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Bioremediation of Pit Lakes – Gilt Edge Mine

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Geochemical And
Redox-Mediated Bio-Transformation™
for
In Situ Pit Lake Remediation Of
Acid- And Metal-Toxic Mine Drainage

2001-2006 Treatability Study
Report of Results

ANCHOR HILL PIT LAKE
GILT EDGE MINE NPL SITE, SOUTH DAKOTA

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This publication is a report of work conducted under the Mine Waste Technology Program that was funded by the Environmental Protection Agency and managed by the Department of Energy under the authority of an Interagency Agreement.

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments, and groundwater; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This project was conducted under the Mine Waste Technology Program. It was funded by the EPA and administered by the U.S. Department of Energy (DOE) in cooperation with various offices and laboratories of the DOE and its contractors. It is made available at www.epa.gov/minewastetechnology by EPA's Office of Research and Development to assist the user community and to link potential users with the researchers.

Sally Gutierrez, Director
National Risk Management Research Laboratory

Abstract

The U.S. Environmental Protection Agency (EPA) Region 8 Superfund Office and the EPA National Risk Management Research Laboratory (NRMRL) Mine Waste Technology Program (MWTP) conducted a field-scale treatability study demonstrating an in situ bio/geochemical treatment technology for decontaminating acid/metal-toxic water within the Anchor Hill Pit lake at the Gilt Edge Mine Superfund site near Deadwood, South Dakota. The purpose of the project, carried out between March 2001 and May 2006, was to develop performance data of the treatment approach for potential use in long-term water treatment/management activities at the Gilt Edge site, as well as other similar sites. The treatment process was applied to approximately 72 million gallons of acidic water, with high concentrations of metals (including iron, aluminum, arsenic, selenium, copper, cadmium, and zinc), sulfate, and nitrate, and the pH was approximately 3.

The treatment process involved pit neutralization, then application of nutrients to stimulate biological activity. The treatment process was successful and approximately 40 million gallons of treated water that met the State of South Dakota’s strict surface water discharge standards were discharged from the Anchor Hill Pit during the demonstration. All project objectives were met, and considerable experience and insight was gained into how operational aspects of such a remediation technique would have to be designed for future efforts.

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Acronyms and Abbreviations

ARARs	applicable or relevant and appropriate requirements
ARD	acid rock drainage
BOD	biochemical oxygen demand
BOR	Bureau of Reclamation
CLP	Contract Laboratory Program
DOE	U.S. Department of Energy
EPA	U.S. Environmental Protection Agency
GWS	Green World Science, Inc.
IAG	Interagency Agreement Number
MSE	MSE Technology Applications, Inc.
MWTP	Mine Waste Technology Program
NRMRL	National Risk Management Research Laboratory
ORP	oxidation-reduction potential
pH	negative log of hydrogen ion concentration
QA	quality assurance
QAPP	quality assurance project plan
RMB^{TM}	Redox-Mediated Biotransformation
SC	specific conductance
SRB	sulfate-reducing bacteria
TSS	total suspended solids

Acknowledgments

This document was prepared by MSE Technology Applications, Inc. (MSE) for the U.S. Environmental Protection Agency's (EPA) Mine Waste Technology Program (MWTP) and the U.S. Department of Energy's (DOE) Environmental Management Consolidated Business Center. For this project, Ms. Diana Bless was EPA's MWTP Project Officer, while Ms. Norma Lewis was EPA's MWTP Project Manager. Mr. Gene Ashby was DOE's Technical Program Officer. Roger Wilmoth was instrumental in accepting this project from EPA Region 8. Ken Wangerud was the site's Remedial Project Manager for EPA Region 8. Ms. Helen Joyce was MSE's MWTP Program Manager and Brian Park was MSE's Project Manager. Additional project-specific contributors that deserve acknowledgement include: Steve Fundingsland, Jim Jonas, Paul Hight, and Marko Adzic (CDM), Jim Harrington (Shepherd-Miller), and Joe Harrington (Green World Science).

Executive Summary

The U.S. Environmental Protection Agency (EPA) Region 8 Superfund Office and the EPA National Risk Management Research Laboratory (NRMRL) Mine Waste Technology Program (MWTP) conducted a field-scale treatability study demonstrating an in situ bio/geo-chemical treatment technology for decontaminating acid/metal-toxic water within the Anchor Hill Pit lake at the Gilt Edge Mine Superfund site near Deadwood, South Dakota. The purpose of the project, carried out between March 2001 and May 2006, was to develop performance data on the treatment approach for potential use in long-term water treatment/management activities at the Gilt Edge site, as well as other similar sites. The treatment process was applied to approximately 72 million gallons of acidic water, with high concentrations of metals (including iron, aluminum, arsenic, selenium, copper, cadmium, and zinc), sulfate, and nitrate, and a pH of approximately 3.

The original objectives for the treatability study were to:

- successfully establish anaerobic and chemical-reducing conditions to reduce nitrate- and metal-sulfate contaminants; and
- reduce toxic-metal concentrations.

As these objectives were successfully achieved, and the effectiveness of the treatment was evident, an additional objective sought was to:

- achieve discharge standards and release “clean” and “non-toxic” water from Anchor Hill Pit lake.

All of these objectives were met, and considerable experience and insight were gained into how operational aspects of such a remediation technique would have to be designed for future efforts.

The first step of the planned two-stage treatment consisted of using a Neutra-Mill (essentially a floating lime slaker developed by Earth Systems, Pty. of Australia), to neutralize the pit water 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 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. The purpose of this step was to induce reducing conditions, and stimulate bacterial activity for nitrate, selenium, and sulfate reduction to create a stable system and improve water quality.

In 2002, the project team concluded that the pH 5.0 condition was inhibiting biological activity so the pH was raised to 6.0 and wood-chips were added as substrate for bacterial growth. Robust bacterial activity rapidly proceeded. 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 these metal sulfide particles, the total metals values of those metals in collected samples were significantly higher. In general, water in the pit met applicable South Dakota Ambient Water Quality Standards (SDAWQS) with the exception of undisassociated 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 20 to 30 feet. During the 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.

While discharge of surface-waters could have begun, it was recognized that the strongly-reducing conditions in the deeper zone might have attributes worth maintaining for additional acid rock drainage (ARD) loading and treatment. It seemed important to better understand the deep-water chemistry and treatment conditions. Because the strongly-reducing deep water condition was believed to be the result of overdosing the carbon-nutrient compounds, it was surmised that the most effective metal reduction and removal could be accomplished by maintaining this reaction-zone with strong reducing conditions. The surface water was thought to be more vulnerable to perturbations, such as contaminated surface runoff into the pit, which might easily result in metals such as cadmium or zinc increasing above discharge limit, with no possibility of decontamination by sulfide precipitation – as would occur in the deeper zone. The deeper zone was, in general, considered to be more stable and controllable; consequently, additional ARD-loading for treatment might be more efficient because reducing conditions already existed, making it unnecessary to add additional carbon to consume dissolved oxygen and establish anoxic conditions. It was envisioned that in the future, contaminated water from the Gilt Edge Mine site might be injected, along with nutrients, into the pit below the stable chemocline, with the surface layer simply serving as the "protective" layer over what would be 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 concerns, which were addressed and managed. Mitigation of the deep water chemistry was attempted by pumping the deep zone waters through an air-sparging unit, followed by a shallow holding-lagoon to complete BOD reduction and solids settling. Since the residual H_2S oxidized to elemental sulfur and formed colloidal particles that were very slow to settle, attainment of regulated values of total suspended solids (TSS) was difficult. Interestingly, metals were not remobilized by this sulfide oxidation, and approximately 150,000 gallons of water was successfully discharged in two separate batches in October 2004.

Even though discharge-quality water was achieved, it was apparent that the time and process phases, along with the area requirements for "polishing-lagoons," made this approach impractical. The notion of operationalizing a treatment system that could be in-loading ARD to a deep reaction zone was deemed to be fraught with too many uncertainties to warrant further consideration. In addition, the team concluded that 1) any operationalized treatment process should assume that high-H_2S conditions could likely occur during each treatment "batch", 2) that a method for rapidly mitigating such a condition be sought, and 3) attention should be turned to eliminating the high-H_2S deep-water concentrations in a "single-step" approach of in situ oxidation. The addition of various oxidants was considered, and hydrogen peroxide was selected as the preferred method to eliminate the dissolved H_2S. Thirty-five thousand gallons of hydrogen peroxide was released into the pit below the chemocline in August 2005. The reaction was successful, and as had been observed in the oxidation-lagoons, the lake experienced a milky-gray coloration as elemental sulfur formed and began to settle.

In late-fall 2005 and spring 2006, large-volume skimming and decanting of surface-waters meeting water-quality standards was carried out, resulting in the release of approximately 40-million gallons of treated water into Strawberry Creek, which runs adjacent to the Gild Edge Mine site. Sampling had shown that approximately 25-million additional gallons of dischargeable water was present in the treated pit lake, when very large spring runoff and storm events required an emergency transfer of ARD-inventory from the Gilt Edge Mine site into the Anchor Hill pit, functionally ending the treatability test in late spring 2006.

1. Introduction

1.1 Background

This document is the final report for Mine Waste Technology Program (MWTP), Activity III, Project 34, *Bioremediation of Pit Lakes (Gilt Edge Mine)*. The MWTP is a program funded by the U.S. Environmental Protection Agency (EPA) and jointly administered by EPA and the U.S. Department of Energy through an Interagency Agreement (IAG). MSE Technology Applications, Inc. (MSE) is the principal contractor for the MWTP.

The EPA Region 8 Superfund office and the EPA National Risk Management Research Laboratory (NRMRL) MWTP, through MSE, conducted 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 from March of 2001 through May 2006. The project goal was to develop 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. EPA's interest in the in situ treatment process was to determine if "semi-passive" treatment of acid rock drainage (ARD) was possible in a pit lake, thereby avoiding some portion of the costs of operating a conventional water treatment plant.

In addition to summarizing the execution of the project over an approximately five-year period, this report also summarizes what was learned over the course of the project, and provides a description of how a similar effort might be conducted in light of the lessons learned during the execution of this project. Figure 1-1 (left) shows an aerial photograph of the Gilt Edge Mine site, Figure 1-1 (center) shows an aerial photograph of the Anchor Hill Pit lake, and Figure 1-1 (right) shows a contoured drawing of the Anchor Hill Pit lake.

Prior to treatment, the Anchor Hill Pit contained approximately 72 million gallons of acidic water, with elevated metals, sulfate, selenium, and nitrate content, and a pH of approximately 3. Table 1-1 presents the initial water composition for samples collected in March 2001 prior to pit neutralization. The table also presents the applicable or relevant and appropriate requirements (ARARs) for the Gilt Edge Mine site that would have to be achieved to discharge water to Strawberry Creek.

1.2 Treatment Description

The treatment approach was originally envisioned to consist of two steps that would occur within the pit lake: (1) neutralize the pit water to near-neutral pH using lime (CaO), applied using a Neutra-Mill (essentially a floating lime slaker, developed by Earth Systems, Pty. of Australia); and (2) utilize Redox-Mediated Biotransformation (RMB^{TM}) technology, developed and patented by Green World Science, Inc. (GWS), to create reducing conditions; stimulate bacterial activity for nitrate, selenium, and sulfate reduction; improve water quality; and create a stable system. The RMB^{TM} process involved addition of nutrients to the pit, including methanol, animal feed-grade molasses, and phosphoric acid, with the goal of stimulating indigenous bacterial activity to first reduce nitrate to nitrogen gas, and subsequently reduce selenium and sulfate. Bacterial reduction of selenium to its elemental state removes it from solution, and reduction of sulfate produces sulfide, which forms metal sulfide particles with copper, cadmium, nickel, lead, and zinc. These metals are reduced to dischargeable concentrations at neutral pH via precipitation as metal sulfides. The metal sulfides were intended to settle to the bottom of the pit, where a permanent anoxic zone would be maintained, ensuring their long-term stability.

Figure 1-1. 300-acre Gilt Edge Mine site (left); Anchor Hill Pit lake (center & right).

Table 1-1. Initial Pit Water Composition and ARARs for the Gilt Edge Mine Site

Parameter	Average Concentration ± Standard Deviation (n=4 unless otherwise noted) (µg/L unless otherwise noted)	South Dakota ARARs Criteria	Special Conditions
Unionized Ammonia as N	No data available	≤0.02 mg/L	30-day average
Dissolved Oxygen	9.0±0.90 (n=3 shallow samples)	≥5.0 mg/L	
pH	3.1 SU±0.07 (n=29)	≥6.5-≤8.8 S.U.	30-day average
Total Suspended Solids (TSS)	6±1.2 mg/L	≤10 mg/L	24-hr composite
Acidity as $CaCO_3$	1115±110 mg/L	N/A	
Chloride	37.3±3.3 mg/L	N/A	
Nitrate/Nitrite as N	85.5±15 mg/L	<50 mg/L	30-day average
Sulfate	3260±30 mg/L	N/A	
Contaminant		**Acute Aquatic Life Value (µg/L)**	
Dissolved Aluminum	224,000±19,000	N/A	
Dissolved Antimony	17±0.5	N/A	
Dissolved Arsenic	73±3	360	
Dissolved Cadmium	576±25	3	Hardness[a]
Dissolved Calcium	506,000±27,000	N/A	
Dissolved Chromium III	No data available	1708	Hardness[a]
Dissolved Chromium VI	<500	15	
Dissolved Copper	43,300±2500	63	Hardness[a]
Dissolved Iron	15,600±	N/A	
Dissolved Lead	31±2.3	281	Hardness[a]
Dissolved Magnesium	196,000±6800	N/A	
Dissolved Manganese	27,100±680	N/A	
Dissolved Mercury	<0.1	2.1	
Dissolved Selenium	26±1.6	20	
Dissolved Silver	<1.3	37.4	Hardness[a]
Dissolved Zinc	14,100±400	370	Hardness[a]
Cyanide (weak-acid dissociable)	No data available	22	

[a] The discharge limits are calculated by formulas incorporating hardness. The values shown are for the maximum allowable hardness value of 400 mg/L as calcium carbonate.

2. Project Chronology

A project chronology, shown in Table 2-1, presents an overall view of how the project was executed. More detailed explanations of selected elements of the project are presented in other sections of this report.

Table 2-1. Chronology of Project Execution

Date	Action Taken
July 2000	The project was selected for execution by EPA-NRMRL's MWTP in collaboration with EPA Region 8. A project kickoff meeting was held at the Gilt Edge Mine including personnel from EPA Region 8, CDM Federal Programs, Inc., the U.S. Bureau of Reclamation, EPA NRMRL, Green World Science, Inc., Shepherd-Miller, Inc., South Dakota Department of the Environment and Natural Resources (SDDENR), MSE, and the U.S. Department of Energy. Responsibilities were assigned as follows: MSE would have a sole-source subcontract with Shepherd-Miller (North American licensee for the Neutra-Mill technology) to neutralize the pit with the Neutra-Mill and a sole-source subcontract with GWS to implement its RMB technology by dosing nutrients after lime neutralization. MSE would also prepare a quality assurance project plan (QAPP) for the project and participate in data collection and evaluation activities. EPA Region 8 would cover analytical costs, including data validation for the project and provide the lime for the pit lake neutralization. CDM would provide quality assurance (QA) oversight and facilitate on-site support along with the U.S. Bureau of Reclamation (BOR). Note that at that point in time, the site was operated by the BOR.
September 2000	Shepherd-Miller personnel visited the site to obtain vertical profiles of physical measurements and collect water for lime titrations, with the goal of establishing water depths for future monitoring, and estimating lime requirements. Initially, the pit only contained 35 to 40 million gallons. Additional water was transferred to the pit in the fall of 2000, including high-nitrate water from the heap leach pad, until the final water volume was about 72 million gallons. The purpose of this was to provide higher nitrate concentrations to challenge the technology, as well as to simply provide more water for treatment.
February 2001	The project QAPP was finalized by MSE after receiving approval from EPA.
March 2001	Initial samples and profiles vs. depth were obtained, continuous monitoring equipment was installed, and lime neutralization was initiated. Various problems were encountered in delivering lime to the Neutra-Mill, as well as Neutra-Mill operation. These are discussed in more detail later in this report.
May 2001	Lime neutralization was completed around May 10, based on pH profiles indicating near neutral pH through the bulk of the water column, with higher pH values near the bottom. Nutrient dosage was planned for two weeks later. Immediately prior to adding nutrients, pH profiles were obtained. These indicated that the pH of the water column had dropped to approximately 5 over the previous two weeks. This is discussed in more detail below. Since trucks containing the nutrients were due to arrive imminently, it was decided to proceed with nutrient dosing, which was completed in late May.
June 2001	Continuous monitoring equipment indicated that dissolved oxygen was consumed within several weeks of nutrient addition.
August 2001	EPA-NRMRL performed a technical systems audit on August 29, 2001. There were four findings related to QAPP deviations, timely receipt of data so that previous sampling event data was available for review, anomalies noted for field pH measurements, and the questionable nature of data gathered from the continuous monitoring probes. All findings, observations, and technical comments were addressed by MSE in a response to EPA. This response memo is contained in Appendix A.
September 2001	Additional nutrients were added to the pit. This was justified by GWS by the presence of much higher nitrate than originally expected due to the addition of high-nitrate heap leach pad water. More nitrate to be reduced requires more carbon to provide the necessary electrons.

