

IN SITU CHEMICAL AND BIOLOGICAL TREATMENT LEADING TO SUCCESSFUL WATER DISCHARGE FROM ANCHOR HILL PIT LAKE, GILT EDGE MINE SUPERFUND SITE, SOUTH DAKOTA, U.S.A.¹

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Extended Abstract. The EPA Region 8 Superfund office and the EPA National Risk Management Research Laboratory (NRMRL) Mine Waste Technology Program (MWTP) have been conducting a field-scale technology demonstration of an in situ treatment of the Anchor Hill Pit lake at the Gilt Edge Mine Superfund site near Deadwood, South Dakota since March of 2001. The project goal was to develop cost and performance data of the treatment approach for potential application in long-term water treatment/management activities at the Gilt Edge site, as well as potential application at other similar sites. The Anchor Hill Pit initially contained approximately 265,000 cubic meters (70,000,000 gallons) of acidic mine water, with elevated metals (including iron, aluminum, selenium, copper, cadmium, and zinc), sulfate, and nitrate content and a pH of approximately 3. The water column was approximately 30 meters deep. The first step of the two-stage in situ treatment consisted of using a Neutra-Mill (essentially a floating lime slaker developed by Earth Systems, Pty. of Australia), to neutralize the pit pH to approximately 7 using lime (March 2001-May 2001). Following a short stabilization period, during which the pH “settled” to a value of approximately 5.0, a patented process for in situ pit lake treatment using an organic formulation of molasses, methanol, and proprietary ingredients was implemented as the second treatment step in May 2001 by Green World Science, Inc. (now licensed to ARCADIS US, Inc.) to create reducing conditions; stimulate bacterial activity for nitrate, selenium, and sulfate reduction; improve water quality; and create a stable system. Denitrification and sulfate reduction did occur, leading to much-improved water quality. The treatment phase of the project, along with site background information, is documented in Lewis (2003)³ and the reader is referred to that paper for treatment details. This poster focuses on subsequent efforts undertaken to discharge water from the pit from both above and below the chemocline; efforts undertaken to evaluate the pit for ongoing

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nitrate treatment at the Gilt Edge site; and efforts to predict the likelihood of turnover of the stratified pit water column and actions taken to decrease levels of dissolved hydrogen sulfide in the deep zone.

Anchor Hill Pit Conditions, Summer 2003.

By the summer of 2003, denitrification was complete and sulfate reduction was well under way. The dissolved form of metals which form sulfide precipitates (e.g., copper, cadmium, zinc) had decreased dramatically upon the onset of sulfate reduction. Due to the slow-settling nature of metal sulfides, the total recoverable values of those metals were significantly higher. In general, water in the pit met applicable South Dakota Ambient Water Quality Standards (SDAWQS) with the exception of un-disassociated hydrogen sulfide (H_2S) (i.e., dissolved H_2S as opposed to HS^-) and biochemical oxygen demand (BOD); the elevated BOD was due to the presence of remaining organic carbon as well as the elevated dissolved sulfide. In addition, the Anchor Hill Pit had become meromictic, with a chemocline at a depth of 6 to 9 meters (20 to 30 feet). Over the ensuing year leading to the summer of 2004, the pit water column became more strongly stratified, with the surface zone being aerated and meeting all applicable water quality standards, and the deep zone having increased dissolved H_2S (~50 mg/L) due to continuing sulfate reduction. The project team began focusing attention on how to potentially utilize the Anchor Hill Pit for future water treatment.

Successful Discharge of Water from Below Chemocline, Summer/Fall 2004.

