and anthropogenic activities, such as oil refining, coal power production, and various mine-related activities (Presser and Luoma 2006). After weathering and oxidation occurs, soluble forms of selenium (selenite and selenate) are generated, thus can potentially contaminate the local water and soil sources. These mobile forms of selenium can bioaccumulate in some plants and animals causing various negative side effects such as selenosis, which is chronic selenium poisoning (Buck *et al.* 2002).

For that reason, selenium is a widespread problem in many wastewaters and a common contaminant in certain regions globally (US EPA 2012). Selenium is commonly found in mining effluents at concentrations that can reach 12,000 µg/L, in extreme cases (Leonard 2001). Because selenium chemically behaves very similarly to sulfur, mining operations where selenium contamination is prevalent are generally comprised of sulfide rich ores. These include copper, nickel, and uranium, as well as sphalerite and chalcopyrite, among others. Fig. 1 shows an example of a mining process demonstrating the potential sources where selenium can enter into aquatic systems.

Additional examples of mining activities where selenium contamination is an issue in-



Fig. 1 Example of a mine site and possible routes for contamination.



Fig. 2 Map providing various sites that reported high levels of selenium contamination (2004).

clude that of phosphate and coal. Fig. 2 shows a map of areas that have experienced issues related to increased selenium contamination. Industries depicted include coal mining/combustion, oil refining, phosphate mining, gold mining, silver mining, nickel mining, metal smelting, and landfill leachate (Moore et al. 2011). Selenium is often found in phosphate ore mining in overburden and mine runoff and oxidized forms of selenium are easily mobilized in runoff or infiltration water (Desborough et al. 1999). Globally, 158 million metric tons of phosphate rock was mined in 2009 and 17.2 % of that was mined in the United States (RMG 2012). In coal processing, effluents generated from leaching of coal combustion residues (CCRs) have high toxic element concentrations, including selenium. In the US, approximately six hundred power plants generate 130 million tons of CCRs annually, of which 56 % is stored in surface impoundments and landfills (Ruhl *et al.* 2012).

The common treatment technologies for removal of selenium from mine effluents to date can be summed up in three major categories: media filtration, chemical treatment, and biomediated removal. These methods often involve high capital and operational expenses that may also be limited by variables such as total dissolved solids, presence of other ions, and ability to maintain microbial health. The EPA listed selenium in at least 508 of the 1,636 sites reported on the National Priorities List (ATSDR 2011). The focus of this work was to introduce a novel chemical treatment for reducing selenium concentrations to the National Fresh Water Quality Standard recommended by the US EPA.

Results and Discussion

A 55 gal (208 L) drum of water was obtained from an industrial minerals processing site in North America. The water, which was contaminated with selenium due to naturally occurring mineral dissolution into a small stream that runs through the mine site, was shipped to and stored in a cooler at 1 °C prior to use. Water analysis was carried out as it is important to understand the other ions present in the water, as they can act as either competing ions (e.g. sulfate, nitrate) for the treatment or provide an alternative coordination possibility for the contaminant itself. The raw water (untreated effluent) comes from a naturally occurring spring and as such only exceeds the discharge permit with selenium. This water contained sulfate levels of 43.1 mg/L, calcium levels of 37 mg/L and a total dissolved solids (TDS) concentration at 410 mg/L, as shown in Table 1. This water also contained 69 µg/L of selenium which needed to be reduced to 5 µg/L or less.

A novel proprietary technology, E-4863 was evaluated in the above mentioned contaminated effluent to remove selenium to below the desired $<5 \mu g/L$ discharge criterion.

IC Analysis	Concentration	ICP Analysis	Concentration
Fluoride (mg/L)	3.8	Copper (µg/L)	7.2
Chloride (mg/L)	8.7	Arsenic (µg/L)	< 1.0
Sulfate (mg/L)	43.1	Selenium (µg/L)	69
Bromide (mg/L)	ND	Cadmium (µg/L)	< 1.0
Nitrate (mg/L)	ND	Sodium (mg/L)	4.7
Phosphate (mg/L)	ND	Magnesium (mg/L)	21
Conditions	-	Aluminum (µg/L)	< 1.0
рН (–)	7.9	Calcium (mg/L)	37
Turbidity (NTU)	0.31	Manganese (µg/L)	< 1.0
Total dissolved solids (mg/L)	410	Iron (µg/L)	27
Hardness (as CaCO ₃)	114	Nickel (µg/L)	16
Conductivity (µS/cm)	438	Molybdenum (µg/L)	< 1.0
Total suspended solids (mg/L)	47	Barium (µg/L)	48

Fig. 3 shows the process of water treatment using E-4863. This treatment could either be continuously fed or applied via a batch process. This single stage treatment takes place in a mixing tank containing the contaminated process water, followed by transfer to a gravity settling tank. Once the solids have settled, they may be discharged to a landfill and the decontaminated process water may be discharged or undergo further treatment, if necessary. Faster solids/liquid separation was accomplished by the addition of common organic flocculants.

A DOE (design of experiment) was developed for the purpose of evaluating effects of dosage, temperature, and filtration techniques on selenium removal. Dosage was examined at 1000, 3500, and 6000 mg/L treatment, shown in Fig. 4. At a dosage of 3500 mg/L E-4863 treatment, selenium removal reached 99 % removal. Fig. 5 shows selenium removal (%) as a function of the amount of selenium remaining in solution. At 99 % removal, the remaining selenium in solution was less than 1 μ g/L, which was the detectable limit of the instrument. At 1000 mg/L E-4863, selenium levels were only reduced by approximately 28 % (to 56 μ g/L remaining selenium). Therefore, no experiments were conducted at concentrations below this dosage level.

Many of the North American mines that have selenium discharge restrictions are in regions that have broad temperature ranges as a function of season. Therefore, the effect of temperature on selenium removal was also





Fig. 3 Schematic representation of water treatment in this work

Fig. 4 Effect of dosage on selenium removal using E4863 Treatment.



Fig. 5 Percent selenium removal as a function of selenium remaining in solution.

studied, as shown in Fig. 6. As temperature was decreased, there did not appear to be a significant effect on the removal. However, an increase in temperature could allow for a lower treatment dosage. Removal of 80 % selenium, or 12 μ g/L remaining selenium, was observed at 2000 mg/L E-4863 dosage.

Another evaluation addressed how treatment, along with filtration methods, affected TDS of the processed water. As mentioned in Table 1, the TDS for the raw water was 410 mg/L. Once treated with 3500 mg/L of E-4863, three filtration methods were applied to study the effect of treatment and filtration on TDS. The standard method of filtration for treated water samples involves using a 0.45 µm filtration membrane. Using 3500 mg/L treatment followed by filtration through a 0.45 µm membrane resulted in an increase from 410 mg/L to 2250 mg/L. Similarly, a smaller membrane, 0.22 μm did not improve the removal of TDS, yielding 2210 mg/L TDS. The least effective filtration method studied was filtration through sand, which yielded 3260 mg/L TDS post-treatment. Therefore, if TDS is a concern, other filtration or TDS removal methods may need to be evaluated in the future. When the three filtration methods were compared for selenium removal after treatment with 3500 mg/L E-4863, the result-



Fig. 6 Effect of dosage and temperature on selenium removal.

ing selenium levels were < 1 μ g/L after filtration through the three methods evaluated.

Experimental *Materials*

The treatment used, E-4863, is an experimental proprietary product. Superfloc A130HMW is a flocculant manufactured and sold by Kemira, Inc. The flocculant is sold as a solid material and was prepared by dissolution in DI Water to 0.25 % solids in solution before adding to selenium containing mine water.

Procedure

A sample of 500 mL of supplied mine water was added to a 600 mL beaker equipped with magnetic stirring. The pH was adjusted to the desired range using diluted nitric acid or 10 % sodium hydroxide. Once the experiment desired pH and temperature was reached and controlled, the E-4863 was added using a 100-1000 µL precision pipette equipped with disposable pipette tips. At the end of the two minutes agitation, flocculant (Superfloc A130 HMW) was added and allowed to agitate at the same speed for 5 minutes. The precipitate was allowed to settle for 10 minutes prior to filtering through a 0.45 µm Millipore filter, unless otherwise stated. The filtrate was then submitted for ICP to obtain selenium analysis.

Instrumentation

In this study, an Agilent ICP-MS 7700x system equipped with a helium collision cell was used for determination of the selenium in water samples. All samples were digested according to EPA 200.8 protocol adapted for Environmental Express digesters. The samples were then diluted 10 times with 5 % nitric acid and analyzed on ICP-MS. An SRM (NIST 1643e) was used to check the accuracy of the instrument. The samples were compared to Ge for precision and results were obtained by comparing samples against a 4-point calibration curve for each element and low detection limits (1 µg/L for selenium) were achieved. The instrument was calibrated with PE Pure Plus Instrument Calibration Standard 1, 10, 100, and 1000 µg/L.

Conclusions

Selenium was successfully removed from water obtained from a mineral mine to levels below the detectible limit of the instrument $(<1 \mu g/L)$ with 3500 mg/L of E-4863. The optimal dosage may need to be better determined by tightening the range between 1000 mg/L and 3500 mg/L E-4863. To examine seasonal sensitivities, the treatment was evaluated toward the effect of temperature on selenium removal. Results suggested that over a range of temperatures between 3 and 40 °C, selenium removal was not negatively affected. Filtration methods were also examined and results yielded no significant difference between samples filtered through 0.22 µm and 0.45 µm membranes. However, a decrease in efficiency of filtration removal of approximately 1000 mg/L of TDS was seen using sand filtration. Work continues to optimize the flocculation package in efforts to improve the solids liquid separation.

References

- ATSDR, Agency for Toxic Substances and Disease Registry (2011) The Division of Toxicology Tox-FAQs. http://atsdr.cdc.gov/tfacts92.pdr (accessed February 2013).
- Buck, BW, Jones, JL (2002) Interagency/Industry Coordination to Respond to Selenium Contamination at

Phosphate Mines in Southeastern Idaho. www.fs.fed.us/geology/buck-jones.pdf. (Accessed March 2013)

- Desborough, B, DeWitt, E, Jones, J, Meier, A, Meeker, G (1999) Preliminary Mineralogical and Chemical Studies Related to the Potential Mobility of Selenium and Associated Elements in Phosphoria Formation Strata, Southeastern Idaho. USGS Open File Report 99–120.
- Hamilton, SJ, Lemly, AD (1999) Water-Sediment Controversy in Setting Environmental Standards for Selenium, Ecotoxicology and Environmental Safety 44, 227–235
- Leonard, B (2001) Selenium Treatment Removal Alternatives Demonstration Project: Mine Waste Technology Program Activity III, Project 20
- Moore, LR, Mahmoudkhani, A (2011) Methods for Removing Selenium from Aqueous Systems. Proceedings, Tailings and Mine Waste.
- Presser, TS, Luoma, SN (2006) Forecasting Selenium Discharges to the San Francisco Bay-Delta Estuary: Ecological Effects of a Proposed San Luis Drain Extension, US Geological Survey, Denver, CO.
- Raw Materials Group (2012) Raw Materials Data, Stockholm (Accessed May 2012)
- Ruhl, L, Avner, V, Dwyer, GS, Hsu-Kim, H, Schwartz, G, Romanski, A, Smith, SD (2012) The Impact of Coal Combustion Residue Effluent on Water Resources: A North Carolina Example, Environmental Science and Technology 2012, 46 (21), pp 12226–12233.
- US EPA (2001) United States Environmental Protection Agency. Selenium Treatment/Removal Alternatives Demonstration Project, Mine Waste Technology Program Activity III, Project 20; MSE Technology Applications, Inc., Butte, MT. EPA/600/R-01/077.
- US EPA (2011) United States Environmental Protection Agency. National Recommended Water Quality Criteria. http://water.epa.gov/scitech/swguidance/ standards/current/index.cfm (Accessed March 2012)
- US EPA (2012) United States Environmental Protection Agency. Identification and Description of Mineral Processing Sectors and Waste Streams.
- www.epa.gov/compliance/assistance/sectors/minerals/processing/technicaldoc.html (Accessed March 2013)

Can treatment and disposal costs be reduced through metal recovery?

Kathleen S. SMITH¹, Linda A. FIGUEROA², Geoffrey S. PLUMLEE³

¹U.S. Geological Survey, PO Box 25046, Denver Federal Center, MS 964D, Denver, CO, 80225, USA, ksmith@usgs.gov ²Colorado School of Mines, Dept. Environmental Science and Engineering, 1500 Illinois St., Golden, CO, 80401, USA, [figuero@mines.edu ³U.S. Geological Survey, PO Box 25046, Denver Federal Center, MS 964, Denver, CO, 80225, USA, *qplumlee@usgs.gov*

Abstract This paper describes a framework to conduct a "metal-recovery feasibility assessment" for mining influenced water (MIW) and associated treatment sludge. There are multiple considerations in such a determination, including the geologic/geochemical feasibility, market feasibility, technical feasibility, economic feasibility, and administrative feasibility. Each of these considerations needs to be evaluated to determine the practicality of metal recovery from a particular MIW.

Keywords metal recovery, copper, zinc, critical and strategic elements, economics, geoenvironmental models

Introduction

Most hard-rock operations will need to treat water at some point during the mining life cycle, and many mining influenced waters (MIWs) require treatment in perpetuity. Commonly, MIWs contain elevated concentrations of metals, such as copper and zinc, which could be potential economic resources to help offset treatment costs. Also, there is a growing interest in many trace elements that historically have had little economic significance but that are now increasingly being used in hightechnology defense and green-energy applications (e.q. solar panels, wind turbines; Eggert et al. 2008; Jaffe et al. 2011). Many of these elements are recovered as byproducts of copper and zinc processing (see Bleiwas 2010), and hence may occur in MIWs. For example, tellurium and selenium are byproducts of copper production, gallium is a byproduct of zinc production, and cadmium and indium are byproducts of zinc and copper production (USGS 2013b). The recent prices of these trace elements (USGS 2013a) warrant investigation into their recovery as a byproduct in a metal treatment and recovery facility. Would the potential economic gains from metal recovery be adequate to reduce treatment costs of MIWs and reduce disposal costs of their associated sludge?

A "metal-recovery feasibility assessment" can be performed for an individual MIW or treatment sludge. The feasibility of economic metal recovery depends upon numerous factors that include (1) chemical/mineralogical composition and consistency, (2) amount and consistency of the available volume (seasonality) or mass, (3) existence, location, specifications, and terms of a potential buyer for the recovered metal(s), (4) availability of recovery technologies, (5) economic factors (i.e. total costs), and (6) regulatory and liability concerns. Fig. 1 summarizes some considerations involved in evaluating the feasibility of metal recovery from MIW and associated treatment sludge.