Date	Action Taken
October 2001-September 2002	Monitoring of the pit conditions continued. Nitrate reduction was proceeding at a rate much slower than expected. This was attributed to a combination of lower than optimum pH along with the presence of elevated aluminum in solution.
April 2002	Additional molasses was added to the pit, along with sodium hydroxide to raise the pH of the water to near neutral.
September 2002	A concerted effort was made to place the pit into optimum conditions for biological activity going into the winter of 2002-2003. These efforts included raising the pH to neutral with sodium hydroxide, as well as adding more nutrients. In addition, wood chips were added with the intention that they would become waterlogged and sink, and thereby provide a suitable substrate for bacteria to attach to and grow on.
October 2002	Foam was observed on the water surface, likely due to nitrogen and carbon dioxide gases produced from bacterial activity. Samples taken indicated a significant drop in nitrate concentration.
April 2003	Samples and profiles taken through the winter of 2002-2003 showed rapid progress in nitrate reduction. Physical evidence of sulfate reduction was observed after ice-off in April 2003, by the presence of black solids and hydrogen sulfide gas aromas whenever the surface water was disturbed.
April 2003 – April 2004	Continued monitoring confirmed the progression of sulfate reduction, as evidenced by a dramatic drop in dissolved concentrations of metals that form sulfide precipitates (e.g., copper, cadmium, zinc); the presence of excess sulfide; very low oxidation-reduction potential (ORP) levels; and the smell of hydrogen sulfide gas associated with samples. The pit water column had become strongly stratified, with aerated water floating on top of strongly reducing, high-sulfide water below.
April 2004	Discussions occurred relating to potential discharge of water from the pit. These discussions focused on how the pit might be used as part of long-term water treatment scenarios at the site. Options considered were directly discharging surface water, or filtering and aerating deeper water. It was decided to focus on discharging deeper water, since it was thought that the deep zone could be better used for long-term treatment. The rationale for this is discussed later in this report.
May-July 2004	Preliminary filtration tests were performed to evaluate the required filtration of deep water, and a filtration apparatus using bag filters was assembled. A shallow aeration/settling pond was created by lining an existing pond. Initial transfer of small amounts of water produced issues with hydrogen sulfide gas management, along with issues related to total suspended solids. The excess sulfide in the water oxidized rapidly to elemental sulfur, which was very difficult to settle or filter. This is discussed further below.
July 2004	Whole effluent toxicity tests of Anchor Hill Pit surface water, as well as water from the shallow aeration/settling pond, showed the water was not toxic.
July-September 2004	In order to evaluate potential use of the high-sulfide, anoxic zone in the pit for future water treatment, two buckets were suspended in the pit. Both buckets contained four gallons of deep Anchor Hill Pit water and one gallon of Surge Pond water, which was neutral pH, containing elevated nitrate and a small amount of metals. One bucket had nutrients (methanol, molasses, phosphoric acid) added, while the other did not. When these buckets were retrieved after six weeks, it was found that the nitrate initially in the bucket with nutrients added had reduced to ammonia. This was surprising and had very significant ramifications for use of the deep water zone for water treatment.
August-October 2004	The initial 100,000-gallon batch of deep water was aerated and successfully discharged after all discharge requirements were met.

Date	Action Taken
November 2004	An evaluation was performed of the stability of the stratification in the Anchor Hill pit, indicating that turnover was very unlikely. A turnover event would be potentially dangerous due to the presence of excess dissolved hydrogen sulfide gas in the deep zone. At approximately the same time, the surface of the pit turned a different color, and a sewage-type smell was produced. This indicated partial vertical mixing to a slightly deeper depth than mixing had previously occurred. The likelihood of a turnover event was evaluated by determination 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 of this analysis indicated that no vertical mixing would be expected under average recorded wind speeds of 10 miles per hour (mph). Under sustained wind speeds at the maximum recorded value of 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 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 H_2S in the deep zone; however, reducing the H_2S levels in the deep zone became an important goal late in the project.
February 2005	About 4 million gallons of surface water from under the ice on the pit was discharged. This took several attempts before a configuration was established that did not draw water from below the chemocline.
May 2005	Since it had been established that utilizing the reducing, anoxic conditions below the chemocline for long-term water treatment was not going to be viable, discussions were undertaken regarding how to best address the high sulfide levels in the deep water in preparation for project completion. Evaluations were performed of using ferrous iron salts, ferric iron salts, and oxidants such as hydrogen peroxide or bleach to eliminate the high sulfide levels. It was ultimately decided to utilize concentrated hydrogen peroxide due to lower cost and ease of handling.
July-August 2005	About 15 million gallons of surface water meeting applicable South Dakota water quality standards was discharged.
August 2005	Concentrated hydrogen peroxide was added to the pit to eliminate excess sulfide by oxidizing it to elemental sulfur. Much of the peroxide initially went directly to the bottom of the pit, leaving a zone of untreated water between a depth of about 10 feet down to about 45 feet. Over the ensuing months, mixing and reactions slowly occurred.
October 2005	Similar to the previous year, the color of the water surface changed and a sewage-type smell was produced. Once again this probably indicated vertical mixing to a deeper depth than previously encountered.
March 2006	Analytical data indicated that the pit water no longer contained any sulfide, indicating that hydrogen peroxide treatment had been successful.
April 2006	An additional 15 million gallons of surface water was discharged from the pit. By this time in the project, over 40 million gallons of water had been successfully discharged from the pit.
May 2006	Due to high amounts of runoff late in the winter at the Gilt Edge site, ARD was transferred from the Sunday Pit to the Anchor Hill Pit. This effectively ended the monitoring phase of the project.

3. Implementation

The following describes how elements of the project were physically conducted and provides more details about implementation of each step of the project.

3.1 Sampling

Sample points were established at two locations along the long dimension of the pit. These were designated NE for northeast and SW for southwest, since the longest dimension of the pit runs from southwest to northeast. Orange marine buoys marking the locations were attached with plastic-coated cable to buckets filled with concrete. Based on original profiles taken in September 2000 by Shepherd-Miller personnel, a thermocline could be expected to extend down to the 20- to 25-foot depth in summer. In an attempt to provide depth and lateral coverage without driving up analytical costs excessively, sample points were established at depths of 5 feet and 35 feet at the northeast location (thereafter designated NE05 and NE35) and at depths of 20 feet and 60 feet at the southwest location (thereafter designated SW20 and SW60). Generally throughout the project, samples were taken at these locations. Occasionally, samples were obtained at additional depths to help answer questions existing at those times. In addition, vertical profiles of temperature, pH, ORP, dissolved oxygen, and specific conductance (SC) were obtained every five vertical feet at the NE and SW locations using either a Hydrolab or YSI sonde. After a history was established showing the NE and SW profiles were generally identical, profiles were typically taken at only the SW location since the pit was deeper at that end. Sediment samples were also obtained on several occasions at the NE and SW locations.

Sampling was usually performed by attaching a tube to the sonde, lowering the sonde to the proper depth and location, and using a peristaltic pump to collect water from that depth. The pump was operated for an extended period prior to collecting samples to allow purging of the tube. Several sampling events were performed using a Kemmerer sampler, in which an open tube is dropped to the proper depth, and a “messenger” sent down the rope to trip the sampler, capturing the tube volume at that depth. Sediment samples from the pit bottom were generally obtained using an Ekman grab sampler.

Early in the project, “Troll” data-collecting instruments, manufactured by In Situ, Inc., were placed in the pit at the NE and SW locations. These turned out to require extensive maintenance to ensure trustworthy values were obtained, particularly after addition of nutrients to the pit and the subsequent initiation of biological activity. The instruments became coated with organic material that looked somewhat like algae. Since on-site labor was not available to undertake this maintenance, those instruments were only used sporadically the first year, and eventually removed and used elsewhere at the Gilt Edge site by CDM Federal Programs.

Safety issues associated with sampling while the pit was frozen over had to be addressed. For work on the ice during neutralization (March-April 2001), a “walkway” was constructed using a series of floats tied together, extending from shore to the NE sample point, and from there to the SW sample point. Each float was essentially a 4-inch thick, 4-foot by 8-foot piece of closed cell foam sandwiched by two 4-foot by 8-foot sheets of plywood. This walkway had a cable running down the middle, and personnel were required to clip in a harness to this cable while using the walkway. This was quite cumbersome since, due to the construction of the system, personnel had to unclip and re-clip to the cable when stepping from one float to the next. This system was used for the first two winters. Subsequently, personnel had to drag one float with them out to the holes cut in the ice for sampling purposes. Ultimately, CDM imposed safety procedures that required a certain minimum ice thickness for work on the ice.

The project highlighted the need for innovative monitoring methods to better understand the progress of each reaction phase. Analysis and interpretation of traditional laboratory data proved to be an inadequate means of evaluating the time-sensitive reactions that were proceeding in real time. In March 2004, a video camera was used to explore the Anchor Hill Pit to provide visual evidence of what was occurring in the pit. The video images captured by the camera (shown in Figure 3-2, left) helped the project team determine that biological processes were underway as evidenced by the gas bubbles seen in the suspended bags of wood chips (Figure 3-2, center) and also allowed the team to view the sediments at the bottom of the pit and also estimate the depth the these sediments (Figure 3-2, right).

3.2 Treatment Methods/Materials

During the project, several different materials were added to the pit lake during the treatment process. The following sections describe the amount of each material added and the methods used to add the materials to the pit.

3.2.1 Lime Addition

Lime addition was accomplished with a Neutra-Mill, developed by Earth Systems, Pty. of Australia. A photograph of the Neutra-Mill is depicted in Figure 3-3. Shepherd-Miller was the North American licensee of that technology at that time. Since lime addition ended up being performed essentially under winter conditions, this turned out to be quite difficult. Initial plans by Shepherd-Miller were to have dump trucks deliver lime to the work site, but the truck drivers were unwilling to back their trucks down the haul road into the pit under icy conditions. For this reason, a lime silo was rented and placed in an accessible location on the rim of the pit above the Neutra-Mill docking location. The silo had an auger system integral to it, and a configuration was assembled in which the auger would transfer lime to a 6-inch pipe, and the lime would flow through the pipe down the pit wall to the working elevation, and then across the haul road to the Neutra-Mill. Note that this was pebble quicklime, and this system did not work. The coarse lime did travel down the pit wall, but could not flow across the relatively level haul road. Ultimately, a conveyor was rented to transfer the pebble quicklime across the haul road to the Neutra-Mill.

Once the problem of delivering lime to the Neutra-Mill was solved, the Neutra-Mill itself presented numerous operational problems. A common problem was that the rotating drum would become out of balance, which would require a shutdown until personnel could redistribute the load so the drum could function, until the next shutdown.

It was anticipated that the Neutra-Mill would be capable of delivering, grinding, and disseminating three to five tons of lime per hour to the pit lake. The throughput was well below this anticipated level. In an attempt to achieve a higher throughput, the project switched to fine hydrated lime delivered in bulk bags. These bulk bags were transported by forklift down the haul road to the Neutra-Mill, which was then fitted with a small hopper and auger. The bulk bag was lifted above the hopper, and cut open, spilling the lime into the hopper. Water was needed to “sluice” the lime from shore to the Neutra-Mill. Throughput never exceeded 1.5 tons per hour.

The Neutra-Mill mixed the lime into the water immediately below the platform on which the Neutra-Mill sits. In an effort to enhance mixing into the pit lake, a portable pump capable of transferring approximately 400 gallons per minute (gpm) was utilized. The pump inlet drew water/lime slurry from beneath the platform, and the discharge was through a 4-inch hose with the exit placed in the southwest section of the pit. A total of 292 tons of lime had been added to the pit when neutralization was considered complete.

3.2.2 Nutrient Addition – May 2001

Nutrient addition was performed by Green World Science in May 2001. This consisted of offloading six truckloads of animal feed-grade molasses and one truckload of methanol into the pit water. These were not blended into the water in a complicated manner, they were simply offloaded through large hoses manned by the truck drivers. Refer to Figure 3-4 (left) for a photograph of molasses addition and Figure 3-4 (right) for a photograph of methanol addition. Due to the high specific gravity of the molasses (1.5 to 1.6), the molasses likely sank immediately to the bottom of the pit. The methanol could be seen spreading out on top of the water surface, and likely mixed in well with the water.

3.2.3 Nutrient Addition – September 2001

Two truckloads of molasses were added to the pit in the same manner as before – offloaded to the pit surface by a hose.

3.2.4 Nutrient and Caustic Addition – April 2002

One truckload of molasses was added to the pit by offloading through a hose onto the ice surface (the pit was still frozen) at the SW end of the pit. Upon the ice melting, the molasses then mixed into the pit water column.

One truckload of 50% sodium hydroxide (caustic) was also added because pH values were still not optimum for bacterial activity despite the first pit lake neutralization with lime that was discussed previously. The caustic solution was added by gravity flow through a pipe out to the middle of the pit, on top of the ice. The solution was quite warm; typically 50% sodium hydroxide is delivered at 120 °F to ensure adequate flowability. This solution melted a hole in the ice, and upon contacting the cold water under the ice, the caustic then probably sank to the bottom of the pit. Anecdotal discussions with others indicated that warm 50% caustic forms “globs” when contacting cold water and does not mix well. It is possible that the caustic sank to the bottom of the pit and never reacted with the water, and it is also possible that the caustic reacted very slowly with the water. No direct evidence of a beneficial pH increase was ever noticed in the vertical profiles after this addition of caustic.

3.2.5 Nutrient, Caustic, and Wood Chip Addition – September 2002

Through the spring-summer of 2002 (due to the continuing absence of indicators of robust bio-reactions) the test-team was concerned that “something was missing” for onset of strong reducing conditions. Debate focused on three contributing factors:

- Dissolved-aluminum concentrations high enough to possibly cause adverse toxicity to bacteria at the cell membrane, inhibiting metabolism, growth and reproduction;
- Insufficient “substrate” for bacterial colonization; or,
- continuation of suppressed pH conditions, not conducive to robust biology for the sulfate-reducing bacteria (SRB).

The project team decided that the test should incorporate changes to optimize the pit conditions for all of the above factors, including:

- Adding caustic to raise the pH to ~6.5, thereby assuring the precipitation of dissolved aluminum, thus minimizing the potential for continuing cellular toxicity from aluminum;
- Adding wood chips (by floating woodchips, by dropping woodchip-filled netting-bags to the sediment interface at the lake-bottom, and by installing suspended vertical columns of woodchip-filled netting-tubes through the water column—spanning the various lake-layers).

These actions were carried out over the fall of 2002 and winter-spring of 2002-03.

Two truckloads of molasses, one truckload of methanol, and two truckloads of 50% caustic were added to the pit. These were approached much differently than previous efforts. A pumping system was set up to draw near-surface water from the NE end of the pit, and discharge it at the surface near the middle of the pit, with the goal of inducing some better lateral mixing than would normally be expected. The pumping rate was approximately 800 gpm. The nutrients and caustic were slowly metered into the pumping loop to ensure they were well mixed into the water when it was discharged to the pit. This avoided the poor mixing observed previously with the caustic addition in April 2002, and provided better mixing of the nutrients into the water as well.

Lastly, 96 tons of wood chips were added to the pit by offloading dump trucks of wood chips into the SW portion of the pit. The purpose of the wood chips was to provide bacteria with a substrate to attach to and also provide a long-term carbon source for the bacteria. It is unclear if these wood chips were required or whether the reactions would have proceeded without their addition, but these wood chips floated for a few weeks before becoming waterlogged and sinking. Physical indications of nitrate reduction were evident nearly immediately; biological "slimes" formed within the floating chips, and within 10-14 days a white froth of gas bubbles appeared and the pit-surface was "fizzing." Figure 3-5 is a photograph showing a white froth of gas bubbles within floating woodchips.

3.2.6 Fertilizer Addition

Monitoring indicated that nitrate reduction was complete by early 2003 and that sulfate reduction was underway by summer 2003. Fertilizer was added to the pit in August 2003 in an attempt to stimulate an algae bloom. This was part of the overall approach put forth by Shepherd-Miller and Green World Science at project inception. The idea was to stimulate algal blooms, so that when the algae dies and sinks, it can serve as an additional nutrient source for the SRB in the deeper water. The fertilizer added was granular triple super phosphate with the formula $Ca(H_2PO_4)_2$ (17% to 23% P; 44% to 52% P_2O_5). It was added by slowly driving a boat around the pit water surface and adding scoopfuls of fertilizer into the surface water. The dosage was sufficient to provide 1 mg/L of phosphorus to the top 3 feet of the water column. An algal bloom was never produced, and it is unclear if this fertilizer addition had any impact on the overall treatment scheme.

Once near optimum conditions for treatment were established, the reducing conditions did occur and the bulk of water in the pit did improve from a water quality standpoint. At this point, the project team began to focus on treatment options to further upgrade the water in the Anchor Hill Pit to meet the very strict discharge requirements for the site. These were very involved efforts, and only a summary will be presented in the body of this report, with a more complete description presented in Appendix B.

3.2.7 Discharge of Deep Zone Water, 2004

Discharge of deep zone water was attempted during the summer and fall of 2004. Bench-scale tests focused on developing a filtration and aeration process to meet discharge requirements. Filtration would be required to remove residual suspended metal sulfides, and aeration would be needed to increase dissolved oxygen and return biochemical oxygen demand (BOD) to dischargeable levels. Safety issues associated with hydrogen sulfide gas release arose and were solved. Problems with TSS arose due to oxidation of excess sulfide to elemental sulfur during the aeration step. Approximately 100,000 gallons were ultimately discharged by the further processing treatment of the deep zone pit water. The difficulties with filtration, hydrogen sulfide, and the very fine sulfur solids were significant, and pursuing discharge in this manner was not practical. Further information about this phase of the project can be found in Appendix C.

3.2.8 Evaluation of Use of Anchor Hill Pit for Ongoing Site Water Treatment, 2004

In parallel with the efforts focused on discharging deep Anchor Hill Pit water described previously, attention was also focused on ongoing water treatment options. 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, 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 1 gallon of Surge Pond water along with 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, and the other bucket received no nutrient addition. The buckets were placed at the 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 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 is surmised 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; however, this was never verified. Judging by the lengthy time (almost two years) since the completion of denitrification, this was 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.

