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 km^2 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 m^3 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 (Fe^{3+}) 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 (Fe^{2+}) type sludges. Therefore, Fe^{3+} is preferable to Fe^{2+}. Since Fe^{2+} is known to be present in the incoming wastewater a pretreatment step using oxidation was tested in bench and pilot studies to oxidize Fe^{2+} 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 bench-scale HDS testing. Titration and oxidant testing was performed at pH 8.8, 9.2, and 9.7. Oxidation was performed via hydrogen peroxide (H_2O_2) 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 (H_2O_2) 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 H_2O_2 somewhat below theoretical requirement for Fe and Mn oxidation at a steady 0.009 mol O_2/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 Fe^{2+}, 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 mol O_2/L	Cd (d) mg/L	Cu (d) mg/L	Fe (d) mg/L	Mn (d) mg/L	Zn (d) mg/L	SO_4 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 influent pilot results*

	Oxidant mol O_2/L	Cd (d) mg/L	Cu (d) mg/L	Fe (d) mg/L	Mn (d) mg/L	Zn (d) mg/L	SO_4 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

Table 2 *Low flow blend influent pilot results*

design was completed. Design parameters defined during bench and pilot testing were incorporated in the design and sizing of full-scale 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, Fe^{2+} 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 Fe^{2+} and Mn may require enhanced oxidation and higher operating pH to meet discharge standards. To neutralize and meet discharge pH requirements, a CO_2 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 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 full-scale 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 mg/L	Ba mg/L	Cd mg/L	Cr mg/L	Pb mg/L	Hg mg/L	Se mg/L	Ag 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

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 full-scale 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=06718550&agency_cd=USGS&format=html