Characterising Environmental Risks Associated with Sulfide-bearing Gold Wastes

Alexander K.B. Opitz[1], Megan Becker[2,3], Susan T.L. Harrison[4,5], Jennifer L. Broadhurst[6]

[1]*Minerals to Metals Initiative, University of Cape Town, South Africa, optale001@myuct.ac.za*
[2]*Centre for Minerals Research, University of Cape Town, South Africa, megan.becker@uct.ac.za*
[3]*Minerals to Metals Initiative, University of Cape Town, South Africa, megan.becker@uct.ac.za*
[4] *Centre for Bioprocess Engineering Research, University of Cape Town, South Africa, sue.harrison@uct.ac.za*
[5]*Minerals to Metals Initiative, University of Cape Town, South Africa, sue.harrison@uct.ac.za*
[6]*Minerals to Metals Initiative, University of Cape Town, jennifer.broadhurst@uct.ac.za*

Abstract

Acid rock drainage (ARD) is one of the most significant environmental challenges associated with the mining of hard-rock sulfidic ores and coal. Environmental hazards associated with ARD generation concern the formation of acidic pollution, which often contains elevated concentrations of deleterious elements and soluble salts. Current characterisation methods tend to mainly focus on the potential for acidity generation under chemical conditions as a proxy for ARD formation, with little initial attention to the risks associated with the elevated elemental concentrations.

This study demonstrates the application of a suite of techniques for the relatively rapid and integrated characterisation of the potential risks associated with acidity generation and the deportment of deleterious elements from two sulfide-bearing gold wastes. The results demonstrate that the novel biokinetic test can be used to validate and compliment the static chemical ARD predictions tests, providing useful information on the relative rates of the acid forming and acid neutralising reactions under conditions of microbial activity. Quantitative information on the mineralogical composition of acid forming and acid neutralising minerals assists in the interpretation of the geochemical test work, with the sequential chemical extraction test provides valuable information on the distribution and potential environmental risks of minor and trace metals.

Key words: Acid rock drainage, environmental risk, mine waste characterisation, metal deportment

Introduction

The extraction of metals from ores generates large amounts of waste material through both mining and mineral processing practice. The environmental effects arising from the disposal of such wastes are far reaching and long-term (Koehnken et al., 2003), with formation of water pollution originating from the runoff of mine waste disposal sites being a major polluting factor. For sulfide-bearing wastes, the generation of acid rock drainage (ARD) is of particular concern. Characterised by low pH values, the highly acidic nature of the solution results in the mobilisation of deleterious elements contained within the mine waste (Nordstrom (2011). The ecological impacts of pollution from gold mine wastes are often cumulative and their true impact may only be felt long after mining activities have ceased (McCarthy, 2011). Most commonly observed, are the immediate effects to the local flora and fauna; however, the contamination of water sources may lead to far-reaching consequences. In a study of the rivers and water sources surrounding the Witwatersrand basin, Durand (2012) reported significant detrimental effects to local communities who use contaminated groundwater for drinking and subsistence farming purposes. The environmental damage is not limited to animals, but may affect the local soils, due mainly to the accumulation of heavy metals and salts (Kitula, 2006). Reliable characterisation of the environmental risks associated with drainage runoff emanating from mine waste, therefore, requires independent assessment of the potential to form acidity and the deportment of deleterious elements.

Evaluation of the ARD potentials of waste samples occurs through the use of standard ARD characterisation and prediction tools which assess the potential of waste samples to generate acidity. The independent quantification of the inherent acid neutralising and acid forming potentials is achieved through the use of laboratory-scale test work, with the difference between the values used to assess overall acidity generation (Price, 1997). Following the classification of the samples, kinetic tests are performed on those which show acid generating potential, or for which some uncertainty in the classification is observed. These tests are aimed at characterising the temporal behaviour of the ARD generation and the composition of the resulting pollution with time (Parbhakar-Fox and Lottermoser, 2015).