Based on the risk of nitrate ammonification described above, it was surmised that any future water treatment within the Anchor Hill Pit would have to be performed on a batch basis (i.e., the pit would be loaded with so much water, neutralized, and dosed with sufficient nutrients to denitrify the nitrate present and achieve a suitable amount of sulfate reduction to produce dischargeable dissolved metals concentrations). After allowing some settling time for the metal sulfide precipitates, the water would need aeration to eliminate any remaining sulfide and BOD, and to raise the dissolved oxygen, possibly along with some clarification. Aerating the water, and settling the sulfur to produce dischargeable water, it is not practical to perform for very large volumes of water so other ways to oxidize the excess sulfide would be employed.

3.2.9 Evaluation of Likelihood of Lake Turnover, 2004

Concerns about the potential for a turnover-mixing event by the meromictic (lake layers that do not mix) 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 10 mph. Under sustained wind speeds at the maximum recorded value of 35 mph, no mixing would be expected, but there would be potential for mixing of the metalimnion (layer of rapid temperature change) with the surface zone. A sustained wind speed of 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 H_2S in the deep zone; however, reducing the H_2S levels in the deep zone did become a project objective. A more complete description of this effort is provided in Appendix B.

3.2.10 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) 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 proceed. 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 would 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 2005, while the pit was still frozen over, approximately 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. The addition of various oxidants was considered to oxidize the excess sulfide to sulfur. Hydrogen peroxide was selected as the preferred method to eliminate the dissolved H_2S. Thirty-five thousand gallons of concentrated hydrogen peroxide were released into the pit (Figure 3-6) in August 2005. The reaction was successful, and as had been observed in the oxidation-lagoons, the lake experienced a milky-gray coloration as elemental sulfur formed and began to settle (Figure 3-7).

Approximately 10 million gallons of water meeting discharge standards was successfully released from the surface of the pit between mid-July and mid-August 2005.

3.2.11 Discharge of Surface Water, 2006

Analytical data indicated that the pit no longer contained any sulfide, indicating that the oxidation with hydrogen peroxide had been successful. In April 2006, an additional 15 million gallons of surface water was discharged from the pit. Since the project began, over 40 million gallons of water had been successfully treated and discharged from the Anchor Hill Pit.

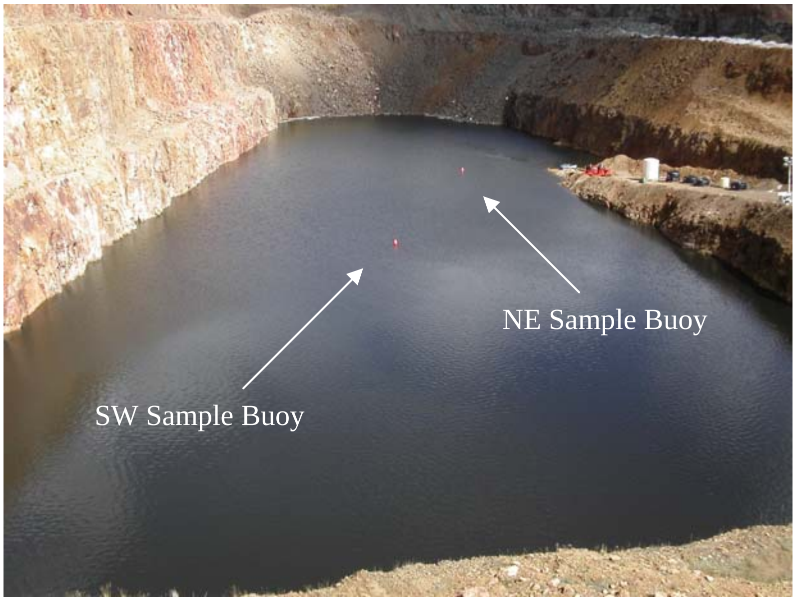


Figure 3-1. Photograph indicating the location of sample buoys in the Anchor Hill Pit.

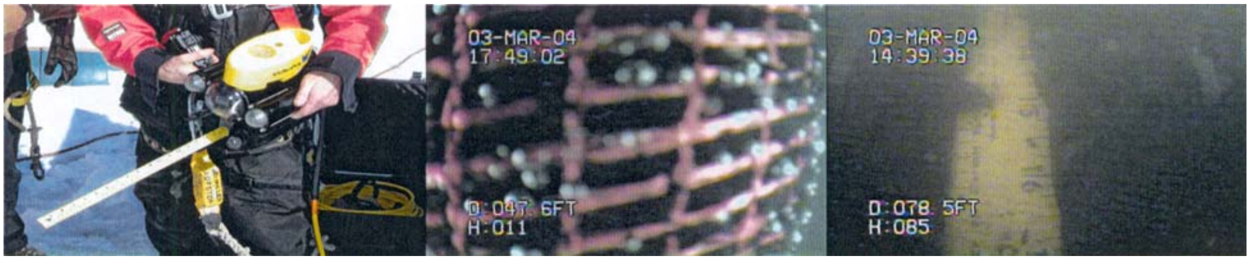


Figure 3-2. Camera used for video camera observations (left), gas bubbles within suspended bags of chips (center), and sludge at bottom of pit (right).

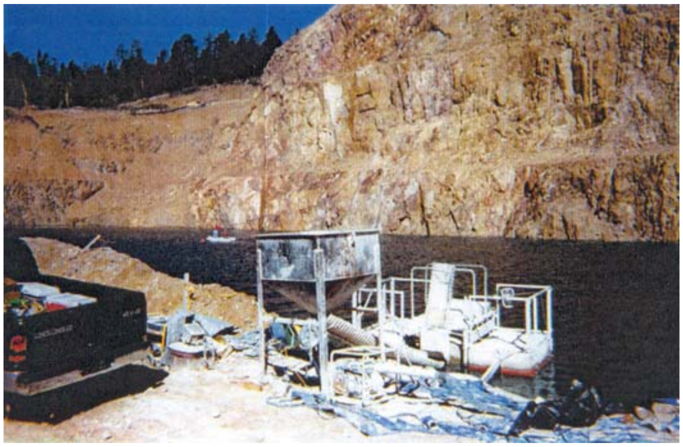


Figure 3-3. Photograph showing Neutra-Mill docking location.

Figure 3-4. Adding molasses (left) and methanol (right) to the pit.

Figure 3-5. Photograph showing white froth of gas bubbles within the floating wood chips.

Figure 3-6. Photograph showing in situ hydrogen peroxide addition.

Figure 3-7. Photograph showing evidence of excess sulfur in the shallow pit water after hydrogen peroxide addition.

4. Results/Discussion

At the beginning of this project, the Anchor Hill Pit contained about 72 million gallons of acidic water, containing high levels of dissolved metals, selenium, nitrate, and sulfate. Table 4-1, which illustrates how water quality improved over the course of the project, presents selected data. Figure 4-1 presents the pH data prior to pit neutralization.

Neutralization of the pit occurred between March and May 2001 using the Neutra-Mill and lime. After a several-week stabilization period following neutralization, the RMB^{TM} process was initiated in May 2001 with the addition of carbon nutrients. Additional sodium hydroxide additions were made to the pit in response to a significant drop in pH (from approximately 7 to 5) observed during the post-neutralization stabilization period. Figure 4-2 shows the pH profiles with depth after lime neutralization. Even after the attempt to neutralize the pit lake, the bulk of the water was still at a pH of approximately 5.

The RMB^{TM} treatment proceeded slower than expected, presumably attributed to starting the treatment at a lower-than-optimum pH. Along with pH conditions deemed lower than ideal for bacterial growth, aluminum dissolved back into solution at concentrations (~40 mg/L) that may have adversely affected bacteria metabolism. Denitrification proceeded slowly through the remainder of 2001 and the bulk of 2002. In September 2002 a concerted effort was made to raise the pit pH to near 7 in order to provide a better pH environment for the bacteria and to precipitate aluminum from solution. Figure 4-3 shows the pH profile following additional efforts to neutralize the pit. This effort was successful – the pH was increased to near neutral, and aluminum concentrations decreased to less troublesome levels.

Wood chips were also added to provide a substrate for bacterial growth, but the effect of the wood chips is unknown. By October 2002, nitrate showed a significant drop, and microbial counts increased.

Nitrate concentrations continued to decrease through the winter of 2002-2003, with non-detectable levels achieved by March 2003. A plot of nitrate/nitrite concentrations at each sample location versus time is presented in Figure 4-4. Note that nitrate reduction occurred more quickly in the deep portions of the pit compared to the shallower portions of the pit until the pH was adjusted to near neutral in September 2002 and nitrate reduction proceeded rapidly when more optimum conditions for biological activity were attained in the pit.

Thermodynamically, significant sulfate reduction was not anticipated to occur until denitrification was complete; and sulfate reduction was expected to begin as soon as a population of SRB could be developed. In mid-April 2003, field personnel observed indications that sulfate reduction was occurring. Whenever the surface was disturbed, they noted black precipitates welling to the surface and hydrogen sulfide gas odors.

Sampling through the summer of 2003 confirmed the initiation and progress of sulfate reduction. Average dissolved copper, cadmium, and zinc concentrations showed a striking decrease. Figure 4-5 plots these parameters along with nitrate, versus time, showing the dramatic decrease in these metals (due to the onset of sulfate reduction) immediately following denitrification. The pit water also showed an increase in alkalinity in the deeper water to approximately 400 mg/L (as $CaCO_3$), providing further evidence that biological nitrate and sulfate reduction was occurring, since bicarbonate is a byproduct of both the nitrate and sulfate reduction reactions. Data through April 2006 is plotted. During May 2006, the test effectively terminated with addition of ARD to the Anchor Hill Pit when precipitation events caused water management issues at the Gilt Edge site, which prompted the addition of site waters to the pit lake.

Water quality in the Anchor Hill Pit continued to improve until it approached discharge standards. Both deep pit water and surface water were successfully discharged from the pit. Discharge of the water was only possible after overcoming many technical challenges; however, the most significant result of the project was that over 40 million gallons of water was successfully discharged from the Anchor Hill Pit lake. In this sense, the project was successful, but there were several lessons learned during the project that would be taken into account if a second batch of water were processed in the Anchor Hill Pit or if a similar project were undertaken at another pit lake.

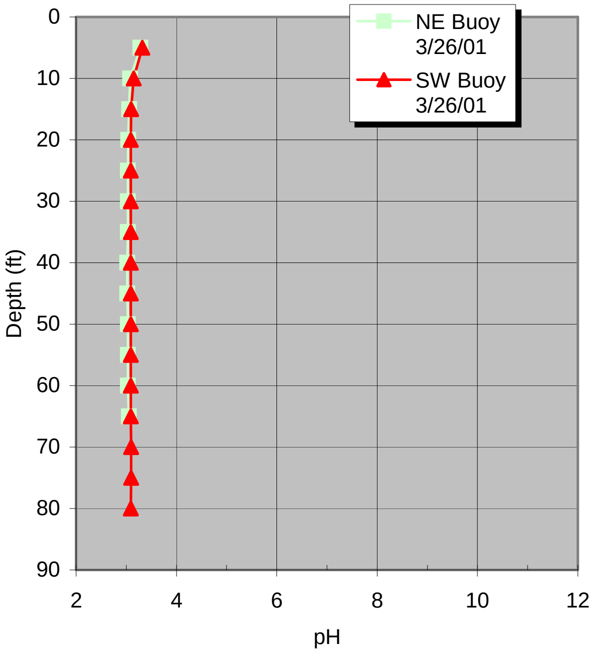


Figure 4-1. pH versus depth prior to pit lake neutralization.

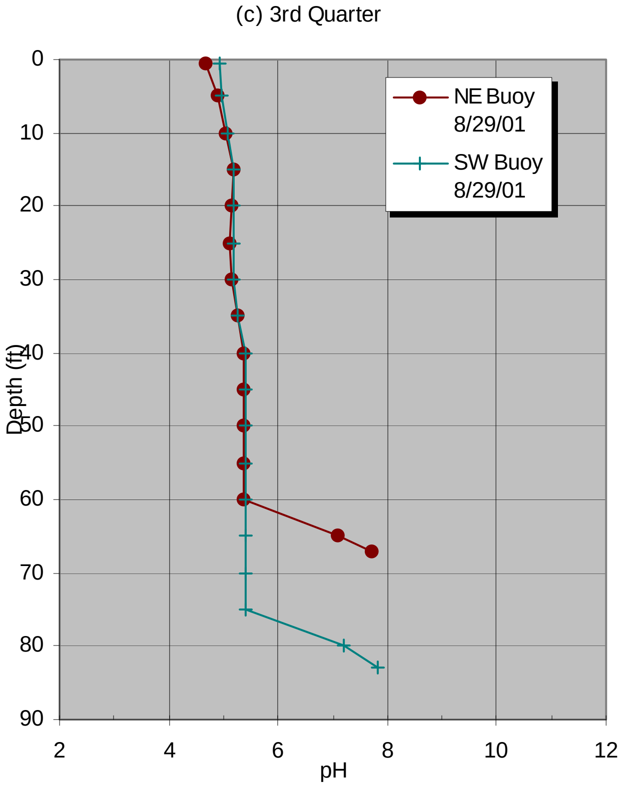


Figure 4-2. pH profiles with depth after initial lime neutralization.

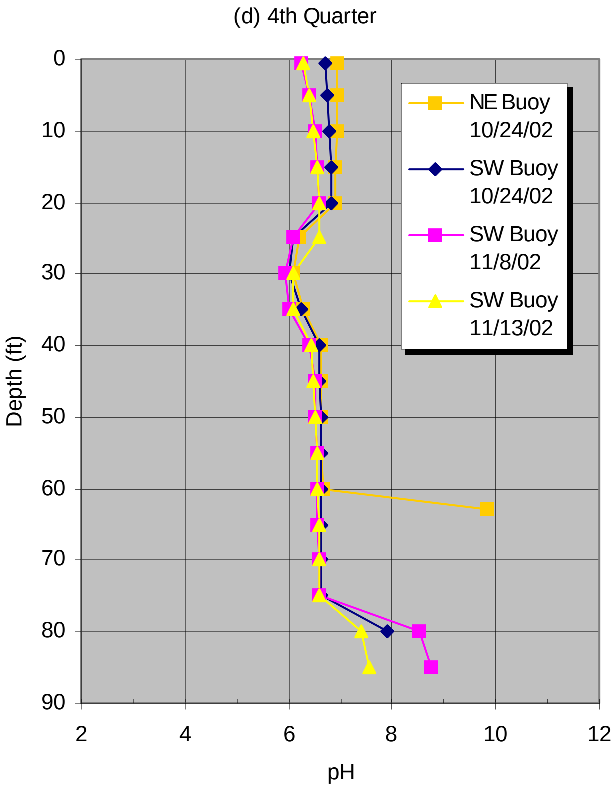


Figure 4-3. pH profile following additional efforts to neutralize the Anchor Hill Pit.

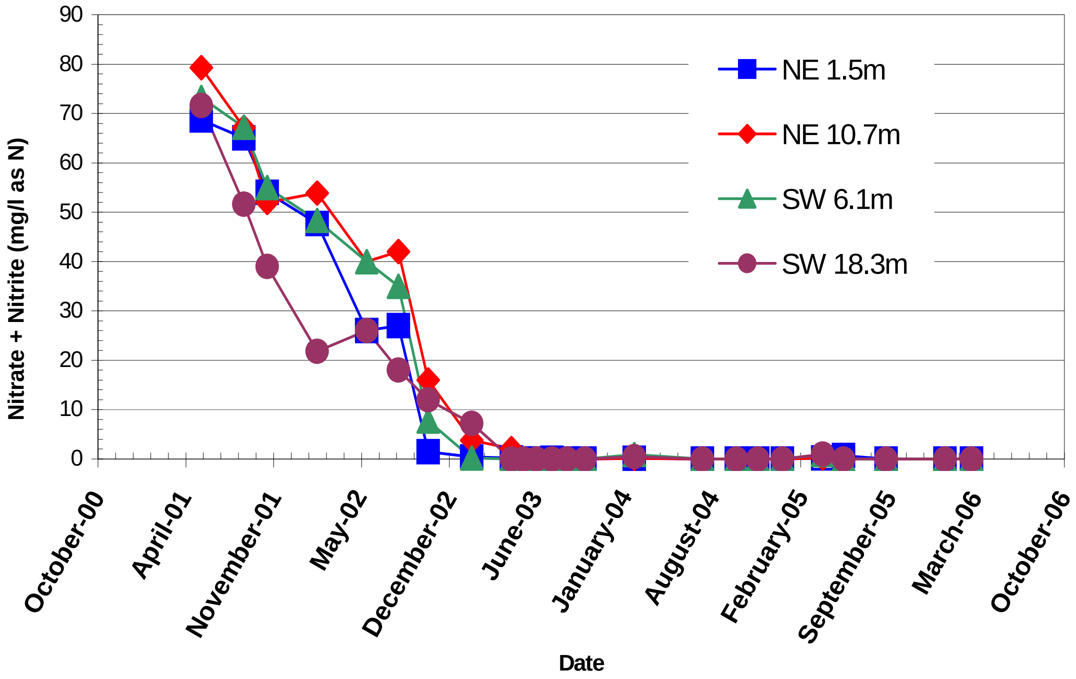


Figure 4-4. Nitrate data at each sample location throughout the demonstration.