Geologic/Geochemical Feasibility

Characterization of the MIW is an important initial step in a metal-recovery feasibility as-



Metal Recovery Feasibility Considerations

Fig. 1 Considerations for the feasibility of metal recovery from mining influenced water and associated treatment sludge. Arrows indicate iterative steps. Transportation costs can be a deciding factor in the economic feasibility of metal recovery.

sessment. Fig. 2 illustrates an approach that can be used to characterize MIW. Potential value in the Fig. represents 30 % of the late 2012 metal prices from the London Metal Exchange (LME; or from USGS 2013b; see http://minerals.usgs.gov/minerals) and can be a useful rough guide to prioritize selective recovery of particular metals. The 30 % factor is mentioned in the case study at Wellington-Oro discussed later in this paper and represents a more realistic price than the gross LME value. Although metal prices for many of the trace elements are considerably higher than those for the major/minor elements, the greater abundance of the major/minor elements provides a greater potential value relative to the trace elements. Nevertheless, if elements can be recovered as a byproduct, their recovery may enhance the overall recovery value if a market can be identified. It is also useful to consider each chemical element as a function of a basis. such as annual mass or the amount of MIW that can be treated during a given period of time. An example calculated from water composition reported for the Berkeley Pit, Butte, Montana, USA (Davis and Ashenberg 1989) and a 30 % factor reveals that treatment of one million liters of water could yield \$U\$500 from copper recovery, \$US300 from zinc recovery, and \$US250 from magnesium recovery. Prior to water treatment, the Berkeley Pit was filling at a rate of 20 ML/d. and the associated Horseshoe Bend water treatment plant, when it is at full capacity, will be treating approximately 26.5 ML of pit water per day (www.pitwatch.org). Some copper currently is being recovered from the pit waters using scrap iron (via passive copper cementation), but these calculations indicate that the potential value of copper, zinc, and magnesium that could be extracted would be in excess of \$US27,000 per day, assuming 100 % recovery and a value of 30 % of the LME price.

The presence of potentially recoverable elements in MIW can be predicted from the mineral-deposit type and identified mineral phases (Plumlee *et al.* 1999). Geoenvironmental models are data compilations of environmentally significant geologic and geochemical characteristics for different types of mineral deposits (du Bray 1995; Plumlee 1999). These models can help target specific mine sites, based on mineral-deposit type being mined,



Fig. 2 Example of mining influenced water characterization for a metal-recovery feasibility assessment. Concentrations (diamonds) are from unpublished 1993 data for the Reynolds Adit, Rio Grande County, Colorado, USA. Potential values (bars) are based on either 30 % of the late 2012 metal price from the London Metal Exchange or USGS (2013b) for each chemical element. Note that metal recovery rates vary depending upon the treatment and recovery technology used. Prior to installation of a bulkhead, peak flows at the Reynolds Adit were 3.3 to 4.9 ML per day with an estimated annual copper load of 65,000 kg (CDPHE 2010).

that would be good candidates for recovery of particular chemical elements from MIW. For example, deposit types that produce highly acidic MIW with the highest concentrations of copper, zinc, aluminum, and magnesium include volcanogenic massive sulfide, epithermal quartz-alunite, and some porphyry copper deposits. All of these deposit types have relatively high concentrations of iron and copper sulfides and relatively low concentrations of carbonate minerals in the ores, wastes, or host rocks compared to other deposit types. These deposits types are potential targets for consideration of copper and zinc recovery. Some energy-critical trace elements that may be enriched in porphyry copper systems include tellurium, cobalt, nickel, gallium, indium, silver, and cadmium (Yano et al. 2013). MIW from mined porphyry copper deposits may therefore be potential targets for the recovery of these trace elements. Rare earth elements (REEs) can be enriched in some deposit types

that generate low-pH conditions, such as volcanogenic massive sulfide and epithermal quartz-alunite deposit types (USGS, unpublished data), so MIW in these deposit types may be potential candidates for recovery of REEs.

Technical Feasibility

Recent increases in the prices of many metal commodities have revived questions as to whether metals can be economically recovered from MIW. Determining which metals might be present in sufficient concentrations to be economically recoverable (and the form and purity of the concentrate required by the market) can help prioritize research into which current technologies can be applied and which new technologies need to be developed for metal recovery. Zinck (2005) reports that the two main approaches for metal recovery from mining wastes are hydrometallurgical (*e.g.* leaching followed by solvent extraction or ion exchange) and pyrometallurgical (*e.g.* smelting). Mosher (1994) describes an industry approach that used MIW treatment sludge as a smelter feedstock, recovering incidental saleable metals, and producing non-hazardous products.

The primary treatment technology for MIW is hydroxide precipitation. The resulting sludge from this type of treatment results in a metal mixture that generally is not suitable for any market specifications. Sulfide precipitation is an alternate treatment technology. In sulfide precipitation, some metals (*e.g.* ZnS) can be selectively removed. Sulfide precipitation lends the possibility of selective recovery due to different solubility products for different metals.

Case Study: Wellington-Oro Water Treatment Plant

The Wellington-Oro mining complex is located near the town of Breckenridge, Summit County, Colorado, USA. The water treatment plant, which began operation in late 2008, uses a sulfide precipitation process to remove zinc and trace cadmium as sulfides in a mixed concentrate. Other metals, such as iron, primarily remain in solution. The water treatment plant has the potential to produce 40,000 kg of zinc per year (based on the design flow of 820,000 L/d and influent zinc concentration of 134 mg/L). The filtercake contains approximately 50 to 57 % zinc on a dry weight basis (unpublished data 2009 and 2011) and is classified as a nonhazardous waste (Bratty et al. 2008). This treatment technology allows for the selective recovery of zinc that is suitable to send to a smelter. The zinc sulfide sludge produced has been purchased by Nyrstar, Clarksville, Tennessee (the primary zinc producer in the United States). Nyrstar covered the shipping costs (\$USO.31 per kg of zinc content) and reportedly paid the town of Breckenridge \$US0.33 per kg of zinc content (personal communication). In this case, the smelter's cost to obtain the zinc was about 30 % of the average 2010 LME price.

Additional treatment technologies exist for MIW. Gusek and Figueroa (2009) provide an overview of MIW treatment technologies. Some alternative technologies include solvent extraction, ion exchange, biosorption (using microorganisms and aquatic and terrestrial plants), electrowinning, and copper cementation (copper reduction on iron metal). Some of these technologies, or hybrids of these technologies, may lend themselves to the selective recovery of metals and trace elements. Different technologies need to be systematically evaluated for their technical, economical, and environmental benefits for metal recovery from different types of MIW.

Market Feasibility

Smelters may be an important market for metal recovered from MIW, but their practicality depends on the physical and chemical properties of the metal-containing concentrate recovered from MIW and also on factors such as the quantities of concentrate generated, distance to the nearest smelter that will accept the concentrate, transportation costs, and contaminants present in the concentrate. In addition to smelters, other possible markets also need to be considered. For example, the fertilizer industry has been a secondary market for zinc recovered from waste sources (USEPA 1999), and a pigment manufacturer has been identified as a secondary market for iron-oxide sludge recovered from abandoned coal mines (Hedin 2003; Silva et al. 2011). Zinck (2005) discusses several sludge reuse options including utilization in construction materials, agricultural land applications, metal adsorbents, and carbon dioxide sequestration. Each market has specific requirements for the forms and purity of the concentrate that they will accept. Marketability must be considered when evaluating the specifications of the potential product(s) produced by the treatment plant.

Economic Feasibility

Economic considerations help drive the interest in metal recovery. Metal prices are published by numerous sources and are based on numerous factors that include specifications, contractual agreements, and other criteria, and are summarized in USGS (2013a). The value of metals contained in MIW concentrates and sludge generally is a fraction of the prices listed for global or domestic markets (see Wellington-Oro case study above). Therefore, total costs (including treatment costs), market values, and potential return on investments need to be (1) estimated prior to making investments, and (2) weighed against the value received from the recovered product(s). Zinck and Griffith (2013) conducted a broad survey of MIW treatment facilities and reported that the average cost to treat one cubic meter of MIW is \$CN1.54. Price fluctuation of metals also impacts the economic feasibility of metal recovery. For example, smelter contracts can vary over time with electric, fuel, and transportation costs and with the changes in metal prices.

Costs that need to be considered include such items as acquisition of capital and working capital, bond, labor costs, maintenance, infrastructure, reagents, insurance, interest, detailed engineering studies, and fees. Additional, less quantitative economic considerations for metal recovery from MIW include (1) energy required to recover the metal compared with the energy required to mine the ore, (2) costs of obtaining required permits for treatment and discharge, (3) preservation of land resources that might otherwise be disturbed by mining, (4) value of clean water as a result of MIW treatment, and (5) reduction in liability and disposal costs when potentially toxic metals are recovered. Even if not currently economic, metal recovery from MIWs can be used to offset treatment and disposal costs, and to reduce liability. Also, treated water may be used at the mining site, which would reduce the costs of acquiring water from other sources

Administrative Feasibility

Administrative feasibility incorporates concerns related to regulatory and liability matters. There are several regulatory and potential liability concerns (in particular with the Clean Water Act and the Comprehensive Environmental Response, Compensation, and Liability Act—CERCLA, also known as "Superfund") that address metal recovery from MIW, as well as mining facilities as a whole. Recently, some of the potential liability concerns have been addressed through the U.S. Environmental Protection Agency's (USEPA) Good Samaritan Initiative, which is "an agency-wide initiative to accelerate restoration of watersheds and fisheries threatened by abandoned hard rock mine runoff by encouraging voluntary cleanups by parties that do not own the property and are not responsible for the property's environmental conditions" (see http://water.epa.gov/ action/goodsamaritan). The USEPA made clarifications to the Good Samaritan legislation in December 2012 (view the memorandum at http://water.epa.gov/action/goodsamaritan). USEPA considers proposals to demonstrate the viability of metals recovery using the Good Samaritan policies for both CERCLA and the Clean Water Act (Carol Russell, USEPA, personal communication).

Conclusions

Most mining operations treat MIWs that commonly contain elevated concentrations of metals, which could contribute revenues to offset treatment and disposal costs. MIWs traditionally have been considered as a waste that must be treated and waste treatment byproducts (*e.g.* sludge) be sent for disposal (either as hazardous or non-hazardous waste). The feasibility of metal recovery from MIWs needs to be evaluated on a case-by-case basis. Even if not currently economic, metal recovery from MIWs has the potential to be used to offset treatment and disposal costs and to reduce liability.

Acknowledgements

Smith and Plumlee acknowledge the USGS Mineral Resources Program for funding this work. We thank Don Bleiwas for his insightful review and helpful discussions. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

References

- Bleiwas DI (2010) Byproduct mineral commodities used for the production of photovoltaic cells. U.S. Geological Survey Circular 1365 (http://pubs.usgs. gov/circ/1365)
- Bratty M, Lawrence RW, Kratochvil D (2008) Reducing water treatment costs while meeting the challenge of environmental compliance for the mining industry. Proceedings of the First International Congress on Water Management in the Mining Industry, Santiago, Chile
- Colorado Department of Public Health and the Environment (2010) Summitville Mine Superfund Site: 2010 Five-Year Review Report (www.epa.gov/superfund/sites/fiveyear/f2010080003754.pdf)
- Davis A, Ashenberg D (1989) The aqueous geochemistry of the Berkeley Pit, Butte, Montana, U.S.A. Applied Geochemistry 4: 23–36
- du Bray EA (ed.) (1995) Preliminary compilation of descriptive geoenvironmental mineral deposit models. U.S. Geological Survey Open-File Report 95–0831 (http://pubs.usgs.gov/of/1995/ofr-95-0831)
- Eggert RG, Carpenter AS, Freiman SW, Graedel TE, Meyer DA, McNulty TP, Moudgil BM, Poulton MM, Surges LJ (2008) Minerals, critical minerals, and the U.S. economy. National Research Council of the National Academies, National Academies Press, Washington, D.C.
- Gusek JJ, Figueroa LA (eds) (2009) Management technologies for metal mining influenced water: Mitigation of metal mining influenced water, Vol. 2. Society for Mining, Metallurgy and Exploration
- Hedin RS (2003) Recovery of marketable iron oxide from mine drainage in the USA. Land Contamination & Reclamation 11(2): 93–97
- Jaffe R, Price JG, Ceder G, Eggert R, Graedel T, Gschneidner K Jr., Hitzman M, Houle F, Hurd A, Kelley R, King A, Milliron D, Skinner B, Slakey F (2011) Energy critical elements: securing materials for emerging technologies. American Physical Society Panel on Public Affairs and the Materials Research Society
- Mosher J (1994) Heavy-metal sludges as smelter feedstock. Engineering and Mining Journal. September 1994: 25–30

- Plumlee GS (1999) The environmental geology of mineral deposits. In The Environmental Geochemistry of Mineral Deposits—Part A: Processes, Techniques, and Health Issues. Reviews in Economic Geology 6A:71-116. Society of Economic Geologists
- Plumlee GS, Smith KS, Montour MR, Ficklin WH, Mosier EL (1999) Geologic controls on the composition of natural waters and mine waters draining diverse mineral-deposit types. In The Environmental Geochemistry of Mineral Deposits—Part B: Case Studies and Research Topics. Reviews in Economic Geology 6B:373-432. Society of Economic Geologists
- Silva RA, Castro CD, Petter CO, Schneider IAH (2011) Production of iron pigments (goethite and haematite) from acid mine drainage. Proceedings of the 11th International Mine Water Association Congress, Aachen, Germany
- U.S. Environmental Protection Agency (1999) Background report on fertilizer use, contaminants and regulations. Office of Pollution Prevention and Toxics, Report Number 747-R-98-003 (www.epa.gov/ oppt/pubs/fertilizer.pdf)
- U.S. Geological Survey (2013a) Metal prices in the United States through 2010. U.S. Geological Survey Scientific Investigations Report 2012–5188 (http:// pubs.usgs.gov/sir/2012/5188)
- U.S. Geological Survey (2013b) Mineral commodity summaries 2013. U.S. Geological Survey (http:// minerals.usgs.gov/minerals/pubs/mcs/2013/ mcs2013.pdf)
- Yano RI, Price JG, Thompson T, Emsbo P, Koenig A (2013) Trace elements in porphyry copper systems as strategic minerals. Proceedings of the Society for Mining, Metallurgy, and Exploration Annual Meeting, Denver, CO
- Zinck J (2005) Review of disposal, reprocessing and reuse options for acidic drainage treatment sludge. MEND Report 3.42.3. Natural Resources Canada (www.mend-nedem.org/reports/files/3.42.3.pdf)
- Zinck J, Griffith W (2013) Review of mine drainage treatment and sludge management operations. MEND Report 3.43.1. Natural Resources Canada (www. mend-nedem.org/reports/details-e.aspx? pub_id=3.43.1)

Water Filtration Innovation to Optimize Recovery and Lower TCO

David R. Stewart

Stewart Environmental Consultants, LLC, 3801 Automation Way, Suite 200, Fort Collins, Colorado 80525, USA; dave.stewart@stewartenv.com

Abstract Point source discharge and acid mine drainage are recognized as serious environmental challenges within the mining industry. The high variability of site-related factors continues to be a challenge with regard to implementing cost-effective long-term treatment. Recent industry sector transition to processes utilizing sulfide ores has driven the need for innovation in high-recovery sulfate-reduction processes. Significant improvements to membrane and filtration process design have allowed for considerably higher recovery ratios and lower remediation infrastructure costs. This paper will provide a technical overview of the most recent innovation in active treatment technologies, their appropriate applications, and normalized total cost of ownership (TCO).