Although results from the standard static characterisation tests provide a rapid assessment of the overall acid generating potential, these results are limited to the extreme chemical condition of the test methods. Thus, no information is gained on the potential for ARD generation under microbial conditions most commonly experienced within waste deposits (Hallberg, 2010). The recent development of the biokinetic tests to account for microbial action has been demonstrated on base metal wastes (Hesketh et al., 2010), gold wastes (Dyantyi et al., 2013) and coal ultrafine wastes (Opitz et al., 2015). Furthermore, the exclusive focus on the potential for acidity generation as a proxy for ARD formation results in a lack of information regarding the deportment of deleterious elements from the waste sample during the characterisation step, particularly the environmental consequences associated with the elevated elemental concentrations within neutral drainage (Plante et al., 2010). These samples are classified as non-acid generating and are, as per the standard screening protocols, not subjected to further test work (Parbhakar-Fox and Lottermoser, 2015).

Measurement of the elemental concentrations in solutions resulting from the static characterisation test may provide information regarding metal deportment under severe conditions, with the addition of sequential chemical extractions allowing for semi-quantitative information of elemental deportment under disposal conditions (Opitz et al., 2015). The inclusion of a detailed mineralogical assessment, allows for a fundamental understanding of the geochemical behaviour of waste samples within ARD characterisation tests (Becker et al., 2015). The inclusion of mineralogical analyses of waste samples in the current characterisation toolbox, either as a co-current characterisation step (Maest et al., 2005) or as preceding characterisation step itself (Parbhakar-Fox et al., 2013), has been suggested previously. However, the integration of such analyses within the common ARD characterisation protocols remains limited.

The present study was undertaken to demonstrate the combined application of techniques for the rapid and effective characterisation of the potential environmental risks associated with two wastes from the extraction and primary processing of different sulfide-bearing gold ores.

Material & Methods

Gold waste samples

Two mine waste samples were used in the completion of this study. Sample A was sourced from a greenstone belt gold deposit. The second waste sample (B) was sourced from a historical tailings dam, generated during the processing of a Witwatersrand gold ore deposit. The compositions of the two waste samples are presented in Figure 1 (Opitz et al., 2016). Acid generating minerals consist of predominately pyrite (A:1.2 wt. %, B: 0.3 wt. %) and pyrrhotite (A: 5.8 wt. %, B: 0.1 wt. %), with small (< 0.1 wt. %) concentrations of other metal sulfides. These trace phases consist predominately of chalcopyrite, galena, and pentlandite. Acid consuming phases within the waste samples consist predominantly of fast-weathering carbonates (A: 0.9 wt. %, B: 0.01 wt. %), with intermediate-weathering silicates such as chlorite (A:1.4 wt. %, B: 1.4 wt. %) and slow weathering Fe-oxides phases such as magnetite (A: 33.4 wt. %, B: 1.9 wt. %) also present. The majority of the waste samples, however, consist of non-reactive silicate minerals such as quartz (A:26 wt. %, B: 70.9 wt. %) and plagioclase (A: 13.5 wt. %, B: 23.9 wt. %).