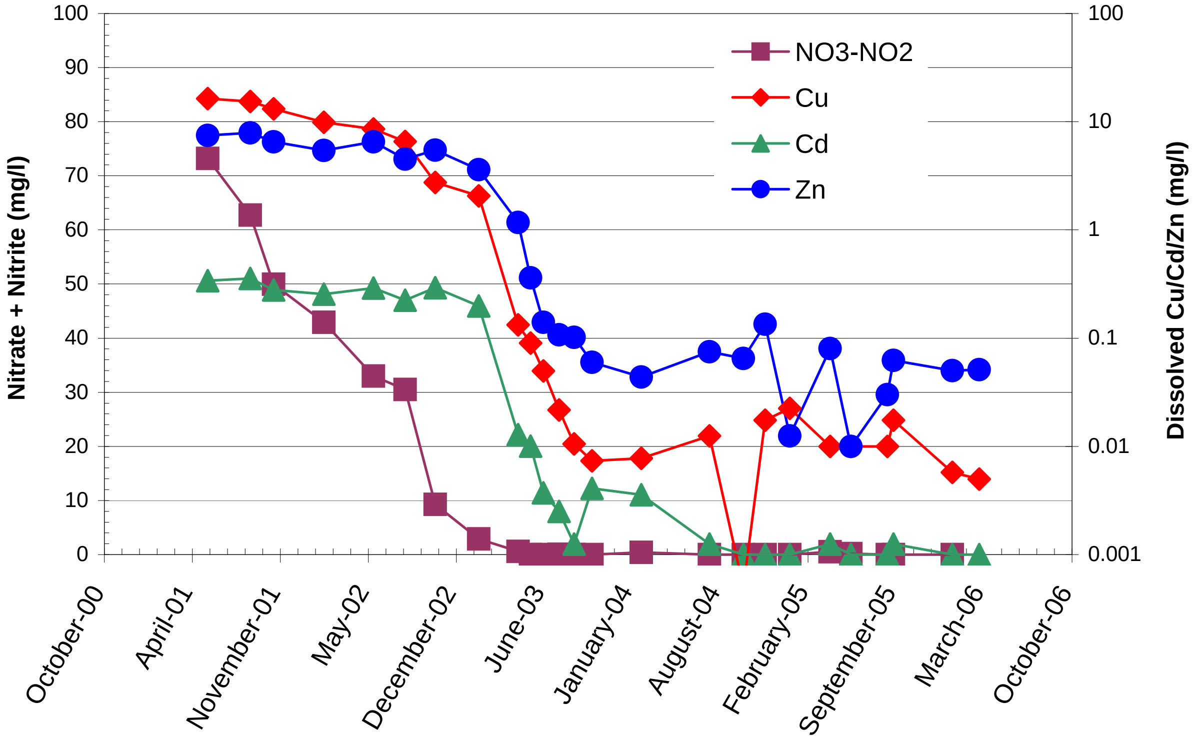


Figure 4-5. Anchor Hill Pit nitrate/nitrite and dissolved copper, cadmium, and zinc concentrations over the project duration. (Note: values averaged over all sampling locations.)

Table 4-1. Water Quality Improvement Over the Course of the Project

Parameter	May 2001				January 2003				February 2004				April or May 2005			
	NE05	NE35	SW20	SW60	NE05	NE35	SW20	SW60	NE05	NE35	SW20	SW60	NE05	NE35	SW20	SW60
Dissolved Aluminum	49.7	45.2	41.8	40.3	3.38	3.43	4.09	3.51	0.127	0.017	0.012	0.019	0.02	0.27	0.02	0.01
Dissolved Cadmium	0.315	0.349	0.35	0.345	0.203	0.206	0.198	0.184	0.0038	0.005	0.005	0.005	0.001	0.001	0.001	0.001
Dissolved Copper	16.3	16.6	16.4	15.9	0.871	1.47	3.3	2.64	0.014	0.008	0.005	0.004	0.01	0.01	0.01	0.01
Dissolved Iron	0.337	0.0867	0.035	0.0479	1.03	1.27	0.976	0.858	0.03	0.048	0.046	0.034	0.04	0.05	0.18	0.08
Dissolved Zinc	7.19	7.65	7.61	7.49	3.38	3.43	4.09	3.51	0.127	0.017	0.012	0.019	0.02	0.27	0.02	0.01
Alkalinity	<5	<5	<5	<5	134	134	176	186	106	366	378	404	98	372	418	452
Nitrate/ Nitrite	68.7	73.2	79.3	71.6	0.4	0.2	3.8	7.21	0.14	0.88	0.14	0.5	0.19	0.9	0.19	0.96
Sulfate	2540	2700	2230	2510	ND	ND	ND	ND	1900	2400	2100	2300	ND	ND	ND	ND
Sulfide	<5	<1	<1	<1	80	100	81	94	4.5	9	8.7	11	1.9	6	6.5	7.3

5. Lessons Learned/Quality Assurance Activities

The following sections are lessons learned over the course of the project that may have value to others attempting similar work in the future. Also included in this section is a discussion of QA activities undertaken throughout the project.

5.1 Neutralization

- If possible, physical profiles should be gathered frequently during times of the year with rapid temperature change (spring and fall) or with potential acidic run-off to more confidently understand the trends observed. Furthermore, regular physical profiles should be gathered for at least one year for an existing pit lake prior to initiating treatment such as that presented here, for comparison purposes. In addition, for pit lakes with uncertain groundwater inflow or flow through, the use of a bromide background indicator would be useful. However, to be useful it must be well mixed into the lake, which is easier said than done. Ideally, it would be added a year or more in advance to allow time for dispersion.

- The Neutra-Mill was not an efficient way to neutralize this pit lake due to the relatively low throughput and the relatively high operator attention required. In fairness, personnel at Earth Systems take the position that the system was not properly configured and operated by Shepherd-Miller. The fact remains, however, that it was difficult to transfer the lime to the Neutra-Mill without "slurrying" it to the Neutra-Mill, and it did require constant vigilance in operation. It is probably quite suitable for smaller bodies of water where the desire is simply to "get in, do it, get out". For a larger body of water, where a larger effort is inherently required, a reliable, less labor-intensive approach would be desirable. One possibility would be to set up a mixed tank at an accessible location near the lakeshore. Bulk bags of lime could be added directly to the mixed tank, which would be constantly agitating, with makeup water being delivered via a pump immediately adjacent in the water body. A second pump could transfer lime slurry from the tank to the water body through a flexible hose, which could be moved occasionally around the lake to facilitate mixing.

- In April of 2002, one truckload of sodium hydroxide was offloaded on top of the iced-over pit lake, with the idea that as the ice melted, the caustic would mix in with the water. In reality, concentrated caustic is delivered at elevated temperature, on the order of 120 °F. This caustic was delivered to the ice surface, where it promptly melted a hole in the ice and probably sank to the pit floor. Concentrated caustic does not mix well in cold water; it simply forms "globs". This type of neutralization approach should not be attempted in a similar, future effort.

- A more effective methodology was used in September of 2002, when the concentrated caustic was metered into a pumping loop. Water was drawn from near the shore at approximately 800 gpm, concentrated caustic was metered into it at a low rate of around 1 gpm, and the mixture was delivered to the water surface in the middle of the pit. This was the approach taken in effectively neutralizing the pit prior to the more rapid commencement of biological activity.

- The choice of lime versus caustic for in situ neutralization depends, in part, on the initial sulfate concentration and the desired final sulfate concentration. Certainly, liquid caustic has some advantages in ease of handling, but will not effect the sulfate concentration as lime can through the production of a gypsum precipitate ($CaSO4\bullet2H2O$). With the high initial sulfate concentration present in the Anchor Hill Pit, the use of lime was advantageous in producing lower total dissolved solids and sulfate values. In the case of a hypothetical pit lake with sulfate concentrations well below the gypsum saturation point, there may be no advantage in using lime.

- Neutralization should not be conducted in the winter. Due to project-specific circumstances, neutralization was performed in the winter, but it was extremely difficult. If a pit lake is located in a climate where it freezes, then neutralization should be conducted in the fall, so nutrients can then be added just prior to freezing over of the lake.

- If neutralizing to a target pH is attempted, adequate time must be allowed for reactions to complete, and the need for additional reagent dosages are likely. Overdosing of the reagent should be considered, as well as the partial use of a reagent providing buffering capacity, such as soda ash.

5.2 Nutrient Addition

- Nutrient dosages should be made based on a recent analysis of the water to be treated, and should be conducted either after the lake freezes or immediately before ice forms (if the climate is such that ice will form).

- Reduction reactions would likely have occurred much faster had neutral pH been maintained from the beginning.

- Nutrient dosage must be estimated carefully so as to not overdose, avoiding excessive sulfide production.

- A good microbial community analysis on the initial water would be helpful to determine the kinds of bacteria that are present and whether bioaugmentation may be necessary. The addition of inoculating bacteria to the pit should be considered. It was not performed on this project because a significant philosophical aspect was that only native bacteria would be stimulated and utilized for treatment. In other applications it should receive serious consideration since it might result in more rapid treatment.

- The wood chips were a relatively cheap material to add to the pit lake to provide substrate for bacterial growth, but it is not clear if wood chips were required for the reactions to proceed.

- If fertilizer is added in an attempt to stimulate algae growth, a liquid rather than solid form should be utilized. In addition, careful thought should be given to the makeup of the fertilizer and its interaction with the surface water. In this case, only granular triple super phosphate [$Ca(H_2PO_4)_2$] was added. It is likely that a small amount of nitrogen should also have been added, and further, it is likely that with the high amounts of dissolved calcium already present in the water, the calcium phosphate could not readily dissolve.

5.3 Monitoring

- In situ physical measurements using a datasonde-type apparatus are favored over the use of a flow cell and peristaltic pump. This is because changes can occur between the deeper zones and the water surface. On one sampling occasion (October 2001) a pump and flow cell were utilized. The temperature of the water in situ warmed up as it was pumped through warmer water to the surface, and was obviously inaccurate. In addition, noticeable degassing of (probably) carbon dioxide was observed in the pump tubing at the water surface. This would tend to result in a pH increase.

- If unexpected dissolved oxygen measurements are encountered, the presence of other dissolved gases (i.e., sulfur dioxide, nitrous oxide, nitric oxide, chlorine, etc.) should be considered and, if necessary, evaluated.

- The use of charge balance calculations as a check of data quality and validity should be utilized as necessary.

- If biological treatment is being undertaken, appropriate analyses (e.g., SRB counts, total direct counts) should be performed prior to treatment and regularly thereafter.

5.4 Discharge

Extraction and oxidation of deep water is not the best way to discharge water. Taking water off the oxygenated surface zone avoids the TSS problem caused by oxidation of sulfide to elemental sulfur. Over 20% of the water initially present in the pit was successfully discharged this way.

5.5 Quality Assurance Activities

At the beginning of the project, responsibilities were assigned to various members of the project team. Quality assurance activities were assigned to EPA Region 8 and their contractor CDM. The following sections discuss data quality issues that were identified during the project by CDM and other members of the project team, the impact of these issues on data quality, and how these issues were addressed.

5.5.1 Field Data Review

Field data (pH, ORP, temperature, dissolved oxygen) was collected by Shepherd-Miller, MSE, and CDM during regular sampling events. Continuous monitoring probes were also installed in the Anchor Hill Pit to give real-time information. As treatment proceeded, field data was reviewed primarily to identify trends. Data anomalies were identified for the continuous measurements when these results were compared to field data from sampling events. It was decided that it was difficult, if not impossible, to maintain valid calibration of these probes, so this data was only used by the project for identifying trends and was not used to determine if project objectives had been met.

There were also occasional issues identified with the field data collected at scheduled sampling events. The pH data collected by MSE using the YSI from the August 2001 sample event should also be considered estimated because after measurements were collected, all buffers measured 0.4 pH units above the accepted value for the buffer. After this event, the YSI was calibrated at each location prior to collecting vertical profiles, thus not relying on one calibration for the entire sampling event.

5.5.2 Laboratory Data

EPA Region 8 began submitting samples to the EPA Contract Laboratory Program (CLP). Over the course of the project, CDM reviewed field and laboratory data as it was generated and prior to release to MSE. CDM did validate the data and indicate through data qualification if any data had data quality issues. The data review process at CDM did cause problems, as the data was not available for review in a timely fashion so that technical adjustments could be made.

Upon review of the data from 2001-2002, MSE personnel noted that the charge balances were not within tolerable limits for the samples collected. To correct this, EPA Region 8 gave CDM approval to send samples to non-CLP labs (Energy in Rapid City, South Dakota and Mid-Continent in Rapid City, South Dakota). CDM also reviewed and validated this data prior to release to MSE. The charge balance issue was corrected and reporting limits improved after sending samples to the non-CLP laboratories.

Also, as a result of the data anomalies reported by MSE, EPA-NRMRL performed a technical systems audit on August 29, 2001. There were four findings related to QAPP deviations, timely receipt of data so that previous sampling event data is available for review, anomalies noted for field pH measurements, and the questionable nature of data gathered from the continuous monitoring probes. All findings, observations, and technical comments were addressed by MSE in a response to EPA. This response memo is contained in Appendix A. As mentioned previously, CLP laboratories being used at the project outset were not providing very defensible data because charge balances were not within tolerable limits.

The only relevant laboratory data that was deemed unusable by CDM included total lead data from the SW60 sample location collected on 8/29/01. Because lead was already below the discharge criteria, this did not impact project objectives.

The most critical sampling events were those that would determine if water met the ARARs and could be discharged from the Anchor Hill Pit. As summarized in Appendix B, much work was performed to determine the best way to obtain water that met the discharge standards. Data relating to discharge requirements was intensely reviewed by the project team and the State of South Dakota to ensure that the data used to make discharge decisions was defensible. CDM did not report any data quality issues for these samples.

6. Conclusions/Recommendations

There is clearly the potential to utilize the pit lake for treating site waters in batch mode. The approach of neutralizing acidic water in the late summer/fall followed by adding nutrients after an extended stabilization time, will likely yield dischargeable water quality at the surface about 1.5 years later (two winters and one summer). Water can then be discharged off the surface. This would probably result in significant cost savings (20% to 40%) over the water treatment plant, but there are many considerations, as discussed in the previous section, to ensure that the technology is applied appropriately.

With the successful discharge of Anchor Hill Pit surface water in 2005 and 2006, it is possible that significantly more surface water could be discharged in a like manner. Water would be discharged from the surface zone (top 5 to 10 feet), and then the new surface water would be allowed to equilibrate with the atmosphere for some period of time. If necessary, the dissolved oxygen and BOD of that water would become acceptable for discharge, along with settling of any precipitates present, be they ferrous sulfide or elemental sulfur. Once the surface water met applicable standards, it could be similarly discharged.

With the knowledge gained during the project, if a new batch of water were ready for treatment, it would be accomplished as follows:

- Good initial characterization over a year to determine seasonal effects on pit lake water quality;
- Bench-scale tests on actual water at appropriate conditions (similar to bucket tests performed in the pit) to assist in determining proper dosages of the various reagents and nutrients;
- Faster and more efficient means of pit lake neutralization;
- Careful dosage of nutrients in the late fall so that biological reactions could occur over the winter;
- Detailed microbial community analysis to determine nutrient requirements and need for bioaugmentation;
- Consideration of adding bacterial inoculum to speed the treatment process, particularly if initial biological characterization indicated that critical bacteria types were not present in the initial water; and
- Discharge of water from the surface water zone incrementally as treatment proceeds and surface water meets discharge standards.

All original project objectives were eventually met, and the project was a success. Also, considerable experience and insight was gained into how operational aspects of such a remediation technique would have to be designed for a future application of this technology. In late-fall 2005 and spring 2006, large-volume skimming and decanting of surface-waters meeting water-quality standards was carried out, resulting in the successful release of approximately 40-million gallons into Strawberry Creek over the course of the project.

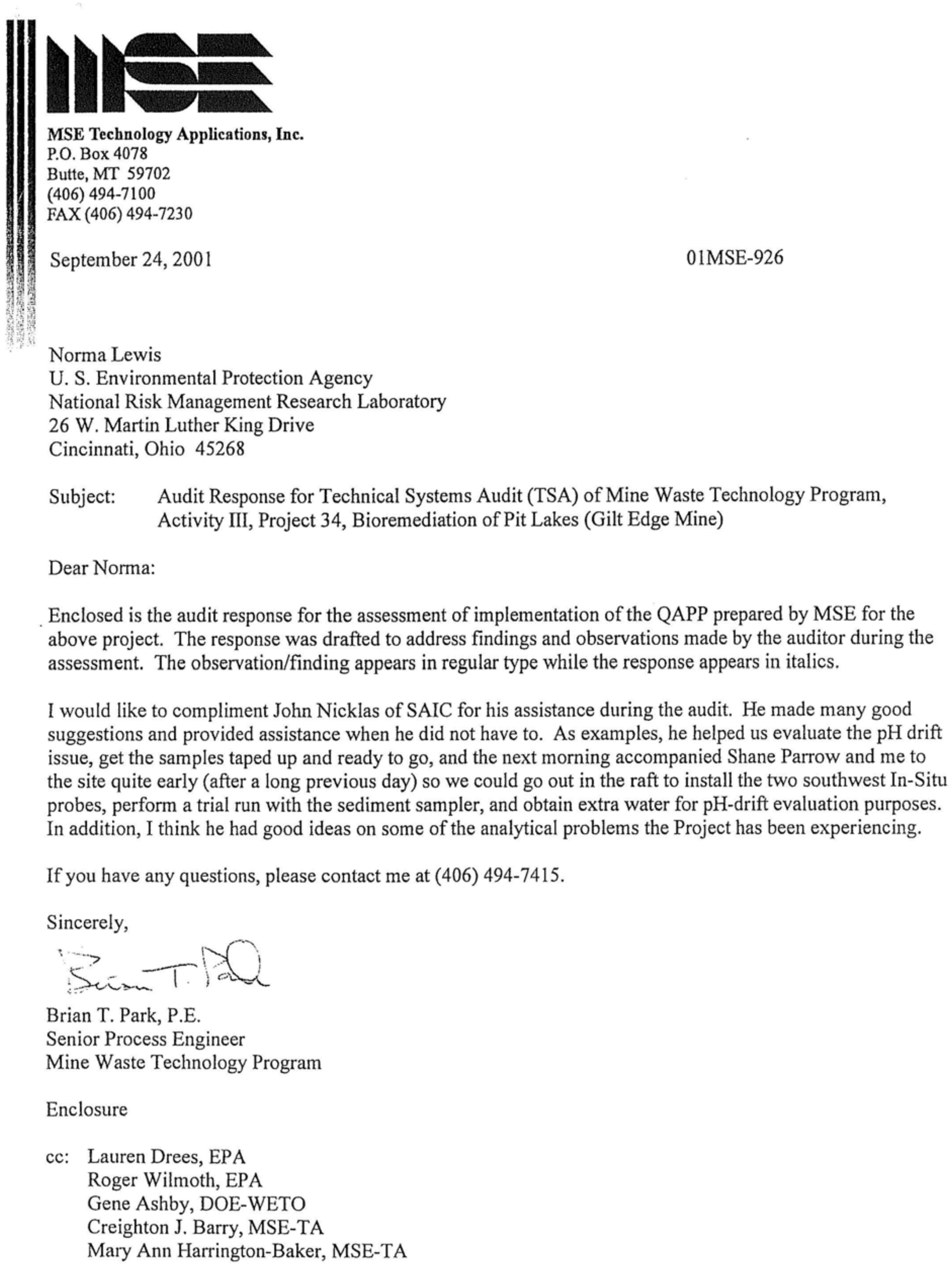
7. References

Lewis, N.M., K.W. Wangerud, B.T. Park, S.D. Fundingsland, J.P. Jonas, "Status of in situ treatment of Anchor Hill Pit Lake, Gilt Edge Mine Superfund site, South Dakota", in Proceedings for *ICARD 2003: Sixth International Conference on Acid Rock Drainage*, July 14-17, 2003, Cairns, Queensland, Australia, The Australian Institute of Mining and Metallurgy (AussIM), ISBN: 1-875776-98-2, 2003.