Keywords IMWA 2013, full paper, AMD treatment, inorganic membranes, lower TCO

Introduction

Acid mine drainage (AMD) from point sources is a significant issue in the mining industry. Pollution from metals in lakes, streams, and rivers causes significant liability and environmental issues. Increased use by the industry of more sulfide ores will result in higher levels of metals and associated water quality issues. There are numerous techniques for AMD treatment. A new consideration for AMD treatment is water reuse. As water becomes scarcer, especially in drought areas, it will be important for the mining industry to consider how and where water can be reused (ICMM 2012). This paper will discuss how several active treatment technologies compare and focus on inorganic membrane treatment to achieve lower overall total cost of ownership (TCO).

Water as a Shared Resource

In mining, water is used in a broad range of activities, including mineral processing, dust suppression, slurry transport, and employee requirements, such as potable water use. The mining industry has moved toward closedloop systems for water use. In addition, mining activities are beginning to interact more closely with agriculture, industrial activities,



Fig. 1 eMalahleni Water Reclamation Plant, South Africa

and municipal/commercial players. This leads to the conclusion that there is now no simple recipe for water management at mining facilities. Examples of interaction around this shared resource are found in companies such as eMalahleni Water Reclamation Plant in South Africa (ICMM 2012). The plant treats contaminated water from its own facility in the coal mining area as well as from other mining operations and delivers treated water directly into the local municipalities' drinking water systems.

Variables to Control

When attempting to control the TCO, it is important to focus on the following parameters: (1) labor, (2) chemicals, and (3) power requirements. These three elements of the overall cost will affect how economical the system can become. In most cases, the incoming water quality for treatment and the resulting end use, such as discharge to a stream or water for reuse, will dictate the type of chemistry required for treatment. Treatment will also be dictated by the environmental permits that are required for discharge or the water quality parameters required for reuse. In addition, mining companies should consider the use of triple bottom line (TBL) accounting (Roucher 2009). TBL reviews the impacts of the overall cost of ownership as well as the bottom lines of financial, social, and environmental impacts. If the mining company controls the above issues of labor, chemicals, and power, it is very likely that the parameters within TBL will also be lowered. This is certainly the case at the Barrick Homestake Mine in Lead-Deadwood, South Dakota. Their Water Conservation Standard was able to protect the company, manage the water cycle, and provide water for the sanitation district as new water for sale (ICMM 2012).

Precipitation Chemistry

Precipitation chemistry is one of the key variables to be controlled. Fig. 2 is a representation of hydroxide solubility curves. In most cases of active treatment, the goal is to remove the metals to their lowest concentrations. This can be accomplished with sodium hydroxide or lime, and by raising the pH, the solubility of the metals of interest decrease.

Iron co-precipitation is also used in precipitation chemistry. This is where metals of interest are ingrained in the precipitant or floc. When decreased metals solubility is combined with iron co-precipitation, it allows for the operation of the treatment system to meet the environmental discharge parameters.

One issue with precipitation chemistry is the precipitation of other compounds, such as calcium carbonate. This is tied directly to the pH value. After a pH of 9.5, alkalinity will be in the carbonate form, which will allow for the precipitation of calcium carbonate and increase the amount of sludge significantly, as much as 100 % in some cases. Therefore, it is important to keep pH increases to a minimum to decrease the amount of solids disposal.

Active Treatment Systems

Three different active treatment systems are compared in this paper. The first is the high density sludge (HDS) clarifier system, as



Fig. 2 Solubility Curves



Fig. 3 High Density Clarifier

shown in Fig. 3. The concept of the HDS system is to recycle the solids formed in the system to allow for better chemical utilization and higher sludge densities. Higher sludge densities allow for smaller treatment systems and thus decrease the footprint of the overall treatment system. In addition, an HDS system will add air in a reaction tank to allow for better oxidation of the metals, such as iron to allow for better efficiency of the precipitation step.

The second and third treatment systems are membrane systems: a polymeric membrane system and an inorganic (ceramic) membrane. Both membrane systems are microfilters and utilize a process similar to that of the HDS system. The difference is that the membrane provides a physical barrier between the AMD and the effluent of the facility. Fig. 4 depicts a membrane treatment system for the ceramic pilot study at the Gregory Incline, Clear Creek County, Colorado. This was an EPA demonstration project, which produced excellent results for water quality and metals removal.

The only difference between this system and a polymeric system is the actual membrane. Both systems will operate at a pressure of 241 kPa and both systems have a backpluse system to decrease flux decline.

The main difference between the two types of membrane is the lifespan of the membranes themselves. At the Blackhawk Colorado AMD treatment facility, the original membranes were tubular polymeric membranes.



Fig. 4 Simplified Membrane Treatment System

The lifespan of these membranes was approximately 6 to 9 months. Due to the replacement cost of these membranes, an alternative was investigated. We installed ceramic membranes in 1995, and these membranes are still in service.

Ceramic Crossflow Membranes

Since installation of the ceramic crossflow membranes at the Blackhawk facility in 1995, over 35 systems ranging from 38 L/min up to 1325 L/min have been installed throughout the world. As shown in Fig. 5, the crossflow membrane is an "inside out" flow pattern. The transmembrane flow is attempting to keep the



Fig. 5 Ceramic Microfilter

Reynolds number very high, which requires a high flow rate. Typical flow rates are 3 m/s. The operating pressure for this type of membrane is 241 kPa. The transmembrane pressure or pressure over the membrane surface is typically 35 kPa. Thus, the power requirements for this type of system are very low.

The advantage over the HDS clarifier is that the high solids in both systems will allow for higher utilization of the chemicals that are added for precipitation. The difference between the HDS and the membrane systems is with the absolute barrier of the membrane between the solids and effluent, there is little chance of a violation of the permit.

Results of Membrane Treatment

A ceramic microfiltration system was installed at the Upper Blackfoot Mining Complex treatment system near Lincoln, Montana (Fig. 6). This was a joint effort between CDM Smith and the State of Montana. At this facility, it was found that the ceramic microfilters were able to operate at a lower pH value when compared to an HDS clarifier. The system has been able to meet the discharge requirements on a consistent basis.

From a cost standpoint, the cost savings resulted from the reduction of labor, lower chemical costs, a smaller footprint for the building, and lower power costs. The labor at



Fig. 6 CMF System at the Upper Blackfoot Mining Complex

the site is typically 8 hours per day, except in runoff season, when the labor is increased to 24 hours per day. The increased labor is typically to handle the additional sludge being generated by the system. The flow increases at the facility approximately 300 % during spring runoff. The lower chemical costs are a result of being able to meet the discharge values at a pH of 8.5. During spring runoff, the pH has to be increased to 9.5 or higher. This has resulted in a significant amount of sludge increase due to the precipitation of calcium carbonate, which then increases both the chemical costs as well as the labor costs.

The smaller footprint is due to the size of the membrane system, which is typically 20 % of the footprint of the HDS clarifier system and significantly shorter in height. The power costs are lower for the membrane system due to the low pressure required for operations at 241 kPa.

Table 1 provides effluent removal values at the Upper Blackfoot Mining Complex treatment system for comparison purposes.

Fig. 7 provides capital and operating costs for the comparison of the HDS, polymeric, and ceramic membrane systems. This figure is based on the comparison of a 1136 L/min system that was identified in the EPA report on the Gregory Incline (MWTP 2002).

Options to Further Reduce Costs

The potential to further reduce costs is found in new precipitation technologies. Specifically, we have found electrocoagulation (EC) and high shear reactors to be beneficial. EC is an expensive and capital intensive process, but allows for precipitation at a lower pH value. The EC process separates the water molecule into hydrogen gas and a free radical of oxygen. It also corrodes the plates and provides iron or aluminum as free metals in solution. This combination allows for precipitation at a lower pH value, which in turn significantly reduces the sludge generated. Also, the precipitation of metal oxides is typically 1 to 2 orders of magnitude in lower solubility. The combination of

Sample Effluent Water Quality Results

Turbidity	0-2 NTU
Total Dissolved Solids	0-10 ppm
Arsenic	66.4% removal
Cadmium	99.98% removal
Calcium	78.27% removal
Calcium, dissolved	78.79% removal
Chromium	99.35% removal
Copper	99.95% removal
Lead	99.95% removal
Manganese	99.8% removal
Manganese, dissolved	99.76% removal
Nickel	99.75% removal
Silver	99.8% removal
Zinc	99.95% removal
Zinc, dissolved	99.93% removal

Table 1. Water Quality Results

Capital Cost Comparison



Annual Operating Cost Comparison



Fig. 7 Capital and O&M Cost Comparison

these factors typically will result in lower operating costs. At the present time, there are not any EC systems of sufficient size to gage their usefulness in the field. However, due to its cost effective at small scale operations, this should be considered as an option for the mining industry.

The other option to reduce costs is a high shear reactor. In the treatment of AMD, it is very important to encourage reaction kinetics. The high shear reactors appear to reduce the time needed for reaction kinetics. The cost of these systems is fairly low and therefore inclusion will typically improve chemical treatment.

Controlling Factors

Earlier in this paper, we discussed the lowest total cost of ownership. This can be achieved by controlling labor, chemistry, and power. As noted above, the cost of labor associated with operating the membrane system is significantly lower when compared to the HDS. The membrane system can utilize three control factors of pressure, turbidity, and pH to control the system. If these parameters are in spec, then the system will be in compliance and will fall directly on the solubility curve. Therefore, the operator only needs to be present to ensure the instruments are working properly and to handle the sludge generated by the system.

The chemistry can be performed at a lower pH due to iron co-precipitation. In addition, if EC is used, this chemistry can be enhanced. The high shear reactor will also improve reaction kinetics and will therefore increase the efficiency of the system.

The power requirements are reduced by utilizing low-pressure systems. The ceramic microfilters allow for treatment at a low pressure of 241 kPa, resulting in low power costs. All of these parameters will decrease the financial costs of treatment. The system's overall metals removal efficiency also benefits the environmental and social values of triple bottom line accounting. These benefits are: (1) environment benefits from the lower levels of pollution and (2) social aspect benefits from reusing clean water discharges.

Conclusions

The conclusions of this paper are as follows: (1) the use of membranes can benefit the mining industry by lowering the total cost of ownership, and (2) membrane system performance provides superior efficiency compared to alternatives in the removal of metals from AMD.

References

ICMM (2012) "Water Management in Mining: A Selection of Case Studies," Environment, May 2012. (www.icmm.com/www.icmm.com/water-casestudies)

- Roucher R (2009) A Triple Bottom Line Assessment of Traditional and Green Infrastructure Options for Controlling CSO Events in Philadelphia's Watersheds, Stratus Consulting, August 2009 (www. michigan.gov/documents/dnr/TBL.Assessment-GreenVsTraditionalStormwaterMgt_293337_7.pdf).
- MWTP (2002) Annual Report, Mine Waste Technology Program 2002, (www.epa.gov/nrmrl/std/mwt/ annual/annual2002)

Zinck J, Griffith W (2013) Review of mine drainage treatment and sludge management operations. MEND Report 3.43.1, 101 pp. Natural Resources Canada. www.mend-nedem.org/reports/files/3.43.1.pdf.

Underwater Nozzle Pipelines (UNP) – A new Process for in-lake Liming

Michael Strzodka¹, Volker Preuss², Konrad Thürmer³

¹GMB GmbH, Knappenstrasse 1, 01968 Senftenberg, Germany, michael.strzodka@gmbgmbh.de ²Brandenburg University of Technology, Siemens-Halske-Ring 8, 03046 Cottbus, Germany, preuss@tu-cottbus.de ³Institut für Wasserwirtschaft, Siedlungswasserbau und Ökologie GmbH, Coudray-Strasse 4, 99423

Weimar, Germany, konrad.thuermer@iwsoe.de

Abstract In fall 2011, one of the largest pit lakes of Eastern Germany has been limed with a novel on-site process. Within 16 weeks of operation, its 110 Mm³ of water could be shifted from the iron buffer to circumneutral pH-values. Due to a thorough consideration of the chemical and hydrodynamic parameters the method prevailed an 80 % efficiency. In this paper we will present the details of this novel UNP-process.

Keywords in-lake treatment, liming, technological solution, pit lake

Introduction

Usually, after open pit mining ceases, the open space fills and leaves back pit lakes. In the Eastern German Lusatian lignite mining area, this will result in Europe's largest artificial lake district. Many of those lakes comprise of large water volumes and surface areas and are therefore amongst the largest lakes in Germany (Nixdorf *et al.* 2001). The inflow of potentially acid groundwater from the adjacent overburden dumps results in sulphate dominated acidic conditions. Many of the newly developed pit lakes have a pH of around 3.0, in the range of the iron buffer (Geller *et al.* 1998).

Back in the 1970ies and 1980ies methods were developed to treat lakes acidified by acid atmospheric depositions (Nyberg 1988, Sverdrup 1985). However, the acidity of the acid sulphate pit lakes exceeds those of the Scandinavian softwater lakes by 2...3 orders of magnitude (Geller 2009). This results in a substantially larger amount of neutralizing agents needed to treat the pit lakes. To minimize the costs for creating and keeping pH-neutral conditions it is essential to apply the neutralising agents as efficient as possible. Current procedures, such as sprinklers (Benthaus and Weber 2012) or ships (Pust *et al.* 2010) that spread the suspension over the water surface, have weaknesses that inhere the procedures and are mainly a result of the hydraulic and logistical circumstances.

This paper presents our work that aimed in developing and testing a highly efficient procedure to lime the pit lakes.

Methods

Usually, lime products are used to neutralize acidified lakes. On-site they are mixed with water to produce a suspension which is then injected into the water body. In order to inject the neutralizing agent as efficiently as possible, it is necessary to disperse the suspension evenly in the lake volume with a minimum amount of energy.

This requirement is best met by applying the free jet principle (fig. 1). Velocity differences between the free jet and the ambient fluid generate exchange processes at the jet boundary (Schlichting and Gersten 1997). Fluid particles of the ambient fluid near the jet boundary are incorporated into the eddies and accelerated. Within the jet the fluid particles are decelerated as a result of turbulent conditions and eddies in the jet direction. Due to the incorporation of ambient fluid into the jet, the jet volume increases with length and the jet ve-



Fig. 1 Velocity distribution inside a free jet flowing into a stagnant and homogenous surrounding fluid

locity decreases while its momentum stays constant. Based on the investigations of Kraatz (Bollrich *et al.* 1989) it is possible to describe the jet's velocity distribution and special development as a function of its initial velocity and length.

By using the free jet for injecting and mixing the lime suspension density differences between the particle loaded jet beam and the ambient fluid are induced. Permanent mixing of the ambient fluid over the length of the jet causes a continuous dilution and consequently a reduction in the suspension's density. Those density effects superimpose the spreading of the free yet and determine the beam's trajectory (fig. 2). The free jet's spread is either limited by the jet reaching the lake's floor or a layer of water with a higher density. Those layers might be a result of thermal stratification during the summer stagnation (thermocline) and the suspension will then spread horizontally along this boundary layer.