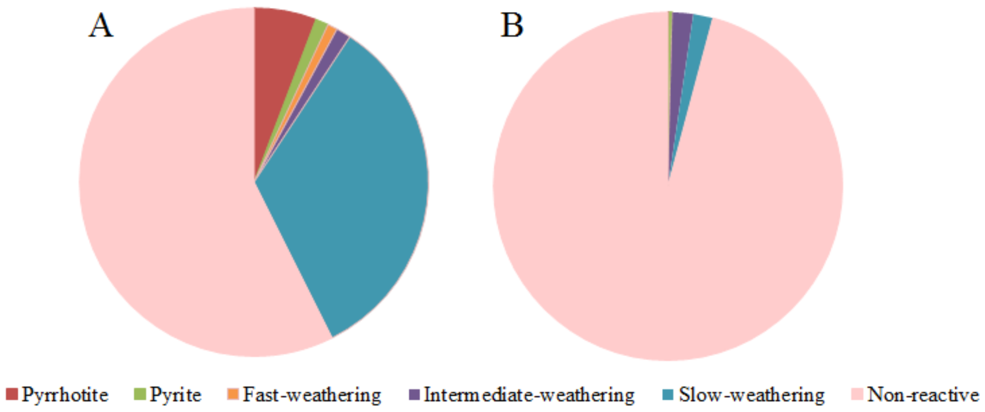

Figure 1: *Results from the mineralogical analysis using QEMSCAN on the two gold waste samples indicating the acid generating minerals, pyrite and pyrrhotite, and acid consuming minerals, carbonates, chlorite and magnetite as fast-, intermediate- and slow-weathering respectively, and non-reactive mineral phases.*

Characterisation of the ARD potentials

The ARD potentials of the waste samples were estimated directly from sample mineralogy in accordance with the method developed by Paktunc (1999) using the difference in the theoretical acidity generated by the acid-forming minerals and consumed by the acid-neutralising phases. Standard acid base accounting tests (ABA, Lawrence and Scheske (1997)) were used to calculate the maximum potential acidity (MPA), on the basis of LECO analysis of total sulfur, and the acid neutralising capacity (ANC), determined empirically, of the waste samples. These tests were performed in conjunction with net acid generation tests (NAG, Miller et al. (1997)) in triplicate. To assess the potential for ARD generation, biokinetic tests were performed according to the method outlined by (Opitz et al., 2016) at 37 °C for 90 days.

Sequential chemical extraction tests

Sequential chemical extraction tests were performed using a method outlined by Broadhurst et al. (2009). In this test, the waste sample is subjected to a sequential chemical leach protocol, to determine the distribution of metals to seven different fractions: water soluble, ion-exchangeable, carbonate, amorphous Fe/Mn-oxide, crystalline Fe/Mn oxide, sulfide and residual/inert.

Environmental risk assessment

The environmental risks associated with the deportment of the deleterious elements were assessed using a ranking and scoring method as outlined in Broadhurst and Petrie (2010). Here, elements are ranked and scored according to their potential environmental significance, as determined from their leachable concentration levels derived from the SCE tests, their acceptable risk concentrations as derived from water quality limits (DWAF, 1996), and their typical crustal abundance. Elements of interest were identified on the basis of common deleterious elements within gold waste deposits (Opitz et al., 2016), with the deportment of As, Cu, Cr, Ni, Pb and U presented. Elemental concentrations were quantified using induced coupled plasma mass spectrometry (ICP-MS) analysis using a Thermo-Fisher X-series II quadruple ICP-MS machine.

Results & Discussion

Characterisation of the potential for acidity generation

- Mineralogical assessment

The results in Table 1 indicate that both samples can be classified as potentially acid generating due to the greater quantities of acid forming phases relative to the acid neutralising phases. The higher acid forming potential for Sample A, as compared to that observed for sample B, can be attributed to the greater quantity of pyrrhotite and pyrite minerals (see Figure 1). Similarly, the higher content of the fast-weathering minerals resulted in a greater acid-consuming potential for sample A, as compared to sample B where the majority of the acid-consuming minerals were intermediate- and slow-weathering phases.

Table 1: *Theoretical ARD estimates using the mineralogical composition*

Sample	Acid-forming Potential [kg H_2SO_4/ton]	Acid-consuming Potential [kg H_2SO_4/ton]	ARD Estimate [kg H_2SO_4/ton]	ARD Classification
A	83.9	9.1	74.8	Potentially acid forming
B	6.7	0.3	6.4	