Lewis, N.M., K.W. Wangerud, B.T. Park, S.D. Fundingsland, J.P. Jonas, "Anchor Hill pit lake two-stage in situ treatment, Gilt Edge Mine superfund site, South Dakota, USA", in Proceedings for *Tailings and Mine Waste'03*, pp. 345-358. Swets and Zeitlinger B.V., Lisse, The Netherlands, ISBN: 90 5809 593 02, 2003.

Appendix A

Technical Systems Review Response from MSE to EPA



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September 24, 2001 01MSE-926

Norma Lewis
U. S. Environmental Protection Agency
National Risk Management Research Laboratory
26 W. Martin Luther King Drive
Cincinnati, Ohio 45268

Subject: Audit Response for Technical Systems Audit (TSA) of Mine Waste Technology Program, Activity III, Project 34, Bioremediation of Pit Lakes (Gilt Edge Mine)

Dear Norma:

Enclosed is the audit response for the assessment of implementation of the QAPP prepared by MSE for the above project. The response was drafted to address findings and observations made by the auditor during the assessment. The observation/finding appears in regular type while the response appears in italics.

I would like to compliment John Nicklas of SAIC for his assistance during the audit. He made many good suggestions and provided assistance when he did not have to. As examples, he helped us evaluate the pH drift issue, get the samples taped up and ready to go, and the next morning accompanied Shane Parrow and me to the site quite early (after a long previous day) so we could go out in the raft to install the two southwest In-Situ probes, perform a trial run with the sediment sampler, and obtain extra water for pH-drift evaluation purposes. In addition, I think he had good ideas on some of the analytical problems the Project has been experiencing.

If you have any questions, please contact me at (406) 494-7415.

Sincerely,

Brian T. Park

Brian T. Park, P.E.
Senior Process Engineer
Mine Waste Technology Program

Enclosure

cc: Lauren Drees, EPA
Roger Wilmoth, EPA
Gene Ashby, DOE-WETO
Creighton J. Barry, MSE-TA
Mary Ann Harrington-Baker, MSE-TA

1. INTRODUCTION

A Technical Systems Audit (TSA) of the quarterly sampling activities at the Anchor Hill Pit, located at the Gilt Edge Mine, was conducted August 29, 2001 by John H. Nicklas of Science Applications International Corporation (SAIC). (SAIC is a subcontractor to Neptune & Co., QA support contractor for EPA.) The audit was conducted using *Mine Waste Technology Program Quality Assurance Project Plan for Bioremediation of Pit Lakes (Gilt Edge Mine)*, Revision 0 dated February, 2001. The following sections represent the response to the findings/observations identified during the assessment.

GENERAL QA/QC ISSUES

Finding #1

QAPP Deviations. Current field activities are not always consistent with the requirements in the approved QAPP. These items include items such as the collection of field measurements with a YSI (as opposed to the QAPP required Hydrolab) and the collection of waste samples with a Kemmerer sampler (as opposed to the QAPP required weighted bottle sampler). In addition, some activities that deviate from the QAPP are not being evaluated for their impact on project objectives.

A letter dated August 24, 2001 from Brian Park to Helen Joyce (MSE QA Officer) itemized 13 recommended changes to the QAPP. This letter was available to the auditor during the audit. Both critical and noncritical items were addressed in the letter. However, these deviations had not been submitted to EPA project personnel for review and approval.

One example of a change which may impact project objectives is that the developer has apparently commented that since the pH of the pit water decreased from pH 7.0 to approximately pH 5, the length of time required to achieve project objectives would therefore increase. However, the August 24 letter proposes a decrease in the length of time of the project due to budgetary constraints. Although separate issues, they need to be evaluated together.

Another example of a deviation identified in the August 24 letter is the required addition of the organic media through a hole in the ice and at a depth of 50 feet below the surface. The organic was actually added after the ice thawed and added to the surface of the pit.

Recommended Corrective Action.

All deviations to QAPP requirements need to be documented. The contents of the August 24 letter should be reviewed by the appropriate personnel for completeness, evaluated for impacts to project objectives, and a determination made regarding the acceptance or rejection of each item. The proposed changes, along with any additional QAPP changes, should be incorporated into an addendum to the QAPP. A formal review and approval process should be used.

An addendum to the QAPP will be developed. No deviations have impacted achieving the project objectives. It must be realized that, due to the decision to try to neutralize the Pit and dose the organic prior to the ice melting (with increased costs associated with work on the ice and severe working conditions), and due to cost overruns on Shepherd-Miller's part, causing MSE to absorb additional work scope, budget issues must be considered in any decisions related to the Project. This is particularly critical in relation to project duration and number of sampling events.

Finding #2

Review of Previous Sampling Event Data. Results from previous sampling events have not all been reviewed for impact upon the current sampling event (i.e., the results from the May sampling event have not been validated and approved for use). Additionally, it appears as though all of the data may not yet have been received from the laboratories. It has been determined that the results from the ICP metals analyses from the pre-neutralization sampling event (conducted in March) show significant matrix interferences and cannot be used to support project objectives. The results from the May sampling event are not yet available to determine if they are capable of meeting project objectives. If the same analytical protocols are used during this sampling event, it is possible that results may not support project objectives.

Recommended Corrective Action. The results from previous sampling events should be evaluated (prior to each sampling event) to determine if analytical methodology and the requested analyses are sufficient to meet project objectives. The turnaround time for the receipt and validation of analytical data should be reduced so the results are available in a timely manner to make necessary project decisions.

MSE concurs with the recommended corrective action. However, EPA Region VIII and their contractor, CDM Federal Services, are responsible for producing analytical data for the Project. As such, MSE is not in control of that aspect of the Project and cannot be held responsible for poor analytical turnaround time. At this point MSE still has not received non-CLP data from the May 2001 sampling event and only very recently received supporting QA information for the CLP data from that sampling event. Note this is now 3.5 months since that sampling event. This has been discussed with CDM. Apparently CDM has begun sending samples to laboratories other than Energy Lab in Rapid City due to their own problems with poor turnaround. CDM had no recommendations for achieving faster turnaround, other than to say that the bottleneck appears to be the generating/formatting/validation of supporting QA information (at CDM for CLP data, at Energy Lab in for non-CLP data). Their suggestion was that data *with no supporting QA would be available much faster, and could easily be obtained for review prior to future sampling events. This suggestion is somewhat dangerous since, without substantiating QA information, there would be no way to know whether the data was good. If EPA Region VIII cannot be convinced to assign priority to the Anchor Hill Pit project samples, CDM's suggestion may be the Project's only alternative.*

Finding #3

Field pH Measurements. A YSI is being used to collect the field measurements. Prior to collecting field pH measurements, the YSI was calibrated using pH 4.0 and pH 7.0, and then a pH 5.0 solution was measured. The YSI appeared to calibrate correctly, and the pH 5.0 solution measured pH 5.0 when checked. During the collection of field measurements, it was noted by the field team that the pH measurements at the sampling locations appeared anomalous. Upon returning to shore, the pH 4.0, 5.0, and 7.0 solutions were measured. All standards were reading 0.4 pH units high (pH 4.4, 5.4, and 7.4 respectively).

Recommended Corrective Action. At the time of the audit, field personnel determined that the pH measurements during this sampling event are not critical to the determination of the achievement of ARARs. The pHs were recorded as measured with appropriate notation, and the water samples collected from the sampling points were measured with the Orion pH meter.

Future pH measurements will be critical for evaluating project objectives and the attainment of ARARs. The cause of the anomalous field pH measurements should be determined, and a method to obtain accurate pH measurements must be determined. Some water was collected during the sampling event to begin investigations. The other field measurements (DO, ORP, specific conductance, and temperature) should be evaluated to determine if they are impacted.

Extra water was obtained and brought back to MSE to investigate this further. Note that the exact cause of the pH drift may not be determinable; a likely suspect is the amount of organic material in the water and the associated "sliminess" noticed when sampling, but this is not a given. Note also that the issue relates to level of accuracy. Based on the probe calibration change, it is likely the measured pH values were high, and this is consistent with what was measured with the Orion meter (Orion measured 4.68 for SW20, 5.01 for SW65, 4.44 for NE05, and 4.80 for NE35, while the YSI gave 5.17, 5.42, 4.89, and 5.27, respectively). The ARAR minimum pH value is 6.0, so even with reduced accuracy the pH was significantly out of compliance. Better accuracy would only be needed if the pH climbs to approximately 6.0, which, if it happens at all, will be a very slow process. Therefore this minor measurement drift is not a crisis. MSE will experiment with the YSI probe and the Orion probe on the extra water brought back, and if a reason for pH drift is established, appropriate corrective action will be taken. Some *possibilities are to clean and recalibrate the YSI probe between profiles; drop the Kemmerer sampler to the proper depths, obtain samples, and measure them with the Orion probe; etc. At a minimum, at the next sampling event, pH values of the four water samples will be measured immediately in the raft with the Orion probe for comparison with the YSI probe. The other measurements, calibrated prior to obtaining the profiles, showed good agreement with calibration solutions after taking the profiles; this would seem to indicate that they were not impacted.*

Finding #4

Continuous Monitoring Probes. Due to the water conditions and the frequency of calibration, the information gathered from the continuous monitoring probes is potentially questionable. The probe at the Northeast location at a depth of 5 feet (NE 5) has failed. The probe at the Northeast location at a depth of 35 feet (NE 35) was not calibrated during this site visit.

Recommended Corrective Action. A decision needs to be made as to whether the continuous monitoring probes are providing some critical or only noncritical measurements. The purpose and necessity of these probes needs to be determined. If the information is required, then the information gathered should be evaluated to determine the accuracy (see finding #4). The continuous monitoring probes are identified within the QAPP. The NE 5 probe should be repaired and replaced if required. The probes should be calibrated quarterly or at another frequency determined to be necessary.

It is MSE's opinion that the data produced by the continuous monitoring probes are not worth the added cost of maintaining their calibration. Realistically, to be trustworthy they would have to be recalibrated every few weeks, and this is not possible with the existing budget. From the beginning of the project the probes were considered a "nice-to-have" (even by Shepherd-Miller), which would show physical variables changing with time, but were not critical to the project goals. The only critical measurements that the probes were originally intended to make were pH and dissolved oxygen, related to draft South Dakota ARARs. In retrospect, it was not a good idea to trust the continuous monitoring probes for this; the vertical profiles generated at each sampling event are much more trustworthy since they are more representative (i.e., vertical profiles rather than four discrete points) and are made with an instrument calibrated just prior to taking the measurements.

Observation #1

Adherence to QAPP SOPs. Specific steps identified in the SOPs attached to the QAPP are not being followed. Two examples are the collection of water samples using a weighted sample bottle and decontamination of sampling equipment. The decontamination procedure requires the cleaning and air drying of all sampling equipment that comes into contact with the samples. However, the cleaning of a Kemmerer sampler (followed by air drying) between the 20' and 65' depths adds no value, since the sampler is passed through the same water to reach the 65' depth.

Recommended Corrective Action. Modifications to SOPs should be documented and distributed to project personnel to ensure consistent procedures are used throughout the study.

The SOPs in the original QAPP were obtained from CDM, and were a carryover from the QAPP prepared by CDM for the Gilt Edge Multicell project. MSE will develop new SOPs as part of the QAPP addendum referred to in Finding #1 above. The new SOPs will reflect actual practices. Note that no problems with actual practices were identified in the audit.

ADDITIONAL TECHNICAL COMMENTS

Additional Technical Comment #1

Field Surveillances or Audits. The QAPP assigns the responsibility for determining the need and conducting surveillances and audits to the CDM Federal QA Manager. No surveillances or audits have been conducted by CDM, nor are any known to be scheduled. Since sampling efforts are now being performed by MSE, responsibilities should be reassigned.

Recommendation. EPA and MSE responsibilities for surveillances and audits should be discussed in a QAPP addendum to ensure that these activities are performed when deemed necessary.

The QAPP addendum referred to in Finding #1 above will reflect actual responsibilities.

Additional Technical Comment #2

Miscellaneous. The following were discussed during the audit.

- An ultra-fine point Sharpie® should be utilized for field logbooks, especially when collecting water samples.
- A contact telephone number should be included on the chain-of-custody forms. This telephone number is particularly critical for samples with short holding times, and should be to a phone where someone is available during the short holding times.

An ultra-fine point Sharpie® will be used in future sampling activities. A contact telephone number will be included on future chain-of-custody forms.

Appendix B

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

Evaluation of Use of Anchor Hill Pit for Ongoing Site 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 and become an integral part of the water treatment strategy for the Gilt Edge Mine site. 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 1 gallon of Surge Pond water along with 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 60-foot depth in the pit in July 2004, to ensure that 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 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 had 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.

Treatment & Discharge Options: In Situ and Ex-Situ Process Considerations

Treatment of the entire pit-lake water body obviously did not occur as envisioned at the outset. Except for the surface layer, the fine suspended metal-sulfide precipitates in the water did not readily coagulate and completely settle. The team’s attention and efforts in 2004 therefore focused on dealing with the fine residual suspended solids in the water column, as well as chemistry issues associated with deep zone waters.

Over the course of treatment, the pit lake had become meromictic (i.e., permanently stratified) with the upper layer separated from the deeper zone by a strong density gradient (or chemocline). The team recognized that the strong redox condition of the deeper zone is where the most robust kinetics for “decontamination” occurred, and that the overlying surface layer served to protect and maintain the thermodynamic conditions of the deep zone. Even though the upper surface-waters were “clean”, the team initially felt that discharge of the surface layer water might compromise the stability and integrity of the multi-layered pit-lake reactor. Accordingly, the team felt that the deep zone (containing the largest volume of pit-waters) should be targeted as the primary extraction zone—recognizing that the issues related to fine residual suspended solids and the inherent chemistry of the deep-waters (residual carbon, excess sulfide, and dissolved non-metal constituents) would have to be dealt with. The team realized that an additional stage of treatment would be necessary to accomplish deep zone water discharge.

Ex-Situ Deep Zone Water Processing

The team developed an approach for filtering the water while pumping from the pit, followed by aeration in a shallow lagoon. Filtering would remove the fine suspended solids, while surface-exposure and aeration would remove dissolved hydrogen sulfide, bio-reduce organic constituents to decrease biochemical oxygen demand (BOD), and increase dissolved oxygen, thereby achieving dischargeable water. Planning began for filtering of the water, and also for construction of a 0.1-acre, 5-feet deep, 150,000-gallon lined lagoon to serve as an aeration and oxidation cell.

Filter testing. In late-January 2004, filtration tests were performed on water from the deep zone in which water was filtered through 0.45-, 1-, 5-, 10-, and 20-micron filter cartridges and the filtrates subjected to total metals analysis. The purpose of this was to determine approximate filtration requirements for sufficiently removing the residual fine metal sulfide precipitates from solution when pumping from the deep zone. Results indicated that filtration at a level of 5-microns or less would be needed. While discharge metals standards are based on dissolved analytical values, a conservative approach focusing on total metals values was followed, since it was thought that suspended metal-sulfide particles might oxidize and re-dissolve upon prolonged exposure to air.

Field-filters and initial pump-runs. A filtration configuration consisting of an initial 25-micron bag filter followed by two 1-micron bag filters in parallel was selected as an inexpensive, simple way to filter initial batches of water. These bag filters were #2-size (7-inch diameter by 32-inches long), contained in standard, off-the-shelf filter housings. The water fed to the filtration system was to be pumped from the 50-foot depth by a Godwin HL80M pump. The pump-filtration setup and the lagoon are shown in Figure B-1. Due to anticipated off-gassing of carbon dioxide and hydrogen sulfide gases released by pumping water from the deep zone to the surface, tests were performed at increasing scale to assure worker health and safety. An initial pumping test of a small batch of 200 gallons confirmed the formation and release of small amounts of hydrogen sulfide gas. As a result, the Site Health & Safety Plan was modified for increased instrumentation and monitoring capability, self-contained breathing apparatuses (SCBAs) were obtained for emergency contingency in the event of extreme off-gassing, and a weather station was set up in the vicinity of the aeration lagoon to assure that pumping into the lagoon was only done under sufficient wind conditions to assure rapid dispersion of H_2S.