In order to neutralize the acid pit lake, the lime suspension's dilution at the end of the jet beam's length must possess the chemically necessary application rate. Best neutralisation results will be obtained if the liming is conducted during the lakes full vertical circulation periods because the complete length of the jet beam can be used for the mixing of the lime suspension (fig. 2). An adequate number of



Wolkersdorfer, Brown & Figueroa (Editors)

nozzles assures that the ambient lake water mixed into the free jet spreads into the whole lake volume at least once during the application period. The method works on a 24–7 basis and consequently even in the case of large water bodies a relatively short period of time is necessary for the liming.

Each pit has an individual chemical composition and morphology. Consequently, the UNP-process requires a configuration specifically designed for each water body. The parameters to be considered include the maximum concentration of the lime suspension, the best treatment period and the location of the nozzles to produce the free jet.

Area of Investigation

A first pilot test of the UNP liming process was conducted within the pit lake *Scheibe*, which has a volume of 110 Mm³ and a water surface of 6.8 Mm². With its length of 5.2 km and a maximum width of 1.7 km it belongs to the largest pit lakes in the Lusatian lignite mining area. As a result of the lignite mining technology used, the lake's morphology is characterised by two distinct features: the eastern part of the lake consists of the former pit's inner dump with a shallow water area of 2... 6 m depth and the western part with a water depth of 35 m (fig. 3). Lake *Scheibe* is characterised by dimictic conditions with full circulation phases in spring and fall.

A determining aspect for the water composition of lake *Scheibe* are the groundwater inflows into the lake: from the south, from the mother rock a slightly acidic groundwater with an acidity of approximately 1.0 mmol/L and from the inner dump water with an acidity of 9.0 mmol/L. Initial lake water conditions used for predicting the treatment of lake *Scheibe* were an acidity of 3.4 mmol/L, a pH of 2.9, as well as calcium and sulphate concentrations of 150 mg/L and 550 mg/L, respectively.

Pilot Project Implementation

Prior to the pilot test, various potential lime products were investigated in the laboratory to determine if they can be used to neutralize lake *Scheibe* with the UNP-process. It could be shown that a quicklime (CaO) provided by Fels-Werke GmbH has the best performance characteristics resulting in a necessary application rate of 150 g/m³ at an efficiency of 70 %. Con-



Fig. 3 Morphometrics of lake Scheibe, sampling points, and a detailed view of the UNP-process

sequently the necessary amount of lime to be added was 16.5 kt.

Technologically, the UNP-process is kept very straightforward: A submersible pump draws water from the lake and supplies the mixing station with this water by ways of a pipe. Two lime silos are dosing the neutralization agent into a mixing tank. From there, the lime suspension is pumped into a maturation tank and finally into a submerged floating pipe transporting the suspension into the lake. At the end of the pipe the lime suspension mixing nozzles are installed in pairs. Lake Scheibe had a nozzle configuration with 6 pairs at a distance of 20 m, which can be considered to be a punctiform injection in relation to the lake's size (fig. 3). On October 4, 2011 the treatment of lake Scheibe started and could be finished successfully on January 25, 2012, after just 16 weeks of operation and two short operation interruptions of the liming installation (fig. 4). For monitoring the liming, 33 water samples were taken on a weekly basis at 12 sampling locations (fig. 3).

Based on the changes of the water quality, the specifications for the further operation of the neutralisation plant were determined. An additional monitoring of the hydraulic conditions of the lake provided the basis for validating a 3D lake model (MOHID-Water Modeling System). Both data were used to verify the previously used design calculation algorithms. In addition, the 3D modelling aimed in identifying the fraction of the momentum input, density driven flow, and wind induced flow responsible for the overall water treatment.

Results

At the beginning of the treatment, lake Scheibe was characterised by stratification with the thermocline being located at a depth of 12 m. Liming started initially with a 10.4 t/h mass flow, equivalent to 250 t/d. Such an application rate makes high demands on the logistics of the lime supply as up to 10 silo trucks were needed on a daily basis. As expected, the application of the suspension was restricted to the epilimnion, but wind induced currents during this phase of the injection supported a uniform distribution of the concentrations throughout the whole epilimnion. Consequently, a treatment effect could already be observed at the two farthest measurement points E1 and E2 in the first week of operation (fig. 3).

A certain proportion of the neutralising agent is stored as a result of its horizontal spreading along the thermocline. Since the samples were always taken from the same depths, part of the injected neutralisation agent is therefore not detected and thus, the average effect in the entire lake is temporarily



Fig. 4 Temporal progress of the lake Scheibe *treatment*

underestimated. In view of a full lake circulation and the subsequent homogenisation of the lake's conditions, eventually, the treatment effect is correctly represented. During the continuation of the water treatment, the thermocline gradually disappeared and the expected treatment effect could fully develop over the entire water depth. This phase of the treatment is purely controlled by momentum input and the density driven flow in the lake.

Fig. 4 shows the temporal development of the average lake's conditions. As a measure of the acidity and alkalinity the modified neutralization potential NP of Schöpke (2008) is used

As planned, at the end of the water treatment, lake *Scheibe* exhibited pH-neutral conditions with a 0.16 mmol/L buffering capacity. The amount of lime used was 15.2 kt, which is less than calculated and the chemical efficiency with 80 % was above the pre-determined value. All project objectives agreed with the client were met and the financial framework was not exhausted. With treatment costs of less than 0.01 \in /mol the UNPprocess is well below other lake treatment costs with lime.

Various boundary conditions for the lake treatment could be identified by the 3D modelling. Wind induced currents are supportive only within the epilimnion. Yet, the main treatment effect is controlled by the momentum input and the density driven flow (fig. 5). Moreover, the pre-determined parameters for predicting the process could be proved to be sufficiently accurate.

Conclusions

As the LMBV pilot test for neutralising lake Scheibe showed, a stationary, continuously working liming installation can treat large pit lakes within a relatively short period of time. The UNP-process described in this paper combines chemical and hydrodynamic conditions within its design calculation algorithm. In order to achieve an optimum treatment, the process is fitted into the natural circulation period of the water body. To our knowledge it was the first time that 15.2 kt of lime were applied within a 16 weeks operation period. The chemical efficiency of 80 % exceeds the expected efficiency obtained during preliminary tests and the treatment costs of less than 0.01 €/mol extraordinarily prove that the UNP-process is a highly efficient treatment option.

Acknowledgements

This pilot project was conducted on behalf of the LMBV (Lusatian and Central German Mining Administration Company). The authors appreciate their financial contribution.



Fig. 5 Longitudinal section of lake Scheibe with discharge of lime suspension under stratified conditions (left) and while full circulation is completed (right) [dimensions in m]

References

- Benthaus FC, Weber L (2012): Innovative Verfahren zur Verbesserung der Gewässerbeschaffenheit. LMBV-Flutungskonferenz 2012 am 08.03.2012 in Leipzig.
- Bollrich G und Autorenkollektiv (1989): Technische Hydromechanik Band 2, Spezielle Probleme, VEB Verlag für Bauwesen, Berlin 1989.
- Geller W (2009): Folgeseen des Braunkohletagebaus und deren Sanierung. WRRL-Seminar 30 am 19.01.2009 in Radolfzell.
- Geller W, Klapper H, Salomons W (1998): Acidic mining lakes: acid mine drainage, limnology and reclamation, Springer, Berlin und Heidelberg 1998.
- Nixdorf B, Hemm M, Schlundt A, Kapfer M, Krumbeck H (2001): Braunkohlentagebauseen in Deutschland
 - Gegenwärtiger Kenntnisstand über wasserwirtschaftliche Belange von Braunkohlentagebaurestlöchern. In: Umweltbundesamt, UBA Texte 35/01.
- Nyberg P, Thørneløf E (1988): Operational liming of surface waters in Sweden. Water, Air and Soil Pollution 41: 3–16.

- Pust Ch, Schüppel B, Merkel B, Schipek M, Lilja G, Rabe W, Scholz G (2010): Advanced Mobile Inlake Technology (AMIT) – An efficient Process for Neutralisation of Acid Open Pit Lakes. In: Wolkersdorfer Ch & Freund A: Mine Water & Innovative Thinking. – p. 175 – 178; Sydney, Nova Scotia (CBU Press).
- Schlichting H, Gersten K (1997): Genzschicht-Theorie, Springer, Berlin und Heidelberg 1997.
- Schöpke R (2008): Experimental Development and Testing of an in Situ Technology to Reduce the Acidity of AMD-laden Groundwater in the Aquifer. In: Rapantova N & Hrkal Z: Mine Water and the Environment. – 337–340; Ostrava (VSB – Technical University of Ostrava).
- Sverdrup HU (1985): Calcite Dissolution Kinetics and Lake Neutralization. Lund Institute of Technology, Dissertation, Lund 1985.

Sulfate Reducing Bioreactor Dependence on Organic Substrates for Long-Term Remediation of Acid Mine Drainage: Field Experiments

Evan Walters¹, Paul T. Behum², Liliana Lefticariu^{1.2}

¹Department of Geology, Southern Illinois University, Carbondale, IL 62901, USA. ²Environmental Resources and Policy Program, Southern Illinois University, Carbondale, IL 62901, USA.

Abstract Excessive concentrations of metal contaminants identified in coal-generated acid mine drainage (AMD) associated with abandoned mines pose environmental challenges in the Midwestern U.S. Although many promising technologies have succeeded in providing short-term, low-cost systems for treatment of acid mine discharges, long-term treatment efficiency has been unsuccessful. Sulfate-reducing bioreactors have been employed as a passive technology for the treatment of AMD. However field studies demonstrate that long-term efficiency critically depends on the properties of organic substrates and their ability to support sustained microbial SO₄ reduction.

Previous laboratory experiments have been incapable of simulating the dynamic physical (*e.g.* temperature) and chemical (*e.g.* AMD composition) parameters represented in the field and thus are of limited practicality when applied to actual remediation efforts. Therefore, this study reports preliminary results from six field-scale experiments conducted at the Tab-Simco site to constrain the role of various organic substrates in remediation of coal-generated AMD. Tab-Simco is an abandoned coal mine located in southern Illinois that discharges AMD with pH \approx 2.7 and average concentrations (mg/L) of dissolves ions: 900 Fe, 220 Al, 40 Mn and 4500 SO₄. We constructed (1) five reactors containing limestone and alternating proportions of herbaceous and woody materials, and (2) one control reactor containing only limestone. For each experiment, we measured temporal trends in field parameters, effluent chemistry, mineralogy of solid precipitates, and microbial communities.

Results from the first four months of operation showed an increase in effluent pH and decreases in SO₄, Fe, Al, and trace metal concentrations in all field experiments. The simulated passive bioreactors removed on average 58 % SO₄, 56 % Fe, and 95 % Al. These results together with the presence of abundant sulfide minerals in the effluent suggest that microbial SO₄-reducing processes have been active. To date, regardless of the organic substrate used, no significant differences in effluent chemistry have been observed among the five simulated passive bioreactors. In contrast, the limestone-only reactor removed on average 33 % SO₄, 52 % Fe, and 49 % Al. In this case, the formation of precipitates has been the main mechanisms of SO₄ removal. Additional mineralogical and isotopic data together with bacterial community analyses will better constrain abiotic and biological processes responsible for effective AMD remediation.

As each reactor matures over 1-year, measurements will reflect genuine temporal changes produced at an actual AMD inflicted site providing practical applications for SRB technology. The results of this study will help improve bioreactor design and reduce the impact of coal-generated AMD.

Keywords Anaerobic Sulfate-Reducing Bioreactors, Acid Mine Drainage, Remediation, Long-Term

Full scale pilot test of a novel technology to remediate alkaline coal mine water using high-surface media at Acomb Mine Water Treatment Scheme, UK

Lee M Wyatt, Arabella M L Moorhouse, Ian A Watson

The Coal Authority, 200 Lichfield Lane, Mansfield, UK, leewyatt@coal.gov.uk

Abstract Acomb scheme is an existing coal mine water treatment scheme, which recently has been struggling to treat the iron-rich water. This scheme, like the majority in the UK, uses conventional methods of aeration cascades, settlement lagoons and aerobic wetlands. At Acomb, a full-scale pilot test of a Deferum treatment unit was installed, which uses high-surface media to remove the iron. This unit at Acomb successfully removed an average of 74 % of the iron from the mine water. Going forward, this type of treatment is likely to be useful where there are difficulties due to restrictions on land and costs.

Keywords Coal mine water, net-alkaline, high surface area media, iron removal, Deferum

Introduction

The mine at Acomb was abandoned by the National Coal Board in 1952, with mining dating back to at least the 19th Centaury using pillar and stall workings combined with the more recent total extraction of the Little Limestone Coal seam. The discharge at Acomb originates from the former mine adit, which commenced soon after the mine was abandoned, resulting in over 30 years of contamination entering the Red Burn. As part of an ongoing mine water remediation programme of existing discharges (agreed between the Environment Agency and the Coal Authority), the mine water treatment scheme at Acomb was constructed in 2002 to treat the mine water discharging from the abandoned adit. The scheme was designed to remove iron from a net-alkaline mine water and comprises of an aeration chamber, hydrogen peroxide dosing system, two parallel settlement lagoons, two aerobic reed bed wetlands and a sludge drying bed (Fig. 1). The discharge effluent, although not in breach of any consent, is higher than expected and desired by the Coal Authority for a treated effluent. Monitoring of the flow rates and mine water chemistry shows mean flow rates of 17 L/s varying between c. 10 L/s and c. 40 L/s; mean iron concentrations for the raw water of 33 mg/L; and mean iron concentrations for the treated water of 8 mg/L.

Subsequent to the construction of the scheme at Acomb, there have been some changes to the environmental regulations. Therefore at this site, and other treatment schemes operated by the Authority, mechanisms are being investigated to aid with improving the treated discharge quality in order to meet the revised regulations. In conjunction, the Authority also have the challenge of treating mine water discharges in locations



Fig. 1 Generalised layout of Acomb Mine Water

where the area of suitable land is limited, in addition to complying with the stringent requirements of cost-benefit analyses. The availability of land influences several factors relating to a mine water treatment scheme including the costs of constructing and maintaining a scheme, the type of treatment (i.e. active or passive) methodology applied and the size or efficiency of a scheme. In order to meet these criteria, the Authority manages a research and development programme to test the viability of novel methods and technologies. One such method is the utilisation of the Deferum high surface media unit to remove the iron. The Acomb site was selected for this trial for a number of reasons. Firstly, the scheme had the necessary infrastructure and security required for this type of technology already in-situ, combined with sufficient space for the installation of a full-scale Deferum system. Finally, the mean iron concentration in the treated discharge is higher than the concentrations preferred by the Authority (c. 1 mg/L), therefore some additional mechanism was required to improve the quality of the treated discharge.

Methodology – The Deferum Unit

The treatment unit (Fig. 2) was installed at Acomb where the trial began in November

2011 and concluded in September 2012. The trial unit was designed to treat 6 L/s, however, throughout the test one line of the unit was not in use, therefore a maximum flow rate of c. 3.5 L/s was achieved (c. 20 % of the mean flow rate). The raw mine water is pumped in to the Deferum unit under pressure (0.4 MPa) and enters the aerator to remove dissolved gasses and oxidise the water. From the aerator the water is passed through the distributor at the bottom of the unit, before moving upwards towards the filter media to remove the iron. After filtration the water passes through a final filter before being discharged to mix with the mine water in one of the settlement lagoons. As the filter media becomes 'clogged' the water level rises until the system switches in to a backwash mode; the slurry from which is discharged out of the unit and, for the trial at Acomb, was transferred to a sludge drying bed.