- Static ARD characterisation tests

Significant discrepancies were observed in the quantitative acid generating and acid neutralising results between the mineralogical and static ARD tests (Table 2). The observed differences in the AP and MPA calculations were due to differences in the sulfide values obtained from the chemical and mineralogical analysis, with the LECO total sulfur method resulting in lower sulfide sulfur (A: 2.3 wt. %, B: 0.06 wt. %) than that calculated from the pyrrhotite and pyrite contents (A: 2.8 wt. %, B: 0.2 wt. %). In an assessment of different methods for the determination of total sulfur in geological samples, Czerewko et al. (2003) observed significant under-estimations in the total sulfur content for low-sulfur samples using LECO analysis. For the samples in this study, an under-estimation in the total sulfur content would explain the lower MPA values as compared to the AP values estimated directly from the sample mineralogy. The differences in calculated acid consuming potentials may be attributed to the presence of intermediate- and slow-weathering minerals not being accounted for in the mineralogical estimates. Previous studies (Becker et al., 2015) have indicated partial dissolution of these mineral phases under the relatively aggressive ANC test conditions, resulting in a higher neutralising capacity than that predicted from quantification of the fast-weathering acid neutralising minerals.

Although differences were observed between the mineralogical estimates and the static ARD test results, the overall ARD classification was the same for all the tests in the case of sample A. Similarly, the NAPP results suggests a potentially acid generating classification ($-20 < \text{NAPP} < 20$) corresponding to that from the mineralogical estimate in the case of sample B. The elevated NAG pH value ($\text{pH } 4.0 < \text{NAG pH}$), however, suggested a “non-acid forming” classification for this sample. The overall classification of the ARD potential for this sample, therefore, remained uncertain due to these discrepancies.

Table 2: *ARD test results following static characterisation tests performed in triplicate*

Sample	MPA [kg H_2SO_4/ton]	ANC [kg H_2SO_4/ton]	NAPP [kg H_2SO_4/ton]	NAG pH [kg H_2SO_4/ton]	ARD Classification
A	70.2 ± 0.7	53.2 ± 1.8	17.0 ± 1.9	2.5 ± 0.0	Potentially acid forming
B	1.9 ± 0.4	3.9 ± 0.5	-2.1 ± 0.3	6.5 ± 0.1	Uncertain

- Biokinetic tests

The pH profiles within biokinetic tests provided an indication of the relative rates of acid formation and acid consumption under the acidic, microbial conditions (Figure 2). The observed initial rise in solution pH for sample A can be attributed to the dissolution of the fast-weathering carbonate minerals. The rapid decrease in solution pH thereafter, was due to ferric iron precipitation and, below pH 3.5, sulfide mineral oxidation using ferric iron, as (re)generated by Fe-oxidising micro-organisms. The biokinetic test results confirmed the potentially acid generating classification of sample A as characterised by the static tests and mineralogical evaluation.

For sample B, the lack of initial changes in solution pH was indicative of the lack of fast-weathering carbonate minerals within the waste sample, consistent with the mineralogical composition (Figure 1). The subsequent absence of significant changes in solution pH with time further indicated no net acidity generation or consumption within the tests, with any acidity generated from the oxidation of the sulfide minerals neutralised by the intermediate- and slow-weathering minerals. The slight increase in solution pH was attributed to a combination of the addition of distilled water to account for the volumes lost to evaporation, and the acid consumption of the intermediate- and slow-weathering mineral phases as determined from sample mineralogy. The biokinetic test results supported a non-acid forming classification for waste sample B as opposed to the potentially acid forming classification from the acid-base accounting and mineralogical estimates.