Figure B-1. (left) Godwin pump and filter-set configuration in the pit; (right) aeration/settling lagoon (ASL) with initial 2,000 gallon run

Scale-Up Operations and Results. After addressing the anticipated hydrogen sulfide gas concerns, a 2000-gallon pumping test was conducted in late June 2004. Initial pumping using the Godwin pump produced erratic, surging flow rates, likely due to the anticipated off-gassing of carbon dioxide and hydrogen sulfide gases resulting from pressure-differentials when pumping water from the deep zone to the surface. A subsequent 20,000-gallon pumping test, also in late-June, at a lower pump speed showed much better pump behavior, with a flow of approximately 350 gpm. Filtration performance was not as effective as desired, with some suspended solids remaining visible in the filtrate in the lagoon. Following both pumping tests, field analyses of sulfide and turbidity were performed in the ensuing days. In both cases, the sulfide level decreased and the turbidity increased. This is believed to be caused by the formation of elemental sulfur precipitates resulting from the oxidation of residual dissolved sulfide. The implication of this was that the aeration lagoon would have to doubly serve as a settling basin upon completion of aeration/oxidation.

Initial Full-Scale Process Discharge. In mid-July an additional 100,000 gallons were pumped from the deep zone through the filters to the ASL. Once again the water initially showed a decrease in sulfide and increase in turbidity from the oxidation of sulfide to elemental sulfur, as shown in Figure B-2. The time required for completion of this process was longer than the previous batches due to (a) the increased volume and depth of the water in the lagoon, (b) conservative operations in delaying active aeration to allow slower release of small amounts of residual H_2S gas, and (c) to gain de-gassing experience. Active aeration initially consisted of recirculation of lagoon water with small submersible pumps (too time consuming), followed by use of the Godwin pump at approximately 500 gpm. This recirculation occurred for about five days, at which time the pumps were shut off to observe settling behavior of the suspended sulfur and the anticipated decay in BOD. Measurements were made regularly during the aeration process with a multi-parameter probe for pH, temperature, dissolved oxygen, and oxidation-reduction potential at the water surface and at the bottom of the lagoon. In addition, the lagoon was sampled regularly for BOD, total organic carbon, as well as daily measurement of dissolved sulfide and turbidity. Laboratory results for BOD and field results for dissolved oxygen at the top and bottom of the ASL are presented in Figure B-3.

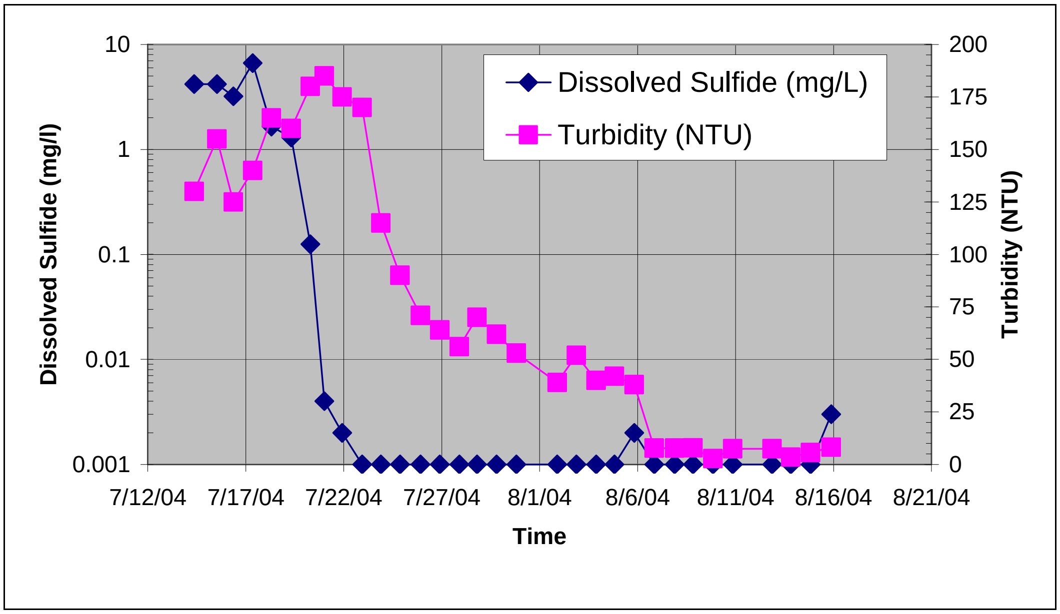

Figure B-2. Dissolved sulfide and turbidity in ASL following 100,000-gallon addition

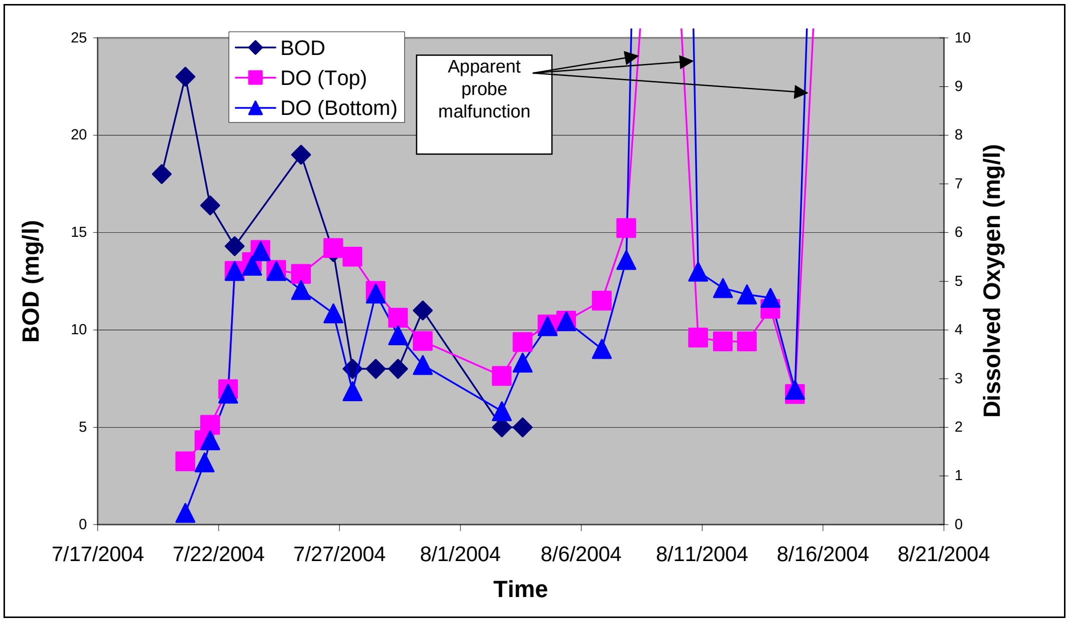

Figure B-3. Biochemical oxygen demand (BOD) and dissolved oxygen in ASL following 100,000-gallon addition

Upon observing the expected decreases in dissolved sulfide, turbidity, and BOD in the several weeks following the final water transfer, it became apparent that the water in the ASL was approaching dischargeable quality. To investigate this, several sampling events occurred to provide further data. The first event was on August 3, 2004 with the analytical results presented in Table B-1.

This dataset was encouraging since all metal values reported were within discharge standards. A further sampling event occurred on August 5 assessing discharge parameters at three different depths within the ASL. (Note: The opportunity was also taken to collect a sample from the surface of the Anchor Hill Pit for comparison.) The results for both of these samples are shown in Table B-2 below.

Table B-1. August 3, 2004 ASL Metals Results

Sample was collected from 0-2 feet
All results are from Energy Laboratories, Rapid City, SD
All units are mg/L

	ASL 8/3/04		**SD AWQC**	
Analyte	**Total**	**Dissolved**	**Acute**	**Chronic**
Aluminum	0.58	<0.05		
Antimony	<0.01	<0.01		
Arsenic	0.04	0.05	0.36	0.19
Barium	0.03	0.09		
Beryllium	<0.005	<0.005		
Cadmium	<0.001	<0.001	0.017	0.003
Calcium	570	590		
Chromium	<0.01	<0.01	0.015	0.01
Cobalt	0.02	0.02		
Copper	0.03	0.02	0.063	0.037
Iron	0.3	<0.02		
Lead	<0.01	<0.01	0.281	0.011
Magnesium	110	110		
Manganese	17	16		
Mercury	<0.0002	0.0002	0.0021	0.000012
Nickel	0.01	0.01	4.569	0.508
Potassium	28	30		
Selenium	<0.005	<0.005	0.02	0.005
Silver	<0.005	<0.005	0.037	
Sodium	360	370		
Titanium	<0.005	<0.005		
Vanadium	<0.01	<0.01		
Zinc	0.04	0.07	0.37	0.338

Table B-2. August 5, 2004 ASL and Anchor Hill Pit Surface Water Compared to Strawberry Creek Receiving Standards

All results are from Mid-Continent Laboratory, Rapid City, SD							
All units are mg/L							
	Anchor Hill Pit Lake	**ASL**			Std.		
	1-2 ft	**0-1 ft**	**1-2 ft**	**2-3 ft**			
pH	7.88	7.97	7.96	8.00	≥6.5-≤8.8	units	See section 74:51:01:07--no change in receiving water greater than 0.5 units
Conductivity at 25 °C	2,460	3,550	3,560	3,560	≤2,500	umhos/cm	30-day average
					≤4,375	umhos/cm	daily maximum
Temperature	Not Analyzed	16 - 27 °C			≤75	°F	See section 74:51:01:31--no temp change over spawning beds, ≤4 °F change
Dissolved oxygen	Not Analyzed	4.7 mg/L (8/9/04)			≥5.0	mg/L	
Total alkalinity as $CaCO_3$	54.4	285	285	279	≤750	mg/L	30-day average
					≤1313	mg/L	daily maximum
Total Dissolved Solids	2246	3428	3303	3454	≤2500	mg/L	30-day average
					≤4,375	mg/L	daily maximum
Suspended Solids	13	11	15	22	≤10	mg/L	24-hr composited sample
					≤17.5	mg/L	Grab sample maximum
Sodium adsorption ratio	2.5	3.5	3.5	3.6	≤10		[Na+]/sqrt(([Ca+2] + [Mg+2])/2) all in meq/L
un-ionized ammonia nitrogen as N (all assuming 22 °C and pH 8.0)	<0.0022	0.055 (total NH3-N 1.25)	0.057 (total NH3-N 1.29)	0.055 (total NH3-N 1.26)	≤0.02	mg/L	30-day average
	<0.0022	0.055	0.057	0.055	≤0.035 (1.75 times the applicable criterion)	mg/L	daily maximum
Nitrates as N	0.068	<0.05	<0.05	<0.05	≤50	mg/L	30-day average
					≤88	mg/L	daily maximum
Undisassociated hydrogen sulfide	<0.4 (total)	<0.4 (total)	<0.4 (total)	<0.4 (total)	≤0.002	mg/L	

BOD5	Awaiting Results	5 (8/3/04)	≤10		mg/L	24-hr composited sample
			≤17.5		mg/L	Grab sample maximum
Fecal Coliform (May 1-Sept 30)	Not Analyzed		≤1,000		/100 ml	geometric mean based on a minimum of 5 samples obtained during separate 24-hour periods for any 30-day period, and they may not exceed this value in more than 20% of the samples examined in this same 30-day period
			≤2,000		/100 ml	in any one sample
TPH	Not Analyzed		≤10		mg/L	See section 74:51:01:10--Cannot impart a visible film or sheen on the surface of the water or adjacent shoreline
Oil and Grease	Not Analyzed		≤10		mg/L	See section 74:51:01:10--Cannot impart a visible film or sheen on the surface of the water or adjacent shoreline

Dissolved Concentrations

Parameter					**Acute**	**Chronic**	
Arsenic (μg/L)	<5	23	23	24	360	190	
Cadmium (μg/L)	2	<1	<1	<1	17	3	
Chromium (III) (μg/L)	<1 (total)	<1 (total)	<1 (total)	<1 (total)	1708	554	
Chromium (VI) (μg/L)					15	10	
Copper (μg/L)	16	15	15	16	63	37	
Cyanide (weak acid dissociable) (μg/L)	<10	<10	<10	<10	22	5.2	
Lead (μg/L)	<1	<1	<1	<1	281	10.9	
Mercury (μg/L)	<0.2	<0.2	<0.2	<0.2	2.1	0.012	based on dissolved conc (for acute) and total recoverable for chronic
Nickel (μg/L)	17	23	23	25	4569	508	
Selenium (μg/L)	12	22	23	22	20	5	
Silver (μg/L)	<1	<1	<1	<1	37.4	---	
Zinc (μg/L)	119	56	79	95	370	338	

Calcium, Dissolved (mg/L)	319	510	518	497
Magnesium, Dissolved (mg/L)	69.2	107	107	105
Sodium, Dissolved (mg/L)	188	333	334	335
Potassium, Dissolved (mg/L)	12.2	25.9	26	25.8

Hardness (in mg/L $CaCO_3$) **400**
use 25 mg/L as a minimum
use 400 mg/L as a maximum

Note: For cadmium, chromium, copper, lead, nickel, silver, and zinc, the discharge limits are calculated by formulas incorporating hardness. The values shown are for the maximum allowable hardness value of 400 mg/L as calcium carbonate.

This dataset showed little variation in metals data vertically, but also identified a potential problem. Selenium values reported by Mid-Continent Laboratory were typically 0.020 to 0.025 mg/L, as compared to nondetectable values at 0.005 mg/L produced by Energy Laboratories. This is significant because the chronic discharge limit is 0.005 mg/L and the acute limit is 0.020 mg/L.

These samples had ammonia-nitrogen concentrations of 1.25-1.30 mg/L, suggesting that the breakdown of nitrogen- and carbon-organics manifested itself as increased ammonia-nitrogen.

With these further encouraging results, it was decided to obtain a sample that would be fully representative of ASL discharge water. It was apparent that dissolved oxygen would need to be boosted from the approximate 4 mg/L present to above the discharge requirement of 5 mg/L. A decant skimmer was set up on the ASL to take water from the upper six-inches, and pump the water through a “riffle run” of corrugated PVC pipe to further aerate the water and increase the dissolved oxygen. The riffle run is shown in Figure B-4. Approximately 2,000 gallons of ASL water was pumped through this riffle run into a tank, with a sample taken from the tank for a comprehensive set of analyses representing the “final discharge” waters. For ease of discussion, the team has coined an acronym for the entire post-Anchor Hill Pit deep-water treatment process—the SOX process. This acronym represents the chemical- and process-operations involved with the removal of residual concentrations of sulfur (S) and organics (O) and the addition of oxygen (X). The comprehensive results for the SOX-process waters are presented in Table B-3 below.

Figure B-4. "Riffle run" for aerating ASL water prior to discharge; the discharge line connects to the fitting on lower tank, connecting with a tributary clean water-diversion pipe near the base of slope.

Table B-3. August 11, 2004 SOX Process Results Compared to Strawberry Creek Discharge Standards

	SOX	**Std.**		
pH	8.04	≥6.5-≤8.8	units	See section 74:51:01:07--no change in receiving water greater than 0.5 units
Conductivity at 25°C	3,680	≤2,500	umhos/cm	30-day average
		≤4,375	umhos/cm	daily maximum
Temperature	22°C	≤75	°F	See section 74:51:01:31--no temp change over spawning beds, ≤4oF change
Dissolved oxygen	6.7	≥5.0	mg/L	
Total alkalinity as CaCO3	271	≤750	mg/L	30-day average
		≤1313	mg/L	daily maximum
Total Dissolved Solids	3551	≤2500	mg/L	30-day average
		≤4,375	mg/L	daily maximum
Suspended Solids	13	≤10	mg/L	24-hr composited sample
		≤17.5	mg/L	Grab sample maximum
Sodium adsorption ratio	3.6	≤10		[Na+]/sqrt(([Ca+2] + [Mg+2])/2) all in meq/L
Un-ionized ammonia nitrogen as N	0.055 (pH 8.0, 22°C) (total NH3-N 1.26 mg/L)	≤0.02	mg/L	30-day average
	0.055	<0.035 (1.75 times the applicable criterion)	mg/L	daily maximum
Nitrates as N	<0.05	≤50	mg/L	30-day average
		≤88	mg/L	daily maximum
Undisassociated hydrogen sulfide	<0.05 (total)	≤0.002	mg/L	
BOD5	< 3	≤10	mg/L	24-hr composite sample
		≤17.5	mg/L	Grab sample maximum
Fecal Coliform (May 1-Sept 30)	Not Analyzed	≤1,000	/100mL	geometric mean based on a minimum of 5 samples obtained during separate 24-hour periods for any 30-day period, and they may not exceed this value in more than 20% of the samples examined in this same 30-day period
		≤2,000	/100mL	in any one sample

TPH	Not Analyzed	≤10	mg/L	See section 74:51:01:10--Cannot impart a visible film or sheen on the surface of the water or adjacent shoreline
Oil and Grease	Not Analyzed	≤10	mg/L	See section 74:51:01:10--Cannot impart a visible film or sheen on the surface of the water or adjacent shoreline

Dissolved Concentrations

Parameter		**Acute**	**Chronic**	
Arsenic (μg/L)	23	360	190	
Cadmium (μg/L)	<1	17	3	
Chromium (III) (μg/L)	<1 (total)	1708	554	
Chromium (VI) (μg/L)		15	10	
Copper (μg/L)	16	63	37	
Cyanide (weak acid dissociable) (μg/L)	<10	22	5.2	
Lead (μg/L)	<1	281	10.9	
Mercury (μg/L)	<0.2	2.1	0.012	based on dissolved conc (for acute) and total recoverable for chronic
Nickel (μg/L)	18	4569	508	
Selenium (μg/L)	11	20	5	
Silver (μg/L)	<1	37.4	---	
Zinc (μg/L)	<50	370	338	

Calcium, Dissolved (mg/L)	526
Magnesium, Dissolved (mg/L)	108
Sodium, Dissolved (mg/L)	345
Potassium, Dissolved (mg/L)	NA

Hardness (in mg/L CaCO3)	**[actual 1758 mg/L CaCO3]**	**400**

use 25 mg/L as a minimum

use 400 mg/L as a maximum

Note: For cadmium, chromium, copper, lead, nickel, silver, and zinc, the discharge limits are calculated by formulas incorporating hardness. The values shown are for the maximum allowable hardness value of 400 mg/L as calcium carbonate.