While the surface water met discharge requirements, it was recognized that the strongly-reducing conditions in the deeper zone might have attributes worth maintaining for future use. While the strongly-reducing deep water condition was believed to be the result of overdosing the nutrients, and could be better managed if implemented in the future, most effective metal reduction and removal could be accomplished by maintaining a condition with strong reducing potential. The surface water was thought to be more vulnerable to disruptions such as contaminated surface runoff into the pit, which might easily result in metals such as cadmium or zinc increasing above their discharge limit, with no possibility of treatment by sulfide precipitation as in the deeper zone. The deeper zone was in general considered to be more stable and controllable. In addition, the overall treatment process might be more efficient since reducing conditions already existed, so carbon would not be needed to consume dissolved oxygen and establish anoxic conditions. It was envisioned that in the future, contaminated water from the site might be injected, along with nutrients, into the pit below the chemocline, with the surface layer simply serving as the “protective” layer over what could be consider the “treatment zone”. Certainly if this approach were pursued, the relative densities of the deep zone water and the contaminated water added for treatment would have to be considered. The decision was made to focus on discharging water from the deep zone. The elevated H_2S present in the deep water posed health and safety issues which were addressed and managed. Mitigation of the deep water chemistry was attempted by air sparging followed by the use of a lagoon to complete BOD reduction and solids settling, since the H_2S was oxidized to elemental sulfur, forming colloidal particles that were very slow to settle. Interestingly, metals were not remobilized by this sulfide oxidation, and approximately 570 cubic meters (150,000 gallons) of water was successfully discharged in October 2004.

Evaluation of Likelihood of Lake Turnover.

Concerns about the potential for a turnover-mixing event by the Meromictic lake was evaluated in October/November 2004. This was accomplished by evaluation of the Lake and

Wedderburn numbers, utilizing historical wind speed information from the site along with the estimated vertical density gradient in the water column. Results were that no vertical mixing would be expected under average recorded wind speeds of 4.5 meters per second (10 mph). Under sustained wind speeds at the maximum recorded value of 15.7 meters per second (35 mph), no hypolimnion mixing would be expected, but there would be potential for mixing of the metalimnion with the surface zone. A sustained wind speed of 28.1 meters per second (63 mph) would be required to produce conditions potentially leading to a turnover of the overall water column. This was considered very unlikely, and no further steps were deemed necessary to address the issue of elevated H₂S in the deep zone; however, reducing the H₂S levels in the deep zone did become a project objective.

Evaluation of Use of Anchor Hill Pit for Ongoing Site Water Treatment.

In parallel with the efforts focused on discharging deep Anchor Hill Pit water described previously, attention was also focused on how the pit might be used for ongoing water treatment. It was envisioned that water from the site could be injected with required nutrients under the existing chemocline, taking advantage of existing anoxic conditions and elevated sulfide, and resulting in rapid denitrification followed by sulfate reduction as seen previously in the pit. As part of the evaluation of injecting water for treatment below the chemocline, bucket tests were performed to gain further information about what results could be expected. Water from the Surge Pond at the site was selected for treatment, since it contained elevated nitrate (120 mg/l as N), was relatively neutral in pH, and had small amounts of dissolved metals present. Approximately 3.8 liters (1 gallon) of Surge Pond water along with 15.1 liters (4 gallons) of deep Anchor Hill Pit water was placed in each bucket. Nutrients sufficient to completely reduce the nitrate were added to one of the buckets, the other bucket received no nutrient addition. The buckets were placed at the 18.3-meter (60-foot) depth in the pit in July 2004, to both ensure no oxygen passed through the bucket wall, and that representative temperatures were maintained. The buckets were retrieved six weeks later. It was anticipated that some or all nitrate would be reduced, and that some of or all of the existing sulfide would be oxidized. The results indicated that sulfide was oxidized, but more significantly, nitrate was apparently reduced to ammonia. This was surprising, but upon investigation, it was found that nitrate ammonification is a known process occurring under extreme reducing conditions. Hydrogen sulfide can serve as an electron donor, along with other compounds. It appeared that a different type of nitrate-reducing bacteria were predominant in the deep water, relative to the oxic conditions existing at the start of the project. Judging by the lengthy time (almost two years) since the completion of denitrification, this is in retrospect not surprising. However, the reduction of nitrate to ammonia has very significant implications for the Gilt Edge mine site, since nitrate is present in varying amounts in essentially all waters existing on-site. Discharge limits for the site are 50 mg/l as N for nitrate, and approximately 3-5 mg/l as N for ammonia, depending on temperature and pH. These results caused the project team to abandon the concept of feeding site waters (with nutrients) below the chemocline for treatment, since nitrate is present in all site waters, and the risk of excessive ammonia production was considered too great. Abandoning the addition of site waters below the chemocline meant that use of the treatment process would have to be accomplished on a batch basis, and the deep zone could not be used as the primary reactor for ongoing water treatment at the Gilt Edge site.