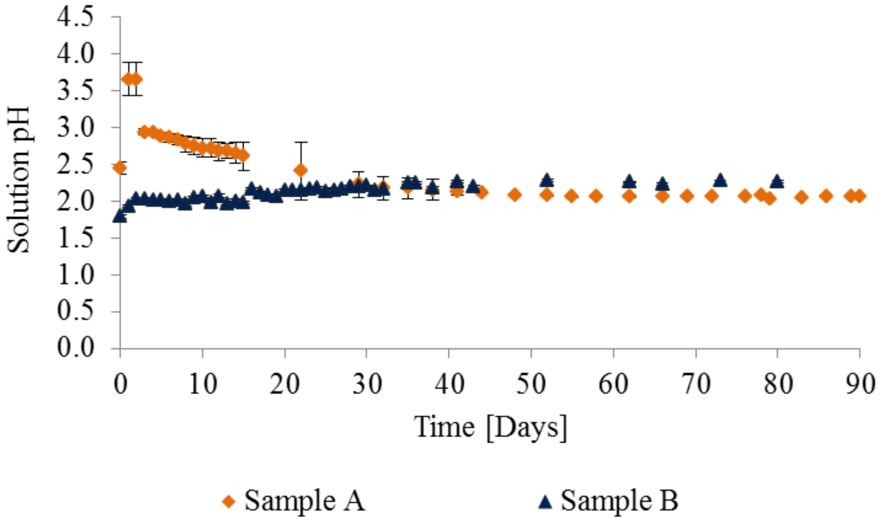

Figure 2: *pH profiles from biokinetic tests performed at 37 °C on waste samples A and B.*

Sequential chemical extraction (SCE) tests

Leachable element concentration levels and relative extents of mobilisation under the SCE tests conditions are presented in Table 3 and Figure 3 respectively. A comparison of results in Table 3 indicates that, whilst leachable concentrations of Cr and the base metals Ni and Cu are higher in sample A, sample B contains higher leachable levels of the toxic elements, Pb, U and, in particular, As. Furthermore, the relatively high mobility of elements in the leach stage 1-5 for waste sample B is indicative of the weathered nature of the sample. This is consistent with the origin of the waste, indicating previous oxidative dissolution of primary sulfide minerals such as arsenopyrite, chalcopyrite, galena, pentlandite and uraninite, and the subsequent re-precipitation of the solubilised metal ions in the form of more reactive secondary minerals and salts. The latter mineral forms are more likely to be readily available for dissolution at circa-neutral pH values and non-oxidative acid leach conditions within the waste deposit.

Although a fairly significant percentage of the As, Pb and U in Sample A is mobilised in the first 5 leach stages, indicating some weathering, leachable concentrations in these stages remain relatively low. The majority of the Cr, Cu and Ni, furthermore, was associated with the primary sulfide phase, and only mobilised under acidic, oxidative leach conditions (stage 6). This was congruent with the sample mineralogy which indicated a significant association of the Cr, Cu and Ni with primary chromite, chalcopyrite and pentlandite minerals respectively.

Table 3: *Leachable elemental concentrations from the SCE tests for sample A and Sample B showing concentrations available for deportment*

Element	Sample A [mg/kg]				Sample B [mg/kg]			
	Stages 1-3	Stages 4-5	Stage 6	Total (Stages 1-6)	Stages 1-3	Stages 4-5	Stage 6	Total (Stages 1-6)
As	2.2	0.7	2.5	5.3	4.5	64.7	27.1	96.3
Cr	5.8	50.0	403	459	1.7	8.7	25.4	35.8
Cu	1.2	12.3	68.3	81.7	70.6	99.5	9.7	180
Ni	15.6	30.0	210	255	7.5	8.7	11.1	27.3
Pb	3.2	3.0	2.3	8.5	13.7	99.6	4.6	117
U	0.1	0.2	0.3	0.7	23.2	5.2	3.7	32.1