This SOX process sample showed that the water was in compliance with standards with minor exceptions. Conductivity and total dissolved solids are above the 30-day average limit, similar to the current situation with the Gilt Edge water treatment plant, and which is pursuant to an interim-waiver for total dissolved solids (EPA Interim-ROD, November 2001). Un-ionized ammonia is above both the limit of 0.02 mg/L for 30-day average and 0.035 mg/L for daily maximum. Selenium is reported at 0.011 mg/L, between the chronic value of 0.005 mg/L and the acute value of 0.020 mg/L. BOD results for the August 11 SOX-process sample were pending, although previous ASL analyses showed BOD to be 5 mg/L, below the 10 mg/L limit.

The continuing elevated un-ionized ammonia levels were somewhat unexpected, since previous analyses in the Anchor Hill Pit had indicated that ammonia levels were within discharge levels. Extended aeration would likely take care of this problem; however, in the interest of timely discharge operations, repeat processing is not preferred. Alternatively, the pH of the water in the ASL could be lowered to approximately 7.5 in order to meet the un-ionized ammonia nitrogen requirement.; this is the preferred option in order to facilitate discharge. Hydrochloric or muriatic acid would be used to lower the pH of the ASL from 8.0 to 7.5 through the addition of a small amount of concentrated acid, thereby achieving the un-ionized ammonia-nitrogen limit.

Biotoxicity Testing Results. Samples of the SOX process water collected August 11 were received August 12 at the ASCI Laboratory in Duluth, MN to test for acute toxicity to both juvenile fathead minnows and Ceriodaphnia dubia. Based on the control organism performance and reference toxicity results, the effluent exposures met minimum performance requirements specified by EPA and produced valid toxicity results. The SOX-process sample collected did not cause sufficient lethality to allow calculation of a 48-hour (Ceriodaphnia) LC50=>100% (i.e., there was100% organism survival). The sample also did not cause sufficient lethality to calculate a 96-hour median lethal concentration for the fathead minnows (i.e., there was 100% organism survival).

To check the toxicity of the surface layer in the Anchor Hill Pit Lake, a surface water sample (2-foot depth) from the pit lake was collected at the same time and likewise sent to ASCI for identical testing. 48-hour Ceriodaphnia results were 100% survival and 96-hour fathead minnow results were 95% survival (reported as no observable adverse effect). The toxicity results indicated that neither the deep zone water treated with the SOX process, nor the surface water from the Anchor Hill Pit posed toxicity issues for receiving waters.

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

Utilizing the results from the SOX process testing, a larger discharge batch from below the chemocline was targeted. 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, and 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 considered 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. In addition, the settling of solids as previously discussed, is important 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 150,000 gallons of water pumped from the deep zone was successfully discharged in October 2004.

Appendix C

Evaluation of Options for Eliminating Dissolved Sulfide, and Subsequent Addition of Concentrated Hydrogen Peroxide

Evaluation of Options for Eliminating Dissolved Sulfide, and Subsequent Addition of Concentrated Hydrogen Peroxide

Following the implementation of the neutralization and RMB^{TM} steps, the Anchor Hill Pit contained about 67 mg/L of excess sulfide in the deep zone below the chemocline (i.e., below a depth of about 30 feet). The presence of this excess sulfide was due to overdosing of carbon nutrients (methanol and animal feed-grade molasses) early in the project. Reducing conditions were established, and subsequently, denitrification and sulfate reduction occurred. Sulfate reduction continued to occur beyond what would have been desired strictly from a water quality standpoint because the sulfide produced was in excess stoichiometrically compared to the metals levels that would form sulfides. Sulfate reduction continued due to the presence of required reactants (carbon, other nutrients, and sulfate) along with suitable environmental conditions.

The presence of excess sulfide posed several problems: 1) potential health and safety concerns associated with possible release of hydrogen sulfide gas if the pit water column were to "turn over" and mix vertically; 2) health and safety concerns associated with release of hydrogen sulfide gas when handling the deep water for potential discharge; and 3) problems associated with generation of suspended solids from oxidation of the excess sulfide to elemental sulfur when handling the deep water for discharge. These risks led the project team to consider possible approaches for reducing or eliminating the excess sulfide. Consuming the excess sulfide via addition of metals-laden site waters was ruled out due to fears of nitrate ammonification occurring. All site waters contain appreciable nitrate (>30 mg/L as N), and bucket tests performed in 2004 in which deep Anchor Hill Pit water was mixed with Surge Pond water did show evidence of nitrate being reduced to ammonia rather than to nitrogen gas. Site discharge standards for ammonia are much lower than those for nitrate, and the only viable process for removing ammonia is to oxidize it back to nitrate via biological nitrification. This would raise other batch treatment process complications, and therefore this option was not considered further.

CDM personnel performed bench-scale titration tests in May 2005. These titration tests evaluated the use of ferric chloride ($FeCl_3$), ferrous chloride ($FeCl_2 \bullet 4H_2O$), and hydrogen peroxide (H_2O_2) to eliminate excess sulfide. Ferric chloride would oxidize a portion of the sulfide to elemental sulfur while the ferric iron would be reduced to ferrous. Subsequently the ferrous iron would remove the remaining sulfide from solution as a ferrous sulfide precipitate. Ferrous chloride would remove the excess sulfide as a ferrous sulfide precipitate. Hydrogen peroxide would remove the excess sulfide by oxidizing it to elemental sulfur, similar to oxidizing it by aeration in the SOX Process in the summer and fall of 2004.

Results were much as expected. All three reagents were very effective, essentially quantitative, in removing sulfide. There had been some interest in what effect the iron salts might have on the pH of the mixture, since the ferric chloride solution (10% strength) was found to have a pH of 0.9 and the ferrous chloride solution (10% strength) had a pH of 2.1. At a stoichiometric ratio of over 200% to remove the 67 mg/L sulfide present, both resulted in a pH drop to about 6.5 from a starting pH of 7.0; the drop in pH was limited by the strong buffering capacity in the deep Anchor Hill Pit water (alkalinity ~450 mg/L as $CaCO_3$). The addition of excess hydrogen peroxide did not show dissolution of the suspended metal sulfide precipitates; this is consistent with what was seen in the SOX Pond in the summer and fall of 2004.

Having gained confidence that any of these three reagents should be capable of successfully reducing or eliminating excess sulfide in the deep water, the issue then became the determination of the best path to take. The following table summarizes some advantages and disadvantages associated with each material.

Table C-1. Comparison of options to oxidize excess sulfide in the Anchor Hill Pit lake.

	$FeCl_2 \bullet 4H_2O$	$FeCl_3$	H_2O_2
Strength	25%	33%	50%
Quantity Needed (assuming 46,000,000 gallons [current volume minus top 20 feet], 67 mg/L sulfide, 100% stoichiometric dosage)	308 wet tons (14 truckloads)	127 wet tons (6 truckloads)	26 wet tons (1.2 truckloads)
Cost (same assumptions as for quantity)	~$59K	~$23K	~$16K
Effectiveness for Sulfide Removal	High	High	High
Handling Issues	Low pH (10% strength was 2.9, 25% strength probably less)	Very low pH (10% strength was 0.9, 33% strength would be less)	pH 4.5 (50% strength), strong oxidizer
Specific Gravity	1.28 (25% strength)	1.33 (33% strength)	1.2 (50% strength)
Viscosity (water at room temperature is 1 cp, olive oil is about 100 cp)	(could not find)	~12 cp	~1.6 cp
Notes	If dosed in excess, could provide "sink" for future sulfide generated		1. Could be an issue with rapid decomposition generating O_2 gas bubbles, could strip H_2S or destabilize water column. This could be avoided by adding H_2O_2 slowly. 2. Could be somewhat overdosed to provide some dissolved oxygen (e.g., 3-5 mg/L) to inhibit further sulfate reduction.

Several other items considered were:

- There are probably sulfide precipitates on the wall of the pit, as the water level in the pit is pumped down, and there was a possibility that these could oxidize and degrade the surface water quality.
- Addition of hydrogen peroxide essentially performs the SOX Process in the pit rather than the aeration pond.
- If hydrogen peroxide were added, the elemental sulfur sludge generated would be very stable, and would cover existing metal sulfide sludge in the pit.
- If a small amount of sulfate reduction continues due to the small amount of carbon present near/in sediments, additional dosage may be needed. This may not be needed if another batch of water is to be treated.
- Some added dosage may end up being needed simply due to inefficiencies of mixing into a large, still body of water.

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).

On August 17-18, 2005, approximately 3900 gallons of 50% hydrogen peroxide by weight were added to the pit in a total of twelve 325-gallon totes. The twelve totes were added approximately four at a time in three locations: the southwest end; the approximate middle of the pit; and approximately midway between those two locations. They were added by simply draining each tote down 2-inch diameter pipe to a 10-foot deep pipe at the point of delivery. Initial totes were drained very rapidly, while later totes were throttled to drain down in approximately 20 minutes. There were occasional disruptions seen at the water surface, resulting from the hydrogen peroxide pushing air ahead of it in the empty pipe between offloading totes, and from apparently vigorous reactions occurring in the deeper zone.

Initial results indicated that the hydrogen peroxide sank through the bulk of the water column and only oxidized sulfide below about the 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 was attempted and appeared to be successful, and as of October 2005 the excess sulfide in the deep water was significantly reduced to between 10 and 15 mg/L. Profiles of sulfide concentrations with depth are depicted in Figure C-1. By March of 2006, excess sulfide had been successfully oxidized (see Figure C-2).

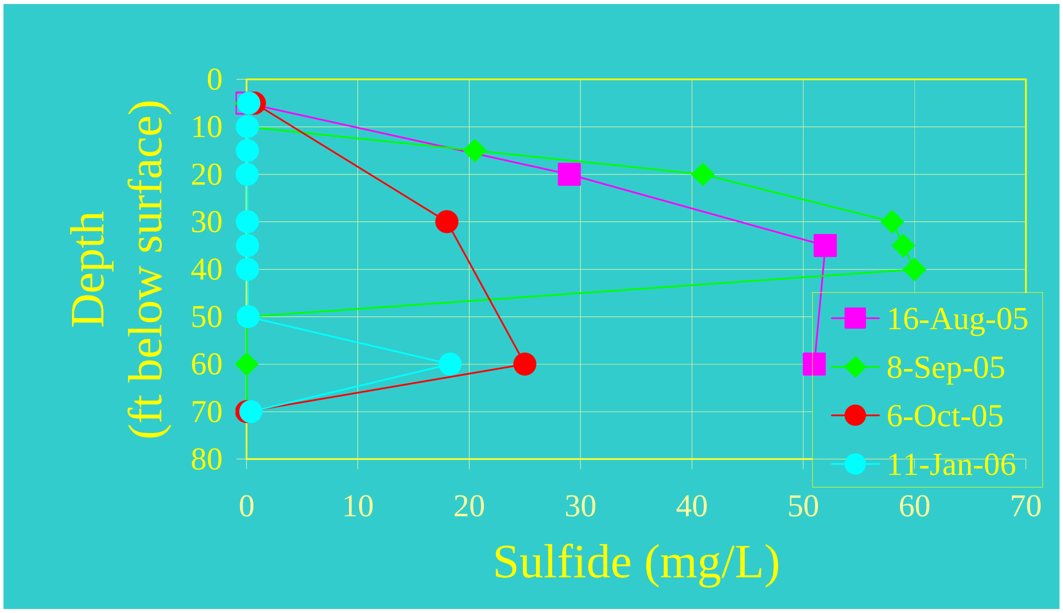

Figure C-1. Change in sulfide with depth after H_2O_2 dosage.

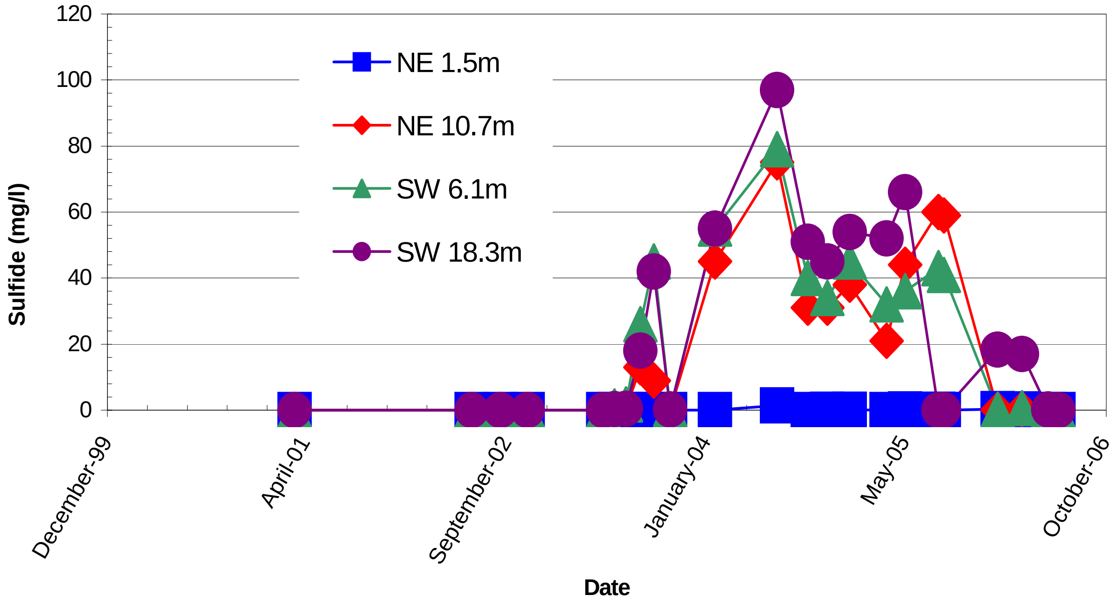

Figure C-2. Sulfide concentrations with time at sampling locations.

Appendix D

Evaluation of Likelihood of Water Column Turnover

MEMORANDUM (VIA E-MAIL)

TO:	Ken Wangerud – U.S. Environmental Protection Agency (U.S. EPA) Richard T. Wilkins – U.S. EPA Mark Lawrensen - South Dakota Department of Environmental and Natural Resources (SD DENR)
FROM:	Steven D. Fundingsland - CDM Federal Programs Corporation (CDM) Marko E. Adzic - CDM
CC:	Brian Park – MSE Technology Applications, Inc. (MSE)
DATE:	November 9, 2004
RE:	Gilt Edge Mine Superfund Site – Anchor Hill Pit Lake

Gentlemen,

As you know in the spring of 2001 and through the EPA's National Risk Management Research Laboratory (NRMRL) Mine Waste Technology Program and the EPA Region VIII Superfund office, a field scale demonstration project demonstrating a two-step in-situ treatment of acidic and metal laden waters was carried out within the Anchor Hill Pit Lake at the Gilt Edge Mine Superfund site. By February 2004, waters within the top 2.5 ft of Anchor Hill (AH) Pit Lake achieved dischargeable standards (i.e., South Dakota Ambient Water Quality Criteria) and contaminants of concern (COCs) were generally decreased by more than 99%. Given the success of the project the U.S. EPA and SD DENR have expressed the possibility of releasing dischargeable waters from AH Pit Lake into Strawberry Creek. Prior to conducting such activities however, CDM evaluated the potential for deep mixing to occur and the subsequent increase in COCs and off-gassing of hydrogen sulfide.

Since the spring of 2003 a distinct horizontal stratification within AH Pit Lake has been observed. This stratification is supported by field recorded measurements (e.g., temperature, conductivity, oxidation-reduction potential [ORP] and pH) collected throughout the water column, see attached. In general, the observed horizontal stratification within AH Pit Lake is driven by a combination of thermal and chemical gradients. As indicated by the attached data with the exception of the fall and winter months (i.e., November to January) where temperature differences within the water column are minimized and/or reversed, a distinct thermocline and chemocline are observed. As a result, the horizontal stratification within AH Pit Lake is driven by both thermal and chemical gradients. Since horizontal stratification within AH Pit Lake has been established there is no evidence that turnover and/or deep water mixing has occurred. This is supported by the continuous negative ORP environment (i.e., reducing conditions) within deeper waters (i.e., depths >20 ft below surface) of AH Pit Lake. As demonstrated by Robertson and Imberger (1994), dissolved oxygen (DO) concentrations within lakes are strongly dependent upon the degree of deep mixing. Therefore, should deep mixing of AH Pit Lake waters have historically occurred an increase in ORP values (i.e., more positive) would have been observed. As confirmed by the historical ORP profiles however, this has not occurred since AH Pit Lake has become horizontally stratified. Nevertheless to better understand lake-hydrodynamics within the AH Pit Lake, first order calculations and quantitative indicators such as the Wedderburn and Lake Numbers were calculated (Imberger, 2001; Hamblin *et al.*, 1999; and Robertson and Imberger, 1994).