Results and Discussion

Throughout the trial, regular on site and laboratory measurements were taken of the raw mine water and the outlet water from the unit (treated). A summary of the key results are summarised below and shown in Figs. 3 and 4 and tables 1 and 2.

Total iron: During the trial the on site total iron had a mean concentration of 31 mg/L (22







Fig. 4 On site alkalinity and acidity measurements.

to 40mg/L). Treated total iron from the unit varied between 2 mg/L and 23 mg/L with a mean concentration of 8 mg/L. In terms of iron removal, the Deferum unit removed a mean value of 74 % (43 % to 94 %); with a mean flow rate of 3.1L/s and a mean removal of 23 mg/L, which equates to a removal loading of 6.6 kg/d. Assuming a footprint area of c. 25 m² for the unit, this converts to a mean area adjusted removal rate of 265 g/m²/d (14 to 847 $g/m^2/d$). The above data uses the more frequently measured on site data, however routine laboratory samples were also taken and tested. The laboratory data includes measurements of total, ferrous and dissolved iron, the results of which are summarised in table 1. The laboratory data shows a mean ferrous iron

concentration of 27 mg/L and a total iron concentration of 31 mg/L (this does not include 3 erroneous values of <5 mg/L). The ferrous concentrations are marginally below the total iron concentrations, thus part of the raw iron is in the ferric form and probably implies the water is at least in part oxygenated before being pumped from the sump – this is evident by the dissolved oxygen concentrations (3.2 mg/L) of the raw mine water. The treated water leaving the unit has a total iron value of 12 mg/L and a ferrous iron concentration of 11 mg/L. The speciation of the iron in the treated water is therefore predominantly in the dissolved ferrous form, rather than the particulate as well as ferric form, suggesting the water has not been sufficiently oxygenated as well as de-gassed

Sample Point	Total Iron	Alkalinity (as CaCO ₃)	Acidity (as CaCO ₃)	рН	Dissolved Oxygen	Temp. ℃	EC μs/cm at 25 °C	T.D.S.
Inlet	31	266	112	6.6	3.2	12.3	1706	1178
Outlet	7	241	96	6.6	3.5	12.1	1600	1109

All values are means as mg/L unless otherwise stated

Table 1 Summary of on site results for the Deferum unit.

Sample Point	Fe (Tot)	Fe ²⁺	Fe (Dis)	Alk	Acy	SO ₄	Cl	Са	Na	Mg	К	Zn	Mn	Al
Inlet	31	27	31	252	49	511	29	212	43	50	13	0.05	0.6	0.02
Outlet	12	11	11	251	20	508	30	211	42	50	13	0.01	0.6	0.02

All values are means as mg/L. Alk = Alkalinity as CaCO₃; Acy = calculated metal acidity as CaCO₃

Table 2 Summary of laboratory results (as total unless stated otherwise) for the Deferum unit.

(*i.e.* dissolved CO_2 may be present in the water) – this is illustrated by the dissolved oxygen concentrations (3.6 mg/L) of the treated water.

Acidity (expressed as mg/L CaCO₃): Acidity was measured both on site and in the laboratory, in addition to calculated metal acidity (Hedin et al. 1994) based on Fe, Mn, Al, Zn and pH. Due to changes in acidity concentrations over time and in transit to the laboratory (i.e. as a result of CO₂ degassing; McAllan et al. 2009), comparisons and analysis have been made using on site acidity and calculated metal acidity. The mean concentration for the raw mine water and the Deferum outlet (treated) are shown in Fig. 4 and tables 1 and 2. On site acidity measurements show a reduction through the Deferum of approximately 16 mg/L, whereas the calculated metal acidity values show a reduction of 29 mg/L. These reductions in acidity by the Deferum unit are predominantly the result of the reduction in iron concentrations through the unit. The differences between on site acidity and calculated metal acidity suggest that the raw mine water contains a significant amount of temporary acidity, probably caused by dissolved CO₂.

Alkalinity (expressed as $mg/L CaCO_3$): This was measured on site and in the laboratory (Fig. 4 and tables 1 and 2). The laboratory results show limited differences between the raw

mine water and Deferum outlet; these are comparable to, and generally correspond with the on site alkalinity concentration. However, the on site alkalinity values do show a minor difference between the raw and treated alkalinity. This 25 mg/L reduction closely matches the 29 mg/L reduction in calculated metal acidity. This is to be expected since the removal of iron affects the alkalinity and metal acidity equally (McAllan *et al.* 2009).

Other parameters: In addition to the parameters discussed above, a series of other chemistry analyses were undertaken. These results, summarised in tables 1 and 2, indicate that the Deferum does not significantly remove or change these parameters; an exception to this is zinc, where a reduction in the mean concentrations of $50 \mu g/L$ to $10 \mu g/L$ was observed. This reduction can most plausibly be attributed to the co-precipitation of zinc with ferric hydroxide.

The trial of the Deferum Unit at Acomb lasted for 290 days between November 2011 and September 2012, during this time the unit was non-operational on 8 occasions of approximately 1 to 5 days duration for each shut down. During the trial, the Deferum successfully removed a mean of 74 % of the total iron; thus resulting in a reduction in the total iron concentration from 31 mg/L to 8 mg/L. This mean value of 74 % (24 mg/L) equates to a mean area adjusted removal rate of 265 g/m²/d. The maximum removal percentage (94 %) was achieved at the end of the trial, when flow rates were approximately 4.3 L/s; with total iron concentrations reduced from 29 mg/L to <2 mg/L. The highest recorded quantity of iron removed during the trial however, was 34 mg/L (reducing concentrations down from 37 mg/L to 3 mg/L), when flow rates were approximately 3 L/s.

If standard settlement lagoons were to be utilised to treat this mine water, then dependent upon the various sizing criteria which could be applied, the lagoon area required is estimated to range between approximately 310 m^2 (based on PIRAMID 2003); 427 m^2 (based on Tarutis *et al.* 1999) and 610 m^2 (based on Hedin *et al.* 1994) in size. These areas are significantly larger than the estimated footprint area of 25 m^2 provided by the Deferum Unit installed at Acomb.

Conclusions

The Deferum unit was designed to remove all of the iron at a flow rate of 6 L/s, and although it failed to achieve this high removal rate, it successfully removed a significant amount of the total iron from the raw mine water. The footprint area (c. 25 m²) required to do this was significantly less than a standard settlement lagoon area between 310 m² and 610 m². In areas where there is restricted land available. the Deferum unit becomes a viable future option to discharge mine water at a lower (although still elevated) concentration, thus reducing environmental impacts. Alternatively, this technique provides an additional option to use in conjunction with a more 'typical' mine water treatment scheme, with the Deferum replacing the settlement lagoons, followed by an aerobic wetland. Both of these options (and other potential scenarios) would still require the need for a sludge drying bed, or other location, to dispose of the backwash slurry. Due to issues associated with non operational time periods and assuming treatment is required to comply with environmental quality standards, additional units as well as the need for water storage may also be required.

Acknowledgements

Thanks go to the staff at Integrated Water Services who monitored and maintained the system deployed at the Acomb Mine Water Treatment Scheme during this trial.

References

- Deferum (2013) www.deferum.com/technologicalprocess.html. Accessed 10th February 2013
- Hedin RS, Nairn RW, Kleinmann RLP (1994) Passive Treatment of Polluted Coal Mine Drainage. Bureau of Mines Information Circular 9389. United States Department of Interior, Washington D.C. 35 pp.
- McAllan J, Banks D, Beyer N, Watson I. (2009) Alkalinity, temporary (CO_2) and permanent acidity: an empirical assessment of the significance of field and laboratory determinations on mine waters. Geochemistry: Exploration, Environment, Analysis 9: 299–312
- PIRAMID Consortium (2003) Engineering Guidelines for the Passive Remediation of Acidic and/or Metalliferous Mine Drainage and Similar Wastewaters. European Commission 5th Framework RTD Project no. EVK1-CT-1999-000021 "Passive in-situ remediation of acidic mine/industrial drainage (PIRAMID). University of Newcastle Upon Tyne, UK, pp 166.
- Tarutis WJ, Stark LR, Williams FM (1999) Sizing and performance estimation of coal mine drainage wetlands. Ecological Engineering 12 315–372

Evaluation of High-Rate Clarification for Water Treatment at a Uranium Mine – A Case Study

Dmitriy ZINCHENKO¹, Patrick SCHAUER¹, Joel MIGCHELBRINK¹, H. C. Liang¹, Joe R. TAMBURINI¹, Michael NKETIA², Nathan ROLSTON², James HATLEY², Tony LAU³, Jeremy WILLIS³

> ¹Tetra Tech Inc., 1576 Sherman St. Suite 100, Denver, Colorado, USA ²Cameco Corporation, 2121-11th Street West, Saskatoon, Saskatchewan, Canada ³Infilco Degremont, 8007 Discovery Drive, Richmond, Virginia, USA

Abstract The performance of a high-rate clarifier with sludge recycle capability was evaluated during a three-month pilot project at a uranium mine in northern Saskatchewan. The pilot unit tested was a 100-gpm DensaDeg[®] system made by Infilco Degremont, Inc. Wastewater from underground processing operations was treated in both high and low pH regimes, generating two dissimilar sludges. Removal was adequate for most targeted contaminants, but high pH sludge presented special difficulties for the mechanical equipment and for process control. Future design of solids-recycling clarifier systems used in chemical precipitation of metals should include considerations for the rheology of the generated sludge.

Keywords Clarifier, Uranium, High-rate, Sludge

Introduction

Cameco's McArthur River mine (MCA) in northern Saskatchewan, Canada is one of the world's largest producers of uranium (U) ore. The mining operation takes place underground and because of the high water table in the area, needs to be constantly dewatered. This water is contaminated with many different metals and needs to be treated before discharge to the environment. The existing treatment process at MCA is currently operating near capacity and with an expansion of the mine being planned, will need to be updated and expanded. Fig. 1 below shows a simplified process flow diagram of the proposed treatment process. Because of the extreme winter weather at the mine site, there is a preference to contain all of the process equipment in a heated building. In order to accomplish this in as small a footprint as possible, high rate clarification was selected. A pilot study was conducted to evaluate the performance of the proposed clarifiers under the expected treatment conditions. The pilot study tested an Infilco Degremont (IDI) DensaDeg[®] clarifier rated for 22.7 m³/h (100 gpm). The pilot unit tested at MCA is shown below in Fig. 2.

The chemistry used for the pilot test was based on the existing chemical treatment process at MCA. The purpose of this pilot test was primarily to evaluate the physical/me-





Fig. 2 DensaDeg® 22.7 m³/h Pilot Unit

chanical separation ability of the high rate clarifier for the specific sludges generated at MCA and not to determine the optimum chemical treatment process.

The pilot test consisted of operating the clarifier under two different pH conditions (low and high) and at several different flow rates (50 %-115 % of rated capacity) in order to mimic the proposed treatment process. At each test condition, the clarifier was allowed to operate for several days, at which point samples were taken from the influent and effluent of the treatment process and analyzed.

The process for the expanded mine water treatment plant (MWTP) called for a two stage pH precipitation system (Liang 2012 SME). Incoming waters would first be treated with barium chloride, ferric sulfate, and an acid or base to achieve a pH of 9-11. The first stage targeted the removal of U, but also had significant removal of many other metals, including arsenic, cadmium, lead, zinc, etc. The effluent for the first stage would then be treated with more ferric sulfate and barium chloride, as well as sulfuric acid to lower the pH to around 4.5. The low pH stage targeted the removal of molybdenum (Mo; Liang 2012 WEFTEC).

The proposed design for the MWTP calls for a blend of mine water and slurry load-out (SLO) water at an approximate ratio of 5:1. The mine water was high pH, highly alkaline, and contained high concentrations of many metals, including U. The SLO water was less alkaline and had less solids loading but had higher concentrations of Mo.

Low pH

One of the driving factors for the construction of the MWTP expansion was the site's desire to decrease Mo loading to the environment. For that reason, the low pH stage solely targeted the removal of Mo. Other constituents were monitored, but process conditions were adjusted to test Mo removal in different situations.

Because only one pilot clarifier was available, the full continuous process could not be modeled. Each pH stage would have to be tested consecutively, instead of concurrently. The flowrates during the test were too great to allow for storage of the water treated during the first stage, so the influent to the low pH stage was simulated by blending water from various sources. A mix of SLO water and effluent from the current MWTP was blended to reach an influent target of 5–10 mg/L Mo. This concentration represented the highest probable Mo concentration that the expanded MWTP could see.

The low pH process was tested at 3 different flow rates: 11.4, 18.2, and 22.7 m³/h (50, 80, and 100 gpm). All tests were run at a pH set point of approximately 4.5. The results indicated that Mo removal was excellent and met the target effluent concentrations at all flow rates. Radium removal was not as effective as indicated in the bench scale testing, but some of the problems could be attributed to the sim-
ulated water. The radium-barium co-precipitation needs adequate sulfate to form proper floc particles, and less sulfate was available in the simulated water than would be in a full scale plant.

The characteristics of the low pH sludge were similar to DensaDeg[®] applications when treating light municipal sludges. The flocculated particles were very light and had a low density. The sludge bed depth varied greatly with flow rate, as the bed expanded and contracted. While the low density of the sludge might seem to decrease its settleability, in practice it still settled very well. Very little solids carryover was observed during the low pH testing, and the effluent was almost always clear and free of flocculated solids. At higher flow rates, some particles were carried through the clarification section, but were caught in the plate settler section. The plate settlers required periodic cleaning.

The flocculant for the low pH stage was not optimized during the pilot testing. The light floc was easy to pump and work with, but a slightly more dense sludge would dampen fluctuations in bed depth and reactor solids concentration. In terms of removal efficiency, there is not much improvement available in flocculant selection. The site polymer was effective at promoting proper flocculation with the low pH sludge. High rate clarification technology is a good application for this type of sludge.

High pH

A total of five different high pH tests were conducted to assess the performance of the DensaDeg[®] system under varying pH and flow. Three different process flow rates of 18.2, 22.7, and 26.1 m³/h (80, 100, and 115 gpm) were tested under the pH 10 control set point while pH 11 and pH 9 tests were both conducted at 18.2 m³/h. The primary constituent of concern was U but other metals and radionuclide contaminants were also removed at high pH.

Ferric sulfate (12 % Fe) and barium chloride (30.5 g Ba/L) were dosed at 0.09 mL/L and 0.4 mL/L, respectively. Sulfuric acid was also dosed to maintain pH set points. An anionic polymer, Magnafloc-351 was the sole flocculant utilized in all tests. Although the manufacturer recommended the use of a different polymer for high pH experiments, Magnafloc-351 was the only flocculant available on site during the course of this project. The polymer dose was varied between 0.25 and 0.5 mL/L from a neat concentration of approximately 0.2 %.