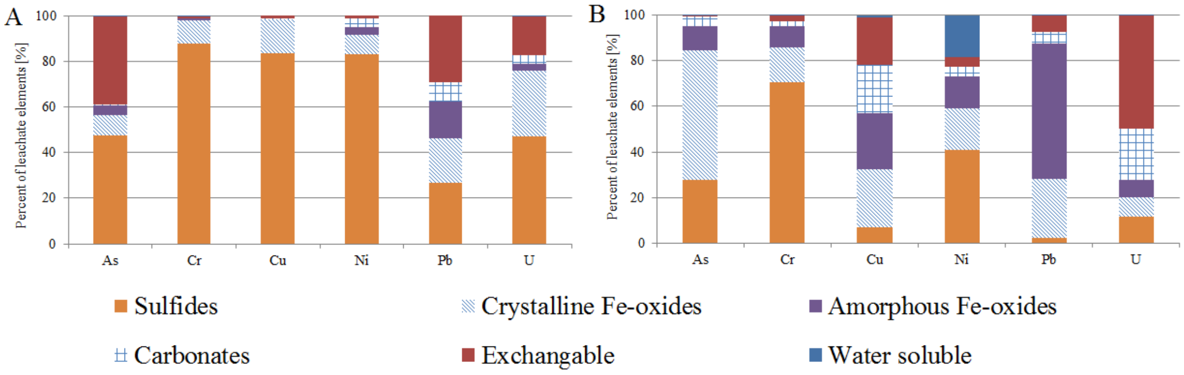

Figure 3: *Relative extents of mobilisation of leachable elements during sequential chemical extraction (where 100% represents the total leachable concentrations over the 6 stages presented)*

Environmental risk assessment

The risks associated with the elemental concentrations from the SCE tests are presented in Table 4. As a result of the relatively low concentrations of leachable elements in sample A, particularly in readily soluble forms (SCE stages 1-5), only Ni and, to a lesser extent, Cr pose a potential risk to the environment, and then only under oxidizing acid leach conditions. As indicated above, this can probably be attributed to the dissolution of primary pentlandite (Ni) and chromite (Cr) under the relatively aggressive leach conditions consistent with stage 6 of the SCE test

The relatively high concentrations of leachable elements and weathered nature of sample B, however, resulted in a significantly higher environmental risk profile, even under relatively mild leach conditions. In particular, a significant environmental risk was associated with the deportment and potential release of As, U and Pb. The relatively high levels of leachable Pb, As and, in particular, U in the water-soluble and carbonates fractions (Table 3 and Figure 3) indicates, furthermore, that this sample may pose a risk to the environment even under circa-neutral and weakly acidic pH conditions. Exposure of the sample to more acidic waters is likely to result in further dissolution of As and Pb at environmentally significant levels, whilst conditions conducive to oxidative dissolution of sulfide minerals may pose an additional risk due to further release of high levels of soluble As.

Table 4: *Environment risk assessment of elemental deportment measurements from SCE tests on wastes samples A and B*

Environmental Significance	Risk factor	Sample A			Sample B		
		Stages 1 - 3	Stages 4-5	Stage 6	Stages 1 - 3	Stages 4-5	Stage 6
High	> 10			Ni	U	As, Pb	As
Moderate	1–10			Cr	As, Pb		
Low	1	Ni	Ni	As		U	Pb, U

Concluding Remarks

The current study highlights the use of a combination of mineralogy, geochemical and chemical leach tests, together with a simple environmental risk assessment method to provide a rapid characterisation of the acid-generating potentials and trace metal deportment risks associated with sulfide-bearing wastes. The integration of the results allowed for an understanding of the minerals responsible for the acid-generating behavior of the waste samples, and the conditions under which the elemental deportment is likely to occur. This information is key in providing guidance for more detailed risk assessment procedures, and to inform relevant risk mitigation strategies.

Acknowledgements

This work is based on research supported by the National Research Foundation (NRF) of South Africa (Grant Number 86054), and on research supported by the South African Research Chairs Initiative (SARChI Chair in Minerals Beneficiation, held by Prof. D. Bradshaw). 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.

References

BECKER, M., DYANTYI, N., BROADHURST, J. L., HARRISON, S. T. L. & FRANZIDIS, J. P. 2015. A mineralogical approach to evaluating laboratory scale acid rock drainage characterisation tests. *Minerals Engineering,* 80, 33-36.

BROADHURST, J. L., MALULEKE, W. J. & VON BLOTTNITZ, H. 2009. Comparison and Application of Sequential Chemical Extraction Techniques for Metal Speciation in Sulphidic Copper Tailings1.

BROADHURST, J. L. & PETRIE, J. G. 2010. Ranking and scoring potential environmental risks from solid mineral wastes. *Minerals Engineering,* 23, 182-191.