Successful Discharge of Surface Water, 2005.

Having determined that (a) processing of the deeper sulfide-laden water for discharge is difficult and likely not economically viable; (b) use of the deep zone for ongoing water treatment is not feasible due to the risk of excessive ammonia production; and (c) therefore, use of the treatment technology in the Anchor Hill Pit would have to be done on a batch basis, it was decided to begin discharge of surface water. This reverted back to the original concept of placing a batch volume of water in the pit, neutralize as necessary, add nutrients, and let the biological treatment processes precede. Surface water would be removed at some rate consistent with sulfur settling through the water column, and enough water would be left in the pit to provide a reasonable cover for the less-stable, higher sulfide at the bottom of the pit. Excess sulfide would probably be present in all batches, due to the need for excess sulfide to drive dissolved copper, cadmium, and zinc down to very low dischargeable levels. However, as the chemocline would come closer to the surface as water is discharged; remaining sulfide would be oxidized to sulfur by interaction with the aerated surface zone. The issue would then be whether the sulfur residues can slowly settle fast enough to accommodate desired discharge rates as water levels drop, and the thermo/chemocline readjusts. Developing this approach began over the winter of 2004-2005.

In March of 2005, while the pit was still frozen over, approximately 16,250 cubic meters (4.3 million gallons, equating to approximately 1 vertical meter of water column) were removed from just under the ice surface, and successfully discharged. This was encouraging, and plans were made to discharge additional surface water and eliminate excess sulfide in the summer of 2005. Options for eliminating excess sulfide included addition of ferric iron salts, ferrous iron salts, and/or oxidants. After bench-scale testing was performed, it was decided to add sufficient 50%-strength hydrogen peroxide to the pit to stoichiometrically oxidize the sulfide present. This selection was made based on the fact that hydrogen peroxide would be the cheapest, it would be relatively easy to handle, and it would chemically mimic the reactions observed during the aeration and discharge of sulfide-laden deep water in summer 2004, i.e., it would result in production of elemental sulfur and should not remobilize metal sulfides.

Approximately 38,000 cubic meters (10 million gallons) of water meeting standards were successfully discharged from the surface of the pit between mid-July and mid-August 2005. Following this, approximately 19,000 kilograms of 50% hydrogen peroxide by weight were added to the pit on August 17-18, 2005. Initial results indicated that the hydrogen peroxide sank through the bulk of the water column and only oxidized sulfide below about the 14-meter (45-foot) depth, with excess hydrogen peroxide remaining below that depth. Subsequent mixing of deep- and mid-level waters by pumping from a shallower depth in one portion of the lake to a deeper depth in another portion of the lake appear to have been successful and as of October 2005 the excess sulfide in the deep water was significantly reduced to between 10 and 15 mg/L. It is likely that additional discharges of the surface water can resume over the winter of 2005-2006.

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Literature Cited

Lewis, N., K. Wangerud, B. Park, S. Fundingsland, J. Jonas. 2003. Status of In Situ Treatment of Anchor Hill Pit Lake, Gilt Edge Mine Superfund Site, South Dakota, USA, 6th International Conference on Acid Rock Drainage, July 2003.