The DensaDeg[®] system facilitated better than expected removal of U at all tested pH values. However, removal of most other contaminants of concern was equal or lower compared to effluent of the current WTP during

Constituent	Units	Pilot Scal Res Value	e Testing ults Removal	Test for Best Effluent Quality (High or Low pH)	Treatment Target	-
Non-Radionucl	ides					-
Arsenic	mg/L	0.0023	47%	High pH	0.03	
Copper	mg/L	0.0024	47%	High pH	0.02	
Lead	mg/L	0.00055	91%	High pH	0.004	
Molybdenum	mg/L	0.073	99%	Low pH	0.1	
Nickel	mg/L	0.00063	21%	High pH	0.12	
Zinc	mg/L	0.0020	89%	High pH	0.14	
Radionuclides						
Lead-210	Bq/L	0.06	95%	High pH	0.21	
Polonium-210	Bq/L	0.21	83%	High pH	0.54	
Radium-226	Bq/L	0.23	98%	Low pH	0.067	
Thorium-230	Bq/L	0.058	95%	High pH	0.09	Table 1
Uranium	μg/L	1.4	96%	High pH	2	

Table 1 DensaDeg® Pilot Test Results this time. Table 1 lists the average final effluent concentrations for pilot plant target criteria.

One of the main purported advantages of the DensaDeg[®] system is that by externally recirculating the sludge, the precipitated flocs can be reintroduced to the influent stream and thus have a second chance to adsorb or bind contaminants. Since the pilot unit consistently demonstrated better U removal than bench scale studies suggested, it may be possible that the sludge recirculation process and the internal recirculation occurring in the Reactor section of the DensaDeg[®] may be responsible for enhanced U treatment. Additionally, on average, better U removal was observed at higher pH conditions (around pH 11) than at lower ones.

During the course of the first high pH test, it became apparent that any previously-established operating guidelines had to be significantly amended to ensure successful performance. The most significant operational challenge encountered throughout the high pH tests was proper sludge handling and flocculation. Ferric hydroxide floc, when laden with U, became significantly denser and heavier than what was seen with the low pH sludge. Therefore, a different strategy for sludge handling was necessary.

For the initial low pH experiments, operators were instructed to build up a sufficiently high solids inventory in the clarifier tank, indicated by sludge bed of approximately 1.8 meters. However, the solids created through this treatment under high pH conditions not only had a fast settling velocity, but also exhibited significant compaction. The progressive cavity-type sludge recycle pump was rated for approximately 4 % solids but the clarifier underflow solids concentration had already exceeded this value and began to plug up the pump before the sludge bed had reached 0.9 meters. At one point, the sludge became so viscous that it could not be pumped out of the clarifier without repeated backflushing through the wasting line.

The unexpectedly high density of the sludge also resulted in over-torque damage to

the gear train of the scraper drive. Multiple power outages occurred during this phase of testing, and it is likely that critical mechanical failure occurred when the scraper mechanism tried to restart against a deep, thick sludge bed. The broken scraper drive led to a few additional problems, most notably an inoperable sludge recirculation system. The sludge bed had a sharp horizontal incline, depressed towards the side of the clarifier that held the sludge waste line and all of the sludge bed sample taps. This caused inaccurate sludge bed readings, and allowed the bed to build above the sludge recirculation intake cone. When the cone plugged, sludge could no longer be pumped and the lack of flow caused the stator of the sludge recirculation pump to fail. Operators developed temporary stopgap measures to continue the testing, but as soon as the scraper mechanism was repaired, similar sludge issues we no longer experienced.

All of the challenges pertinent to dense U sludge were further compounded by inconsistencies in polymer concentration. The mechanical problems with the polymer make-up system would occasionally lead to very dilute batches of flocculant. This resulted either in under-dosing of polymer before the problem was discovered, or over-dosing when operators had already adjusted for the previous, dilute concentration. Insufficient polymer dose resulted in light, disperse flocs of varying size (including pinfloc) but this effect was partially reduced when good quality sludge was being recirculated concurrently. Overdosing of polymer, however, led to the formation of large, spherical flocs, some over 1 cm in diameter. This type of floc created sludge that was nonhomogenous, amorphous, globular in appearance and would expel water readily upon physical compression. This phenomenon was observed repeatedly when over-polymerized sludge was being pumped for recirculation or wasting. Initial pumping would only produce water, followed by a dilute sludge stream, until the frictional headloss became too great and all flow stopped. Bed depth samples taps were

thus found to be unrepresentative of the clarifier conditions when this type of sludge was present because water would be separated from sludge solids in the small-diameter sample tap piping. Once issues with the flocculant make-up system were identified and repaired, flocculant dosing for subsequent tests was considerably more consistent.

Several changes to system operation were made to address issues with sludge and polymer dosing. The previous operational metric of sludge bed height was eschewed in favor of reactor tank solids, which were measured every 3-4 hours with a 1-L graduated cylinder and were maintained between 5-15 % (by volume) after a 10 min settling time. Sludge compaction was best accomplished through direct visual observation of the sludge recirculation stream, which led to a brief but consistent wasting and a resulting sludge bed depth of about 0.3-0.6 m. Consistent qualitative checks of the reactor tank flocs also helped to safeguard the process against any unexpected mechanical malfunctions with the polymer deliverv system.

Inconsistencies in the main influent stream presented the remainder of the operational challenges associated with running the DensaDeg[®] system. The original pilot plant configuration called for influent water to be provided via a series of underground dewatering pumps but the resulting flow rate soon proved to be too unreliable for steady state conditions so influent water was rerouted from a large equalization pond. Grit, cement, and other debris were present in the influent water and could be found in the settled sludge as well. While this may have contributed to increased sludge density, some amount of each is likely to occur in all mine water treatment operations.

Recommendations

A flocculant study should be performed in order to determine the proper polymer dose and type best applicable to the process water and its coagulant(s). Brief on-site bench scale

testing performed during the course of the experiment concluded that at least some polymer was necessary to settle ferric hydroxide flocs. Pure recycle of settled, flocculated solids was not sufficient enough to completely eliminate the need for polymer addition. However, decreasing polymer dose gradually while maintaining sludge recirculation is a viable method of slowly reducing the amount of over-polymerized solids when they are already present in the system, without significantly impacting effluent quality. Operators found that a dense and fast-settling sludge like the one generated in the high pH tests requires only a very small bed depth to attain good compaction in the clarifier underflow. This information should have been communicated by IDI to the pilot team so that proper operational changes could have been implemented.

High pH, U-laden sludge presents special challenges to the operation and design of the DensaDeg[®] system. In the interest of redundancy and good safety factors, it is recommended that special operating procedures be developed for handling sludge that is thicker than typically encountered or anticipated in the initial design. Accidental overdose of flocculant or coagulant can lead to sludge that exhibits a rheology different from the one typically encountered during normal plant operation, so sludge handling equipment needs to capable of addressing these occasional upsets. It was the operators' observation that the overall performance of the DensaDeg[®] process for high pH U treatment was good, but some modifications in sludge handling procedures and equipment, with special consideration of U sludge properties, could make the system perform even better. Increased diameter piping, long radius fittings, emergency or even routine operation flush water connections, and pumps rated for highviscosity, high-solids sludge transfer with rundry capability, and higher torque rake mechanisms are just some of the ways the sludge handling capability of the DensaDeg® system should be specified in a full-scale installation.

Conclusion

The DensaDeg[®] high rate clarification technology tested at MCA was demonstrated to be effective and feasible for the type of sludge produced by the expected low pH treatment condition. Though the pilot unit worked adequately and produced acceptable effluent under high pH treatment conditions, there are some areas for optimization in future designs specific to this type of application. Specific detailed operating procedures and specification of more robust sludge handling equipment will allow this technology to be utilized for dense metal sludges.

Acknowledgments

We thank the Colorado School of Mines for hosting the IMWA 2013 Conference. We also

thank Cameco and IDI for allowing the results of the pilot test to be published.

References

Liang, H.C.; Zinchenko, D.; Billin, S.J.; Barta, J.; Jones, R.; Willis, W.B.; Tamburini, S.J. "Membrane vs. Chemical Treatment to Remove Mine Water Contaminants – Determining Which Process Works Best for Mine Water Treatment Needs," SME, 2012, Seattle, WA

Liang, H.C.; Wright, G.; Tamburini, J.R.; Willis, W.B. "Water Chemistry Considerations for Improving Molybdenum Removal at a Mine Water Treatment Facility," WEFTEC, 2012, New Orleans, LA

LAGNIAPPE YOUR GOODIES LAGNIAPPE YOUR GOODIES



Author Index

Volume I pages 29–760 👁 Volume II pages 807–1246

Α		Bloom, Jack	119
		Blum, Alex	287
Abfertiawan, Sonny	341	Boehlke, Adam R	1187
Adeniyi, Amos	507	Bogert, Henry	1009
Adolph, Amundson	1157	Borbely, Caitlin	1157
Aerts, Peter	705	Bouzalakos, Steve	1193
Allard, Bert	391, 551, 625, 1119	Bowman, Jennifer R	639, 643
Alpers, Charles	287	Bozeman, Lauren R.	1011
Alvarez, Rodrigo	399	Bratty, Mike	717
Amaral Filho, Juarez	245	Bravo, Luis	807
Annandale, John	417	Breckenridge, J. Larry	97, 269, 331, 397
Anornu, Geophrey	451, 457	Bredenkamp, Brendon	103
Ardau, Carla	983	Briest, John	1217
Atanasova, Maria	307	Broadhurst, Jennifer	245, 275
Auckland, Adam	371	Broschek, Ulrike	807
Ávila, Paula	313	Brown, Adrian	525
		Brueckner, Friedemann	925
B		Bryan, Christopher	275
		Buchanan Jr., Ronald J.	581
B. B. Gagné, Emmanuelle	91	Byrom, A. James	519
Baacke, Delf	1081		
Bäbler, Matthäus	855	C	
Bäckström, Mattias	391, 463, 513, 551		
Bai, Haibo	219	Cabon, François	1205
Bailey, Matthew T.	519	Cadle, Sonya	207
Banning, Jessica	1089	Camden-Smith, Bronwyn P	281
Barnard, Tobias	843	Campana, Patricia	843
Barnekow, Ulf	1047	Campbell, Kate Marie	287
Barnes, Andrew	405	Castiglia, Peter	105
Beale, Geoff	119	Cath, Tzahi	1199
Becker, Megan	275	Ceranski, Helena	925
Beddoes, Paul	251	Chahbandour, John	813
Behum, Paul T.	747	Chapin, Thomas	295
Bekesi, Gabor	29	Chatwin, Terrence Doyle	301
Bender, Michael	371	Cheng, Cheng	105
Benthaus, FriedrCarl	919	Chesnaux, Romain	91
Bern, Carleton R	1187	Chironga, Lordrif	887
Bezkorowajny, Andrzej	257	Christoffersen, Lee	347, 967
Bhattacharya, Jayanta	263, 325	Cichy, Dan M.	1125
Bickford, Fred Eric	97, 269	Cidu, Rosa	931
Biddau, Riccardo	931	Clements, Nathan	819
Billing, David G	281	Cloutier, Vincent	91
Bittner, Arnold	35, 47, 1017	Coetzee, Henk	307, 475, 937, 943

Conroy, Kevin	533, 539, 711, 717	E	
Cornejo, Jorge	807		
Costa, Maria Clara	693	Effner, Scott	133, 487
Costa, Maria Rosário	313	Eger, Paul	545
Cottingham, Christopher Todd	111	El Idrysy, Houcyne	175
Cravotta, Charles	319, 949	Engle, Mark A	1187
Creek, Mike	301	Everett, Brent	133
Crouch, Caitlin	447		
Crozier, Trevor Wade	213	F	
Cunha, Osmar	705		
Curiel, Eli	1009	Fahlqvist, Anna Linnéa	551
Czop, Mariusz	257, 1139	Fereira da Silva, Eduardo	313
-		Fernández Lorca, David	837
D		Fernández Rubio, Rafael	837
		Ferreira, Adelaide	313
Da Pelo, Stefania	983	Figueroa, Linda A.	729, 1023
Daigneault, Réal	91	Firpo Vasquez, Beatriz Alicia	977
Das, Bidus Kanti	263, 325	Florence, Kay	557
Davis, Andy	955	Foote, Randy	105
de Bary, Alejandro	867	Forero Garcia, Felipe	229
de Wet, Louis Daniel	825	Fornarelli, Roberta	563
Dean, Daniel Miller	337	Fosso-Kankeu, Elvis	843
DeDycker, Phil	347, 967	Franzidis, Jean-paul	275
Dee, Kato T	1157	Frau, Franco	983
Defossez, Anne-Julie	1205	Fricke, James Ross	337
Dennis, Ingrid	961, 1003	Frippiat, Christophe	989, 995
Dennis, Stefanus Rainier	961	Funcken, Luc	995
Dev, Subhabrata	325	Furuya, Hisatoshi	587
Diana, Melinda Rose	341		
Digges La Touche, Gareth	117	G	
Ding, Dong	157		
Dipple, Gregory M	593	Gale, John Edward	139
Divine, Craig	347, 967, 1125	Gallagher, Neal T	533
Dobr, Michal	229	Gammons, Chris H.	493, 1041
Dong, Guiming	893	Gao, Ming	151
Dong, Shuning	831	Gast, Martin	611
Dore, Elisabetta	931	Gautama, Rudy Sayoga	341
Dorey, Robert	331	Gericke, Mariekie	569
Dowling, Jeremy	119, 125	Geroni, Jennifer	949
Drennan, Dina	1023	Geza, Mengistu	1199
Drewes, Jörg	1199	Gillow, Jeff	347
Duaime, Terence E.	1041	Girão, Ana	693
Durand, Jean Robert	661, 723	Giraudo, Joe	237
Duren, Sabre Miel	973	Gorsuch, Joseph	499
Dwyer, Robert	499	Govender-Ragubeer, Yageshni	569
		Grandin, Anna	625, 1119
		Greenway, Gillian	383