CZEREWKO, M., CRIPPS, J., REID, J. & DUFFELL, C. 2003. Sulfur species in geological materials—sources and quantification. *Cement and concrete composites,* 25, 657-671.

DURAND, J. F. 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.

DWAF 1996. South African Water Quality Limits. Pretoria.

DYANTYI, N., BECKER, M., BROADHURST, J. L., HARRISON, S. T. L. & FRANZIDIS, J. Use of mineralogy to interpret laboratory-scale acid rock drainage prediction Tests - A gold case study. World Gold 2013, 2013 Brisbane, Australia. AusImm, 159-526.

HALLBERG, K. B. 2010. New perspectives in acid mine drainage microbiology. *Hydrometallurgy,* 104, 448-453.

HESKETH, A. H., BROADHURST, J. L., BRYAN, C. G., VAN HILLE, R. P. & HARRISON, S. T. L. 2010. Biokinetic test for the characterisation of AMD generation potential of sulfide mineral wastes. *Hydrometallurgy,* 104, 459-464.

KITULA, A. 2006. The environmental and socio-economic impacts of mining on local livelihoods in Tanzania: A case study of Geita District. *Journal of cleaner production,* 14, 405-414.

KOEHNKEN, L., CLARKE, N., DINEEN, R. & JONES, W. Present staus of remediation of Mt Lyell acid drainage. Sixth International Acid Rock Drainage Conference, 14-17 July 2003 Cairns, Australia. 65-70.

LAWRENCE, R. W. & SCHESKE, M. 1997. A method to calculate the neutralization potential of mining wastes. *Environmental Geology,* 32**,** 100-106.

MAEST, A. S., KUIPERS, J. R., TRAVERS, C. L. & ATKINS, D. A. 2005. Predicting Water Quality at Hardrock Mines.

MCCARTHY, T. S. 2011. The impact of acid mine drainage in South Africa. *South African Journal of Science,* 107**,** 01-07.

MILLER, S. D., ROBERTSON, A. & DONAHUE, T. Advances in Acid Drainage Prediction using the Net Acid Generation (NAG) test. 4th International Conference on Acid Rock Drainage, 1997 Vancouver, BC. 533-549.

NORDSTROM, D. K. 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.

OPITZ, A., BROADHURST, J. L. & HARRISON, S. T. Assessing Environmental Risks Associated with Ultrafine Coal Wastes Using Laboratory-Scale Tests. Advanced Materials Research, 2015. Trans Tech Publ, 635-639.

OPITZ, A. K. B., BECKER, M., BROADHURST, J. L., BRADSHAW, D. J. & HARRISON, S. T. L. The Biokinetic Test as a Geometallurgical Indicator for Acid Rock Drainage Potentials. The Third AusIMM International Geometallurgy Conference, 15-16 June 2016 Perth, Australia.

PAKTUNC, A. 1999. Mineralogical constraints on the determination of neutralization potential and prediction of acid mine drainage. *Environmental Geology,* 39**,** 103-112.

PARBHAKAR-FOX, A., LOTTERMOSER, B. & BRADSHAW, D. J. Cost-effectuve means for identifying acid rock drainage risks - Itegration of the geochemistry-mineralogy-texture approach and geomettallurgical techniques. The 2nd AUSIMM International Geometallurgy Conference, 2013 Brisbane, QLD.

PARBHAKAR-FOX, A. & LOTTERMOSER, B. G. 2015. A critical review of acid rock drainage prediction methods and practices. *Minerals Engineering,* 82**,** 107-124.

PLANTE, B., BENZAAZOUA, M. & BUSSIÈRE, B. 2010. Kinetic Testing and Sorption Studies by Modified Weathering Cells to Characterize the Potential to Generate Contaminated Neutral Drainage. *Mine Water and the Environment,* 30**,** 22-37.

PRICE, W. A. 1997. Draft guidelines and recommended methods for the prediction of metal leaching and acid rock drainage at mine sites in British Columbia. British Columbia Ministry of Employment and Invetment.