Greer, Briana	353, 365	Johnson, Kelly S	643
Griffin, Adam	347, 967	Johnson, Raymond H	281, 377, 1237, 1241
Grmela, Arnost	181, 1097	Johnston, Katherine Sylvia	213
Gunawan, Firman	341	Johnstone, Andrew	961, 1003
Gusek, James Joseph	575, 581	Jones, Ashley	383
Gutierrez, Luis Ventura	687	Jones, Perry M.	1095, 1117
		Jonsson, Stefan	855
H		Jordan, David	105
Hamai, Takaya	587	K	
Hanson, Rachel	711		
Hardwick, Ed	655	Kahl, Sandra	1165
Harley, Andrew	359	KairiesBeatty, Candace	545
Harmon, Makinsey	83	Kaliaperumal, Raj	441, 1035
Harrison, Anna Lee	593	Kamika, Ilunga	613, 619
Harrison, Sue	275	Kaminsky, Jon	133
Hasche-Berger, Andrea	1165	Karlsson, Lovisa	391
Hatley, James	755	Karlsson, Stefan	391, 625, 1119
Hay, Michael	347	Kasedde, Hillary	855
Hazelton, James	69	Kauffman, Mary	487
Hedin, Benjamin C	605	Keller, Jason	237
Hedin, Robert S	599, 605	Kennealy, Jamie	125
Helgen, Steve	353, 365	Kershaw, Steven	519, 1173
Henkel, Sebastian	905	Kingston, Scott	1089
Hernandez, Aurora Maria	41	Kinser, Karla	633
Herrell, Michael	251	Kirabira, John Baptist	855
Hill, Steve	667	Kirk, Allan R	1009, 1011
Hinck, Peter	435	Kirk, Lisa Bithell	1011
Hocking, Crystal Marie	899	Klauder, Wiebke	905
Hoey, Dave	71	Klaus, Reinhard	861
Hoos, Rick	1089	Knoller, Kay	611
Hoth, Nils	611	Komischke, Holger	1165
Hou, XinWei	151	Kortatsi, Ben K.	451, 457
Howell, Roger Lynn	145	Kos, Paul	1073
Hudson, Amy	849, 1105	Kosinski, Sean	353
Hull, Brian D	533	Kotoane, Mpno	307
1 1		Kotze, Jonanita Kramor, David	157
1		Kranta Frieles	133
Ikada Manami	-0-	Kruse Dapiele Natalie Alveen	899
ikeua, mananni	507	Kruse Colin	397, 039, 043
1 1		Krzeszowski Światosław	397
5		KIZESZOWSKI, SWIALOSIAW	101
Jenk IIIf	10.81	Külle Christoph	1139
Jenn, on Jeschke Christina	1001 611	Kuma Jerry S V	4/, 101/
Jiang Jianhua	011	Kusuma Ginting Jalu	454,457
Johnson Kathryn Olive	3/1	Rusuina, Ontenig Jaiu	341
joinison, Kaun yn Onve	699		

| L

| M

LaBar, Julie A.	1143	Mackenzie, Ian	371
Lachmar, Thomas	1211	Mackey, Amy L	639
Lagos, Josué	807	MacSween, Jessica	441, 1035
Landkamer, Lee L.	1023	Mahoney, John J	411
Lane, Terre	105	Makgae, Mosidi	417, 475
Lau, Tony	755	Malisa, Rejoice	655
Laubrich, Jan	1047	Mansel, Holger	925
Laurence, David	69	Mao, Xianbiao	219
Lazarim, Helio Alexandre	837	Maree, Jannie	417, 507, 655, 875
Le, Vinh-Luu	163	Marks, Mary Beth	1009, 1011
Lee, Ilsu	1023	Marx, Vera	47
Lefticariu, Liliana	747	Mathuthu, Manny	1145
Lengke, Maggy	955	Mavunganidze, Taimos	425
Leone, Gaston	469	Mayes, William Matthew	383
Leong, Shane	69	Mbaya, Richard	507
Lestari, Iin	341	McCullough, Clint D	1029
Li, Xiangquan	151	McGeeney, Dayna	1193
Liang, H. C.	755	McGeorge, Norman	1003
Licbinska, Monika	1097	McGivern, Amber L.	1041
Lilley, Tim	649	McKnight, Diane	447, 973
Lin, Yun	881, 911	Mengistu, Haile	1179
Linderfelt, William	105	Metschies, Thomas	1047, 1081
Liu, Houmao	157	Meyer, Joseph	499
Liu, Jingcun	219	Meyer, Jürgen	1081
Liu, Lingxia	151	Meyer, Troy	849
Liu, Shucai	219, 893	Migchelbrink, Joel	755
Liu, Yong	219	Milczarek, Mike	237
Liu, Zaibin	831	Mill, Taylor J	1157
Llanos Lopez, Freddy S.	1143	Mkandawire, Martin	441, 1035
Lobos, Jorge	807	Moderski, Anna M	539
Logsdon, Mark J.	53	Moleiro Cabrera, Manoel Camilo	169
Londe, Louis	1205	Momba, Maggy	613, 619
Long, Dejiang	371	Monteiro, Olinda	693
Lopez, Dina	639	Moore, Lucas R.	661, 723
Loredo, Jorge	399	Moorhouse, Arabella M. L.	519, 667, 749, 1173
Lotfiazad, Farshad	867	Morgan, Philip	557
Lourenço, João	693	Morr, Dennis	1073
Lucke, Beate	919	Motlakeng, Tshepo	429, 1067
Lukas, Eelco	1151	Mulaba-Bafubiandi, Antoine Flori	bert 843
Lund, Mark Andrew	1029	Müller, Jürgen	1047
Lupo, John	223, 873	Müller, Mike	1055
Lupton, Sarah	111	Mullett, Mark	563
Luscz, Emily	163, 269	Musiolik, Aleksandra	1061
Lusk, Karel	1097		
Lyle, Sarah Louise	405		

229

967

741

295

1193

563

705

1211

499

1157

717

705

837

1105

281

1105

71

705

307

383

499

1125

441, 1035

181, 1097

Ν

Nairn, Robert W.	673, 679, 691, 1143
Nason, Peter	681
Nel, Elaine	157
Netshitungulwana, Robert	429, 1067, 1179
Nicholson, Andrew	59, 353, 365
Niejalke, Darren	29
Nketia, Michael	755
Nordstrom, D. Kirk	287
Noske, Craig	819
Novhe, Ntshengedzeni Obed	429, 875, 1067, 1179
Nowak, Neil	1217
Nyabeze, Peter K	1179

0

441, 1035
875
1073
633
1223
655
399
59
899

Ρ

P		Rolston, Nathan	755
		Rouleau, Alain	91
Pacyna, Daniel	989, 995	Roux, Estelle	71
Palmer, Kelsea J.	1143	Roux, Pierre	1205
Pan, Guoying	881, 911	Rowe, Jerry	1111
Paños, Nora Hilda	687	Roy, Denis W.	91
Parker, Stephen R.	493	Rüde, Thomas R.	905
Pastorinho, Ramiro	499	Rudnick, Deborah	59
Paul, Michael	1047, 1081	Rue, Garrett	447
Pedder, Rosalind Katherine	175	Rutkowski, Tom	711, 717
Peer, Rebecca A. M.	691, 1143	Ryan, Adam	499
Perzoff, Tania	1089		
Piatak, Nadine M.	1095, 1117	S	
Pint, Tina	435		
Pinto da Costa, João	693	Sackey, Michael Ampim	451, 457
Plumlee, Geoffrey S.	729	Sakala, Emmanuel	1067, 1179
Pluta, Irena	699, 1061	Sanders, Laura	723
Podda, Francesca	983	Sansom, Stephanie	633
Popoola, Patricia	507	Santore, Robert	499
Power, Ian Malcolm	593	Sartz, Lotta	463, 513, 551

L R

Preene, Martin

Preston. Kelli

Preuss, Volker

Progess, Christina

Rahman, Priom

Raman, Chandra

Randall, Kevin

Ranville, James

Rapantova, Nada

Relego, Melissa R

Rhodes, Melissa

Ribeiro, Mauricio

Ribeiro, Vinícius Viera

Richardson, Robert

Richers, Dave

Robbins, Sarah

Rodrigues, Fabio

Roelofse, Frederick

Rogerson, Micheal

Rogoff, Eric

Rolston, Nathan

Rogevich-Garman, Emily

Richardson, Charles Doc

Ramos, Renato Giani

Ralph, David

Scassiotti, Walter	705	Thürmer, Konrad	741
Schauer, Patrick Jordan	755	Tilliander, Anders	855
Schlekat, Christopher	499	Timms, Wendy	69, 1193
Schneider, Ivo	245, 977	Tinklenberg, Annelia	105
Schoenbacher, Jeff	63	Titone, Brian C.	195
Schramm, Andrea	1081	Tlowana, Supi	475
Schüttrumpf, Holger	905	Todd, Andrew	295
Seal, Robert R.	1095, 1117	Trein, Camila Maria	977
Selker, Frank	111	Trindade, Tito	693
Selker, John	111	Tshivhase, Victor Makondelele	1145
Senese, Ana Alicia	687	Tutu, Hlanganani	281, 377, 425
Seok, Eunjeong	139	Tyler, Murray	29
Sharp, Jonathan O.	1023		
Shea, Joe	441	U	
Shi, Xianxin	831		
Sidu, Sibusiso	825	Uhlig, Christiane	925
Simbolon, Reynaldi	341	1	
Simon, André	611	V	
Sjöberg, Viktor	391, 625, 1119		
Smith, Jessa	717	Vacca, Andrea	931
Smith, Kathleen S.	729	van den Berg, Elmer	125
Smith, Ross E.W.	77	Van Etten, Eddie J.B.	1029
Song, Xin	469	van Tonder, Gerrit	887
Sorells, Duff	581	Vandenberg, Jerry	251
Spurlin, Matthew S.	1125	Veil, John	1229
Sraj, Nina	117	Vermeulen, Danie	1151
St. Louis, Robert Michael	1131	Veschkens, Mathieu	989, 995
Stephen, Smith	705	Vink, Sue	71
Stewart, David	735	Vitale, Matt	111
Stewart, Michael David	405	Volker, Karien	807
Steyl, Gideon	887		
Stochel, Bernadetta	257, 1139	W	
Strickland, Forrest	661		
Strosnider, William H. J.	691, 1143	Wallace, Michael Gary	899
Strzodka, Michael	741	Walters, Evan Robert	747
Sui, Wanghua	189, 893	Walton-Day, Katherine	1157
Sun, Yajun	893	Wang, Changshen	219
Swanson, Eric E.	195	Wang, Hao	831
Szczepinski, Jacek Jozef	201	Wang, Zhengxing	151
		Warren, Bartholomew James	481
T		Waterhouse, John	29
		Watson, Ian A.	667, 749, 1173
Tamburini, Joe R.	755	Weidner, Christoph	905
Taplin, Ros	69	Weiler, Jéssica	245
Thomas, Abraham	1179	Wendland, Edson	169
Thompson, Keith Steven	207	Wessels, Lize	1151
Thompson, Randi Lee	213	Wheelan, Mark	1193

Whitmore, Christa	487	X	
Whittle, Phillip	77		
Wiedhartono, Arief	341	Xu, Pei	1199
Wilbur, Stephen Crawford	213		
Williams, Amy	287	Y	
Williams, Dean	301		
Williams, George P.	493	Yibas, Bisrat	429, 1067, 1179
Williams, Les	59	Youlton, Cristian	169
Williamson, Jacob	499	Yu, Jincun	893
Willis, Jeremy	755	Yungwirth, Grace	117, 229
Wilson, Daniel	105		
Wilton, Michael John	223	Z	
Winfrey, Brandon K.	691		
Wolhuter, Alexandra	71	Zhan, Guosheng	237
Wolkersdorfer, Christian	181, 1165	Zimmerlund, Ben	125
Woodruff, Laurel G.	1095, 1117	Zinchenko, Dmitriy	755
Worsa-Kozak, Magdalena	257, 1139	Zingelmann, Markus	35
Wu, Yazun	881, 911	Zupancic, John W	1187
Wyatt, Lee M.	667, 749, 1173		
Wyman, Susan	83		

Keyword Index

Volume I pages 29–760 👁 Volume II pages 807–1246

This keyword index is based on the keywords submitted by the authors. It is not an index for the pages in these proceedings. Each keyword directs to the paper's first page.

0-9		artificial recharge	97
		Australia	29
3D Models	1035	availability	313
3D visualization	1125	AVS/SEM	1095

| A

В

abandoned mine	313, 319, 931, 949, 1165, 1173	Baccu Locci mine	983
acid base accounting	397	bacteria	687
Acid mine drainage	287, 295, 307, 319, 341, 475,	bacterial growth	325
533, 563, 691,	705, 747, 937, 973, 1067, 1143	bacterial sulfate reduction	611
acid rock drainage	97, 275, 331, 447, 525, 1143	Barium Sulphate	1061
acidity	463	Barium	699
active treatment	533, 639	bark compost	1119
Adsorption	545, 569, 575	barometric efficiency	995
Agrostis capillaris	1119	Bauxite stripping mine	837
Airlift	145	Beneficial Reuse	1199
alkaline addition	639	best practices	251, 301
alkalinity	337	bioavailability	481
alluvial aquifer	47	Biofilm	383
Alternative filter pack m	nedia 861	biokinetic tests	275
alum shale	391	biological recovery	643
Aluminum	691	bioremediation	613, 619, 693, 843
Amazon	837	Biosorption	687, 843
AMD treatment	417, 735	biotic ligand model	1117
AMD	429, 499, 655, 1179	biotreatment	337
amendments	347	Black shale	391
anaerobic bioreactor	587	Bochnia	257
Anaerobic Sulfate-Redu	cing Bioreactors 747	Bofedal	163
Analytical methods	91	Boron	633
Antimony	931	brackish water	105
aquifer characterization	111	Brine	855
ARD prevention	301, 581	bulkhead	1157
ARD	245, 301, 1011, 1111	Bushveld Complex	1179
arid environment	59		
Arizona	125	C	
arsenic contamination	983		
arsenic	313, 399, 525, 931, 1081	Cadmium	525, 691
Artesian pressure	29	calibration	103, 207, 223

Wolkersdorfer, Brown & Figueroa (Editors)

carbon dioxide	673	COSED-UF	371
carbon footprint	673	cost calculation	557
carbon mineralization	593	cover performance	237
carbon sequestration	593, 605	Cr(VI)	569
carbonate precipitation	593	criteria	77
case study	1047	critical and strategic	elements 729
cat ion-exchange	655	Cu-Ni-PGE deposits	1095
catastrophic events	41	curtain grouting	881
Catchment	1029, 1179	Cyanide Decay	457
Cation Exchange Capacity (CEC)	451		
centrifuge core testing	1193	D	
characterization	967		
chloride contamination	1131	damage function	989
circum-neutral mine water	557	data analysis	1125
Clarifier	755	data validation	83
climate	463	database	411
closure	1205	decant	1003
CO2 degassing rate	949	Deferum	749
Coal Bases	151	depressurization	119, 893
coal bed methane	1187	desalination	105, 507
coal bed natural gas	1187	design consideration	s 229
coal combustion ash utilization	341	design	507, 1125
coal mine drainage	599, 949	design-basis	53
Coal Mine Water Hazard	831	dewatering test	881
Coal mine water	667, 749	dewatering	103, 125, 157, 163, 175, 207, 887
coal mine	643, 1067	discharge	77, 1125
coal seams	1035	dissolved organic ma	tter 973
coal waste	245, 977	DMT Box Model	961
coalbed methane extraction	1193	Drainage Tunnel	119
coalbed methane	1211	drawdown	29
collaboration	1055	drillstem tests	145
Colliery	1151	dry cover	341
column leaching tests	487	dynamic methodolog	gy of water investigation 1173
compaction	341		
compartmentalized	157	E	
complexation	545	•	
compliance monitoring	83	ecohydrogeology	117
Compliance	825	Ecohydrology	117
Compost reactor	263	ecological risk assess	ment 59
Concentration	1145	ecological risk	955
confined aquifer	893	ecology	117, 1029
confining strata	1193	economics	729
copper chelation	661	efficiency	687
copper mine	1139	efflorescent crusts	281
copper removal	661	effluents	723
copper 125, 493, 499, 525, 545, 729, 11	17, 1119, 1119	electrical conductivit	y 1151
correlation analysis	995	electrodes	557

elution column experiments	905	G	
Emalahleni	429		
end-uses	1029	GARD Guide	301
engineering plans vs. discounted cost	s 53	geochemical modeling	181, 281, 287, 1011
environment	71	geochemical processes	1017
environmental database	83	Geochemical	457
Environmental Geology	151	Geochemistry	493, 681, 899, 1041, 1105
environmental impacts 4	69, 1081, 1097	geoenvironmental model	s 729
environmental issues	983	geo-environmental provir	nces 1179
eochemistry	451	Geomembrane	1217
EPANET	961	geophysical survey	189, 1067
Ermelo Coal Field.	1067	geotechnical logging	175
eutrophication	679	geothermal energy extrac	tion 1035
Evaporation	807, 855, 1217	GIS	63, 989
Evapotranspiration (ET) cover	237	global	633
experimental clogging model	905	glycerol	611
Exploration	831	gold mining	475
exsolution	673	Gold tailings	425, 1131
external organic carbon dosing	263	GoldSim	435
extreme events	53	Gram-negative bacteria	843
		Gram-positive bacteria	843
F		grass cover	625
		Great Artesian Basin	29
fabricated soil	977	greenstone	1179
faulting	887	ground freezing	111
faults	157, 1211	groundwater inflow	103
Feed pH	563	groundwater investigation	n 1125
FEFLOW	441, 1035	Groundwater Modeling	125, 133, 163, 925
Felsendome Rabenstein	1165	groundwater protection	35
ferricrete	493	groundwater supply	213
Fe-Ti oxide deposits	1095	groundwater use	35
fiber optics	111	Groundwater Vistas	125
Field analysis	943	groundwater 47, 117, 20	1, 207, 469, 1035, 1105, 1131
filter	507	Groundwater-flow model	441
finite element analysis	1035	grouting	189
flow and transport modeling	35	guidelines	77
flow model	157		
flux and head targets	103	ГН	
forward modelling	281		
Frac-flowback	1199	hdraulic conductivity	451
Fracture deformation	139	HDS	717
fractured rock	91, 175	heap leach	849
fragmented aquifuge	219	HFO	519
freeze desalination	655	High Altitude	163
Freeze	507	high density sludge (HDS)	533
Fully grouted vibrating wire piezomet	ters 229	high surface area media	667, 749
		High-rate	755

high-resolution sampling	295	Issues	151
historic operations	1089	Italy	983
Historic sulphidic mine waste	625		
historic	1143	J	
humic substances	425		
humidity cells tests	245	jarosite	1011
HybridICE	507, 655		
hydraulic adit plug	1009, 1011	K	
hydraulic fracturing	1223, 1229		
hydraulic integrity	1193	karst water-filling coal field	911
Hydraulic properties	91	kinetic cells	331
hydrochemistry	911, 1211		
hydrodynamic containment	899	L	
hydrodynamics	1165		
hydrogeochemistry	257, 359, 1139	laboratory simulation	307
hydrogeology 111, 119, 151, 175, 195, 89	99, 1131, 1205	Lake Katwe	855
Hydrological impact assessment	405	leach pad	237
hydrological properties	861	leachate	875
hydrology drilling	881	leaching	391
hydrology	973	Lead	397, 525, 691
Hydrous Ferric Oxide: see HFO		Leadville	1237
		legacies	937
		legal and regulatory	1223
		Lewatit monoPlus S108	655
Impoundments	1217	Life of Mine	867
in situ water sampler	295	lignite mining	611, 925
inflow prediction	133	lime precipitation	533
in-lake treatment	741	limestone aquifers	189
Innovative treatment	919	Limestone	717
inorganic membranes	735	liming	741
internet based	301	limit	365
Ion rejection	563	long term metal release	905
IRM	525	Long-Term	747
iron fertilization	605	low cost	525
iron incrustation	905	low molecular weight organic acids	425
iron oxidation rate CO ₂ degassing rate	949	Lubin region	1139
iron oxidation rate	319	Lugeon	195
iron oxidation	599	lutocline	371
iron oxyhydroxide filter	551	lysimeter	169
iron pyrite	475		
iron removal	667, 749	M	
Iron	463, 691		
iron-rich material	525	management	77, 873, 887, 1151
irrigation	417	Manganese	691
Iso-electric point	563	Marinobacter	613
Isothermal Evaporation	855	mathematical model	201
isotope fractionation	611	membrane	649

mercury mining		300	Minewater	383
mercury		539	mining application	35
Mesocosm		383	mining hydrology	47 133
metal binding prote	ins	8/3	mining impact	169
metal contaminants	3	525	mining influenced w	rater (MIW) 533, 575, 581
metal mine water	-	1173	mining legacy	1173
metal pollution		1067	Mining Modeling	469
metal recovery		720	mining	63 110 125
metal sulfides		603	Minnesota	1117
metals removal		661	Missouri	337
microbial diversity		613	mixing equation	181
microbial iron oxid:	ation	287	model validation	130
microbial sulfate rec	luction	919	modeling	47 207 365 377 849 887 1125
microfiltration	auction	649	MODFLOW	201 269
mid-conference tou	r	1237	MODELOW-SURFACT	·
mill tailings	-	1047	monitoring	402 825 821 1002 1157 1205
mine closure	227 1000 1	020 1007 1105 1111	MSWI ashes	493, 023, 031, 1003, 1137, 1203
Mine deposits	237,1009,1	1061	multidisciplinary	1055
mine dewatering		201	mannaiscipinnary	1055
mine discharge		60	I N	
mine drainage		1157	1	
Mine dump		11/7	NAF lavering	241
Mine flooding prog	nosis	061	Namihia	25 47
mine flooding	10010	1081	nanofiltration	562 705
mine leachates		1001	nanonarticles	602 602
mine permitting		423 82	Natura 2000 protect	ion area 405
Mine Peru		717	natural attenuation	207
mine planning		122	Navaio Sandstone	1211
mine reclamation		642 1072	net-alkaline	667 740
mine tailings		502	neutral mine drainad	Je 10/1
mine voids		395 475	neutral mine water	50 1041
Mine waste geocher	nietry	473	neutralised mine wat	+CC 50
mine waste geoener	iiisti y	201 1110	Nevada	417
mine water manage	ment	222 425 812 1047	Nickel	
mine water manage	mem	1111 1125	nion Exchange Cana	525, 545, 015, 019, 091
mine water quality		251	nitrate	610
mine water release i	egulation	231	Nitrogen source	225
Mine water sources	nroportions	181	NMFD	545 62
mine water treatme	nt	551 557	nuisance constituent	ts 670
mine water	257 AA1 525	605 612 622 600	Numerical Modeling	110 212
mille water	207,441,525 875 8	00 1061 1007 1120	nutrient exhaustion	262
Mine	029,0	872	nutrient exhlustion	205
MINEDW		075 157	0	
mineral salts		+37 8		
mineral solubility		10/1	ochre	E10
mineralogy		1041	oil and gas	519 1220
MineSite		400	Oil sands	1229
		123	- 11 DM1140	5/1

olorado	499	POSTGRES	1105
Omitiomire Copper Mine	35	potash	105
open water table	169	precipitation	307
open-pit coal mining	181	Predicting	831
open-pit	125	predictions	435, 463
Operations	873	predictive modeling	955
opper	691	Preventing and Controlli	ing Technology and
optimal grouting strata	219	Equipment	831
optimize	735	prevention	245
Ordovician limestone	893	Principal Component Ar	nalysis 429
organic carbon	1095	proactive monitoring	359
Otjikoto Gold Mine	35	probabilistic model	867
oxicology	499	probable hydrologic con	sequences 1073
oxidation	365, 475	produced water	1187, 1199, 1217, 1223, 1229
		protozoa	619
P		public participation	41
-		pumping test	213
packer testing	195	Purification	699
Passive barrier	1017	PXRD	281
passive treatment	581, 587, 599, 673, 1111	pyrite	955
passive	525		
PCGEOFIM	925	Q	
peat	545		
permeability	887, 1193	quality	1003
Permitting	469	Quaternary gravel pack r	material 905
Perpetual management	53		
Petrel	125	R	
рН	463		
PHAST for Windows	411	radionuclides	1145
phosphate	619, 619	radium	1097
photochemistry	973	rare earth elements	447, 973
PHREEQC	397, 411, 1105	rate	365
physical	861	raw and discard coal	875
piezometeric head	229	reaction paths	281
pipeline scaling	287	reactive transport	377
piper diagram	911	re-aeration	679
pit lake chemistry	353	recharge channels	881
Pit Lake 59, 405, 741, 955, 102	9, 1041, 1055, 1073, 1105	reclemation	967
pit slope depressurization	125	redox	359
pit wall runoff	353	Regional aquifer	91
planning	1125	regulations	41
platinum-group metals	1117	regulatory	63
Poland	257, 1139	remediation	383, 681, 747, 983, 1047, 1131
pollution atlas	1179	re-rising groundwater le	vels 925
pollution	613, 619	resuspension	371
post-closure monitoring	41	reuse	819
post-conference tour	1241	rganic Matter Content (C	DMC) 451

rice husk	587	Static and kinetic tests	875
risk assessment	189, 989	static tests	275, 331
risk of abandoned mines	1173	statistical analysis	83
riverbed extension measures	925	stemming flow	1009
Rudna mine	1139	strata reinforcement	219
		strategic water risks	813
S		stratification	1003
		stream recovery	639
saline water	105	stream restoration	643
salinity	71	Stream sediments	429
salt mine	257	stream tracer	493
Saxony	1165	sulfate reducing bacteria	325
scaling factors	251	sulfate reducing bioreactor	1023
screening level assessment	943	sulfate reduction	325
seasonal variations	295	sulfate-reducing bacteria	587
sediments	399	sulfide mine waste	275
seepage chemistry	487	Sulfide	365, 717
seepage	347	sulfidic mining waste	513
selective chemical extraction	313	sulphate	687, 699
selenium biological water treatment	711	surface gas emanation	989
selenium removal	723	surface water	201, 399, 469, 1117
Sequence Batch Process	417	suspended solid	837
sequestration	673	sustainability reporting	69
sewage sludge	681, 977	sweetmeat waste	263
Sewage	691	Sydney Coalfields	441
Short and long term solutions	417	system upgrade	867
silver	397	, 10	
Silverton	1241	T	
site investigation	1125		
slimes	875	tailingstailings consolidation	269
slope depressurization	139	tailings management strategies	593
Sludge	755	tailings pond	371
soda ash	919	Tailings Storage Facility (TSF)	457, 819
sodium adsorption ratio	1187	tailings water treatment	539
solid phases	1061	tailings 269	9, 347, 405, 967, 1143
solution chemistry	625	technological solution	741
sorption	377	temperature	111, 687
source control	347	test analysis	145
South Africa	429	thermal budget	849
Southeast Idaho Phosphate District	487	three-dimensional image	1151
speciation	481	Total Dissove Solids (TDS)	457
spectral analysis	995	toxicity	481, 679
Spinner logging	175	trace elements	513
sprinkler irrigation	807	trace metals	313, 1041
St. Louis River	1095	tracer test	1165
Stability Analysis	163	tracers	967
stable isotope	911	tracing experiment	881

trading		71	water infiltration	837
transpo	ort modeling	411	water inrush	189, 219, 893
transpo	ort	1017	water licence requirements	and expectations 1089
treatme	ent technologies	633	Water losses	807
treatme	ent	481, 525, 825, 1125	water management strategy	813
TSS		371	water management	819, 967, 1081
			water quality modeling	251, 1055
U			water quality permits	63
			water quality	77, 435, 1029, 1089, 1157
Underg	round cavern storage	1205	water resources	269
underg	round mines	91, 1081	water reuse	539
underly	ving karst aquifer	219	water shortage	867
unsatui	rated flow	849	water sources	1223
update		223	Water supply	105
Upper S	Silesia	1061	water treatment	649, 661, 723
Uraniu	m surface complexation	411	water	873, 1003
uraniur	n 347, 377, 551, 7	755, 1017, 1081, 1097	watershed	69
useful r	nodels	223	wavelet analysis	995
USEPA		63	Weak Acid Dissociable (WAI	D) 457
Utah		1211	weathering	391
			well performance	861
V			WET	337
			wetlands	425
vanadiı	ım	613	Whole Effluent Toxicity	337
vegetat	ion	931	wire-line packer system	195
vertical	flow bioreactors	679	Witbank coalfied	875
			Witwatersrand	475, 937

| W

		Z	
wastewater treatment	337		
wastewater	619	zeolite	569
water balance	169, 181, 223, 867, 1111	zinc	383, 397, 493, 499, 525, 691, 729
water bursting source	911	Zn-removal	557
water disposal	1211		

IMWA - INTERNATIONAL MINE WATER ASSOCIATION

Application Form	
Inividual or Student Member	
Name and Surname	
Title/Major	www.IMWA.info
Business Name and Address	
Telephone No Fax No	E-mail
Residence Address	
Telephone No Fax No	E-mail
For student membership only: University and the anticipated year	ar of graduation
Please indicate address for correspondence:Image: BusinessMembership Class (Please check one):Individual	ResidenceStudent (less than 30 years)
Date of Birth Country	of Birth
Citizenship	
Signature	Date of Application
Payment enclosed for calendar year(s) 20□Individual Member:EURO €50.00 annually or payment by□Student Member:EURO €25.00 annually or payment by	Credit Card: EURO €53.00 Credit Card: EURO €27.00
Use current exchange rate to convert EURO to US Dollars when the Treasurer!	sending checks. Do not send EURO checks to
Method of Payment:	
□ Check** □ Wire funds transfer*** □ □ Visa Card* □ MasterCard* □	Invoice web page http://www.IMWA info/card
* Name on Card:	Security code:
Card N°:	_ Exp. Date:
Signature:	
** Please send US checks payable to IMWA to: *** Ple	ase wire funds to:
Dr. Lee C. ATKINSON (Treasurer) c/o Itasca Denver, Inc. 143 Union Blvd. Suite 525 Lakewood, CO 80228, USA Telephone: +1 303 969-8033 Fax: +1 888 611-7938	send an e-mail to Treasurer@IMWA.info to obtain our bank account details. Please note that a \$US 7 bank fee will apply for payments to IMWA's US account

IMWA - INTERNATIONAL MINE WATER ASSOCIATION

Application Form

TRAINING AND EXPERIENCE (Please use extra sheet if necessary)





The 2013 International Mine Water Association Conference at the Colorado School of Mines takes place at a time of rapid growth in global mining and concomitant increase in mine water use and discharge.

Sustainable mining requires reliable mine water technology, to ensure that mining will meet all resource and environmental protection goals, and to assure all stakeholders that their water resource interests will not be adversely impacted by mining.

IMWA 2013 covers the state of the art and practice in reliable mine water technology, with over 200 papers on mine water use, mine water flow and control, mine water treatment and quality protection. It showcases the remarkable progress achieved in regulation, evaluation, use, extraction, treatment, and discharge of mine water, which makes mine water use and protection reliable and mining hydrologically and geochemically sustainable.

CONFERENCE THEMES

- I 🗩 Mine Water Permits and Regulation
- 2 m Mine Water Hydrology
- 3 🥂 Mine Water Geochemistry
- 4 **Mine Water Treatment**
- 5 📻 Mine Water Operations
 - Mine Water Closure

6

7 🎹 🛛 Mined Hydrocarbon Water