The Wedderburn Number (W) evaluates the potential for metalimnetic water to uplift into the epilimnion; while the Lake Number (L_N) evaluates the potential for deeper hypolimnetic water to uplift. One of the required input parameters in calculating the aforementioned quantitative lake indicators is water density. The presence of horizontal stratification within AH Pit Lake confirms a definite difference in water density throughout the water column (i.e., denser waters are near the bottom). These density differences are the result of thermal and chemical differences within the water column. Thomann and Mueller (1987) have put forth the following relationship that calculates water density as a function of temperature and salinity:

$$\rho = 1 + \{(10^{-3}[(28.14 - 0.0735T - 0.00469T^2) + (0.802 - 0.002T)(S - 35)]\}$$

(Equation 1)

Where: ρ = Water density as a function of temperature and salinity (g/cm^3)
T = Water temperature (ºC)
S = Salinity (‰)

As indicated within Equation 1 a measure of salinity is required. Typically and to date, salinity has not been analyzed at the Gilt Edge Mine Superfund site. As a result, salinity levels were estimated using the relationship between conductivity and total dissolved solids (TDS). Eighty data points (i.e., sampling events) were identified where both conductivity and TDS measurements were recorded within AH Pit Lake over a period of time from October 26, 2000 to July 8, 2004. To better understand the relationship between conductivity and TDS within AH Pit Lake, a scatter plot of the aforementioned data set was generated, a best-fit relationship determined, and a correlation coefficient calculated using Excel. A summary of this data is presented within Figure 1.0.

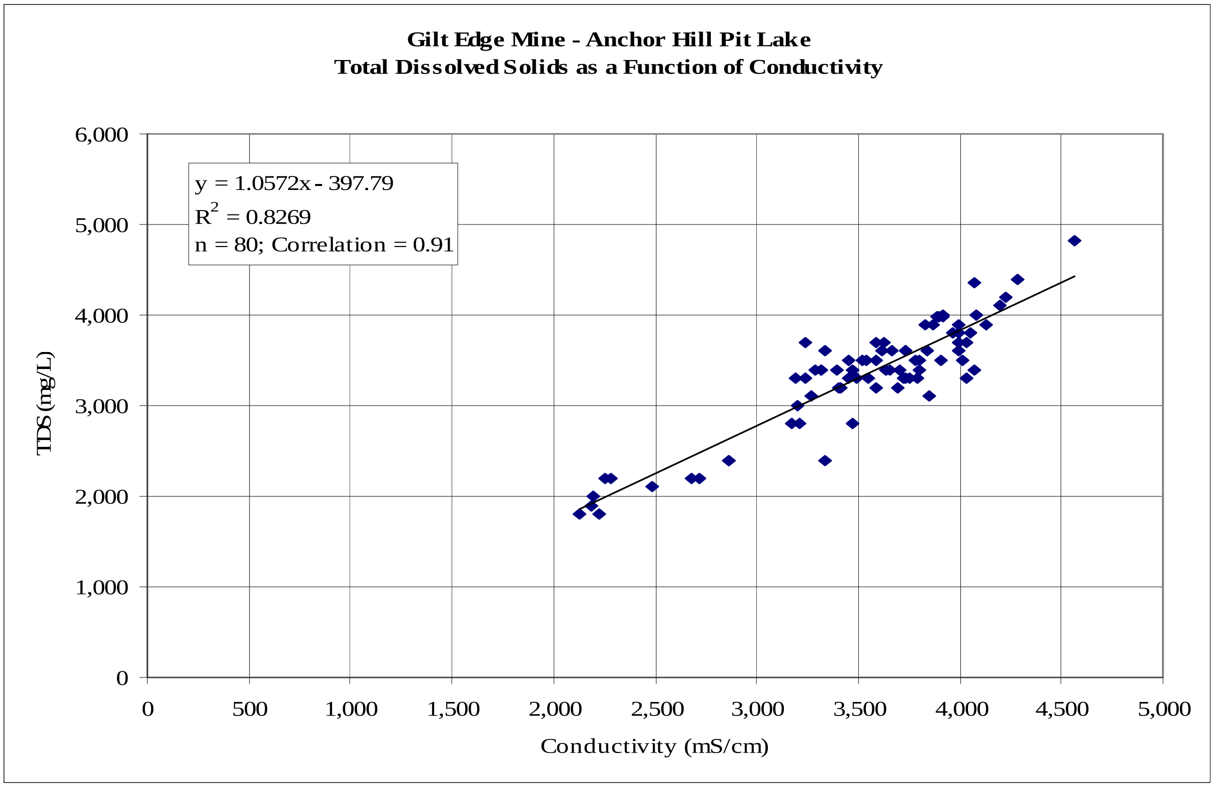

Figure 1.0. Relationship between Measured Total Dissolved Solids and Conductivity within Anchor Hill Pit Lake.

As indicated within Figure 1.0 there is a positive correlation between conductivity and TDS (i.e., r = 0.91); and with an r^2 value of 0.83 a linear relationship was identified as being the best-fit. Using the linear relationship noted within Figure 1.0, TDS levels were calculated for historic profile sampling events within AH Pit Lake. Subsequent salinity levels were determined using the following relationship (Thomann and Mueller, 1987):

$$S \cong \frac{TDS}{1{,}000 mg/L \big/ perthousand} \qquad \text{(Equation 2)}$$

Where: S = Salinity (‰)
TDS = Total dissolved solids (mg/L)

Corresponding water densities were then calculated for each sampling event and density profiles as a function of depth generated.

In general, there appears to be three distinct layers present within AH Pit Lake. They include: the epilimnion (0-5 ft), the metalimnion (5-20 ft) and the hypolimnion (>20 ft). Average water densities for the aforementioned layers were calculated to be approximately 1,001.2 kg/m^3, 1,002.3 kg/m^3, and 1003.3 kg/m^3, respectively. The overall average density was calculated to be approximately 1,003 kg/m^3.

Since September 2004, using hydrometer measurements water densities have been recorded at depth intervals of 3 ft and 25 ft below surface within AH Pit Lake. As indicated by Figure 2.0, for water samples collected at depths of 3 ft below surface, a negative correlation between water temperature and density (i.e., as water temperature decreases, water density increases) has been observed. On the other hand, water temperature does not appear to any have measurable effect on density at a depth of 25 ft. At this depth 'salinity' would appear to dominate water density effects. These results support the historical observations of a diminishing thermocline but a persistent chemocline during the winter months, see attached field water quality profiles.

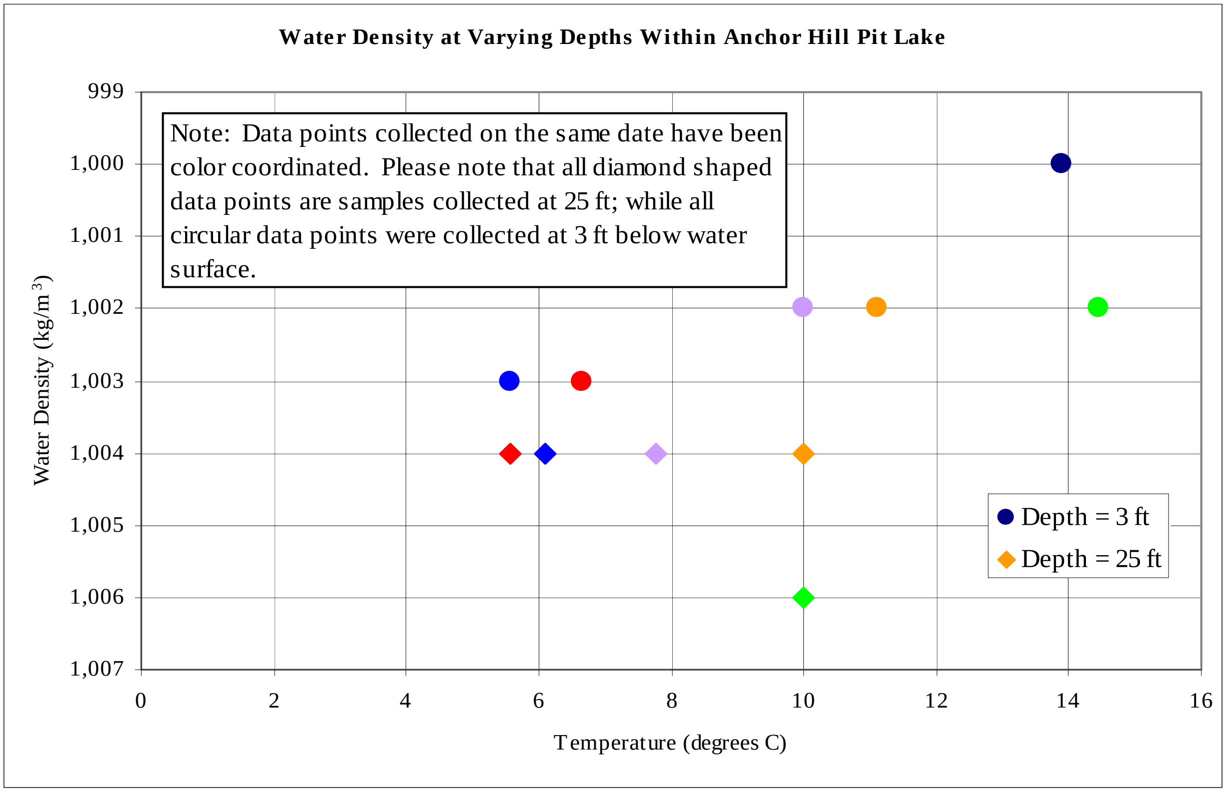

Figure 2.0. Hydrometer Density Measurements Recorded within Anchor Hill Pit Lake (September 24, 2004 to November 5, 2004).

Using the aforementioned calculated average water densities, Wedderburn and Lake Numbers were determined. The Wedderburn Number can be used to examine the extent of upwelling of metalimnetic water (Imberger, 2001). It is the ratio of the restoring moment about the center of volume of a lake to the disturbance moment for two-layer stratification. Mathematically it is expressed as follows (Imberger, 2001):

$$W = \frac{g\delta' \times h^2}{u_*^{\ 2} \times L} \qquad \text{(Equation 3)}$$

Where: W = Wedderburn Number (unit less)

h = Depth to thermocline (m)
u_* = Water shear velocity (m/s)
L = Fetch length (m), and

The L_N is a quantitative index of the dynamic stability of the water column and is defined as the ratio of the moments about the water body's center of volume and of the stabilizing force of gravity (resulting from the density stratification) to the destabilizing forces from wind, cooling, inflow, outflow, and artificial destratification devices (Robertson and Imberger, 1994). In general, a L_N of one indicates that the wind energy is just sufficient to deflect the thermocline, a $L_N << 1$ means that lake stratification is weak with respect to wind stress and strong seiching would occur on the surface and turbulent mixing within the hypolimnion is expected. A $L_N >> 1$ typically means lake stratification is strong and dominates forces introduced by the wind. Little to no seiching and/or turbulent mixing within the hypolimnion is expected (Imberger, 2001; and Robertson and Imberger, 1994).

Assuming that wind is the dominating force for mixing (i.e., inflow, outflow, and any artificial destratification devices have minimal destabilizing force) the L_N can be calculated as follows (Imberger, 2001; Hamblin *et al.*, 1999; and Robertson and Imberger, 1994):

$$L_N = \frac{(z_g - z_0)Mg(1 - \frac{z_T}{z})}{A^{3/2}(1 - \frac{z_g}{z})\rho_0 {u_*}^2} \qquad \text{(Equation 4)}$$

Where:

z_g = Center of volume (m)
z_0 = Center of mass (m)
M = Total mass of water (kg)
z_T = Height to thermocline (m)
z = Total depth (m)
A = Lake surface area (m^2)
ρ_0 = Average water density (kg/m^3)
u_* = Water shear velocity (m/s)
g = Acceleration due to gravity (9.81 m/s^2)

It should be noted that the center of volume (z_g) and center of mass (z_0) were calculated as follows:

$$z_g = \frac{\sum z \cdot A \cdot dz}{\sum A \cdot dz} \times \frac{1m}{3.2808\,ft} \qquad \text{(Equation 5)}$$

Where:

z_g = Center of volume (m)
dz = Incremental depth (i.e., 0.5 ft)
z = Depth (ft)
A = Incremental surface area (ft^2)

$$z_0 = \frac{\sum \rho(z) \cdot z \cdot A(z)}{\sum \rho(z) \cdot A(z)} \times \frac{1m}{3.2808\,ft} \qquad \text{(Equation 6)}$$

Where:
z_0 = Center of mass (m)
$\rho(z)$ = Water density as a function of depth (kg/m^3)
z = Depth (m)
A(z) = Surface area as a function of depth (m^2)

Meteorological data (i.e., wind speed) collected from the on-site weather station as maintained and operated by the State of South Dakota was reviewed for the purpose of this evaluation. Based on data collected from September 2, 2003 to August 31, 2004 the average wind speed recorded at the Gilt Edge Mine Superfund site during that time was approximately 10 mph (miles per hour). Maximum wind speeds of approximately 35 mph were recorded during that same period of time. A plot of the historical wind speeds recorded at the site is provided within Figure 3.0. It should be noted that the average wind gust recorded at the Gilt Edge Mine was approximately 15 mph. Using Equations 3 and 4, a sensitivity analysis with respect to wind speed was conducted for AH Pit Lake.

Under average wind conditions of 10 mph and the existing water level (i.e., water depth = 89.5 ft) no seiching or turbulent mixing within AH Pit Lake is anticipated. Wedderburn and Lake numbers of 12 and 39 were respectively determined. As a result, under typical conditions AH Pit Lake would appear to be a very stable lake and no seiching and/or mixing would be expected. This is confirmed based on field data collected to date. Should a sustained wind speed of approximately 35 mph (i.e., site recorded maximum) be observed, there is the potential for seiching to occur (W = 1) while no turbulent mixing within the hypolimnion is anticipated (L_N = 3).

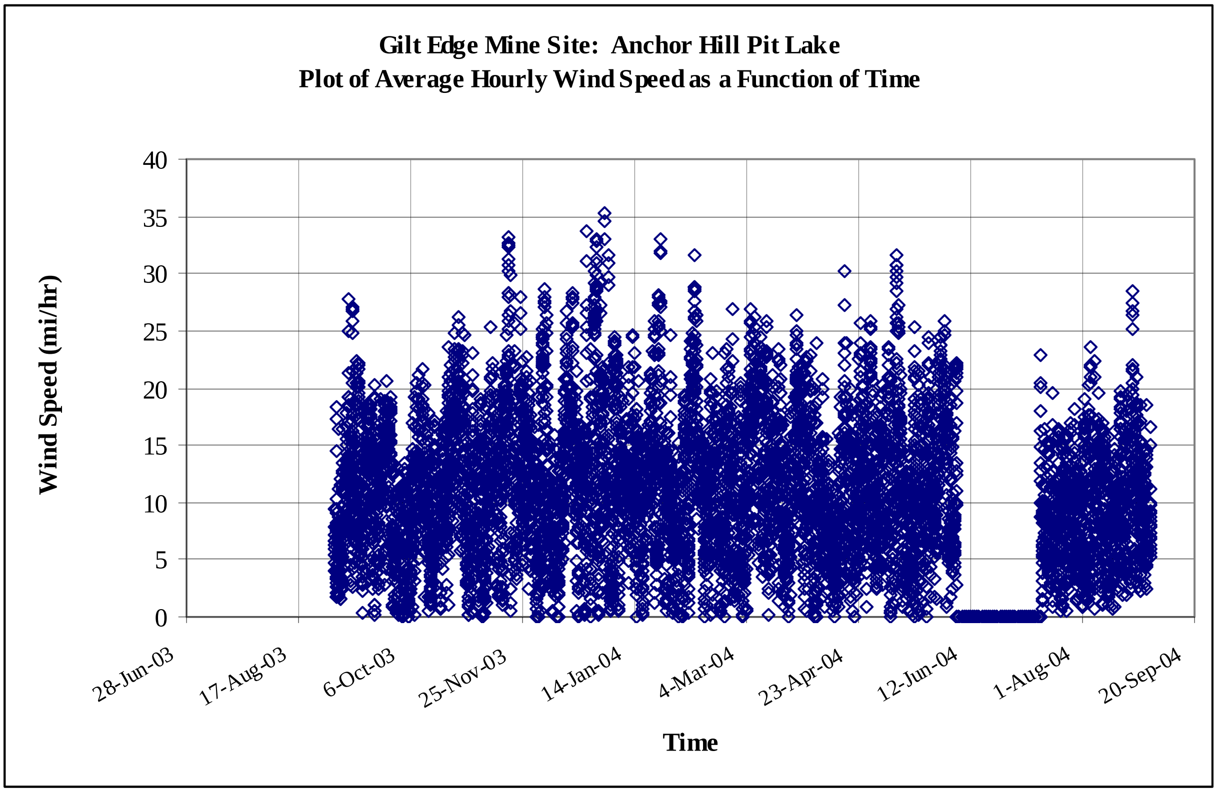

Figure 3.0. Average Wind Speeds Recorded at the Gilt Edge Mine Superfund Site from September 2003 to September 2004 (data recorded by the State of South Dakota).

To assess the potential for deep mixing to occur within AH Pit Lake a wind speed sensitivity analysis was conducted. Based on our findings, turbulent mixing of the hypolimnion is not expected until a sustained wind speed of approximately 63 mph was observed over the lake surface. It is important to note that the only variable within the sensitivity analysis was wind speed. All other variables such as fetch, water depth and depth to thermocline were held constant. It should be noted that the calculated 63 mph wind speed is the required minimum to generate turbulent mixing within the hypolimnion, and that it does not preclude mixing will occur but rather that it is possible. As demonstrated by Robertson and Imberger (1994), even during weakly stratified periods (i.e., low lake stability), deep mixing only occurs when the wind force is sufficiently strong to cause L_N values to drop below one.

Similar calculations were conducted assuming that 5 ft of water was discharged (i.e., approximately 7.1 million gallons) from AH Pit Lake. Should such an activity be conducted it is anticipated that AH Pit Lake would become a two-layered stratified lake as opposed to the existing three-layered; and that a reduced wind speed would be required to stimulate turbulent mixing within the deeper sections of the lake (i.e., approximately 31 mph). Recall that the maximum recorded on-site velocities were approximately 35 mph. A summary of our findings is presented within Figure 4.0, with a detailed summary of calculations attached.

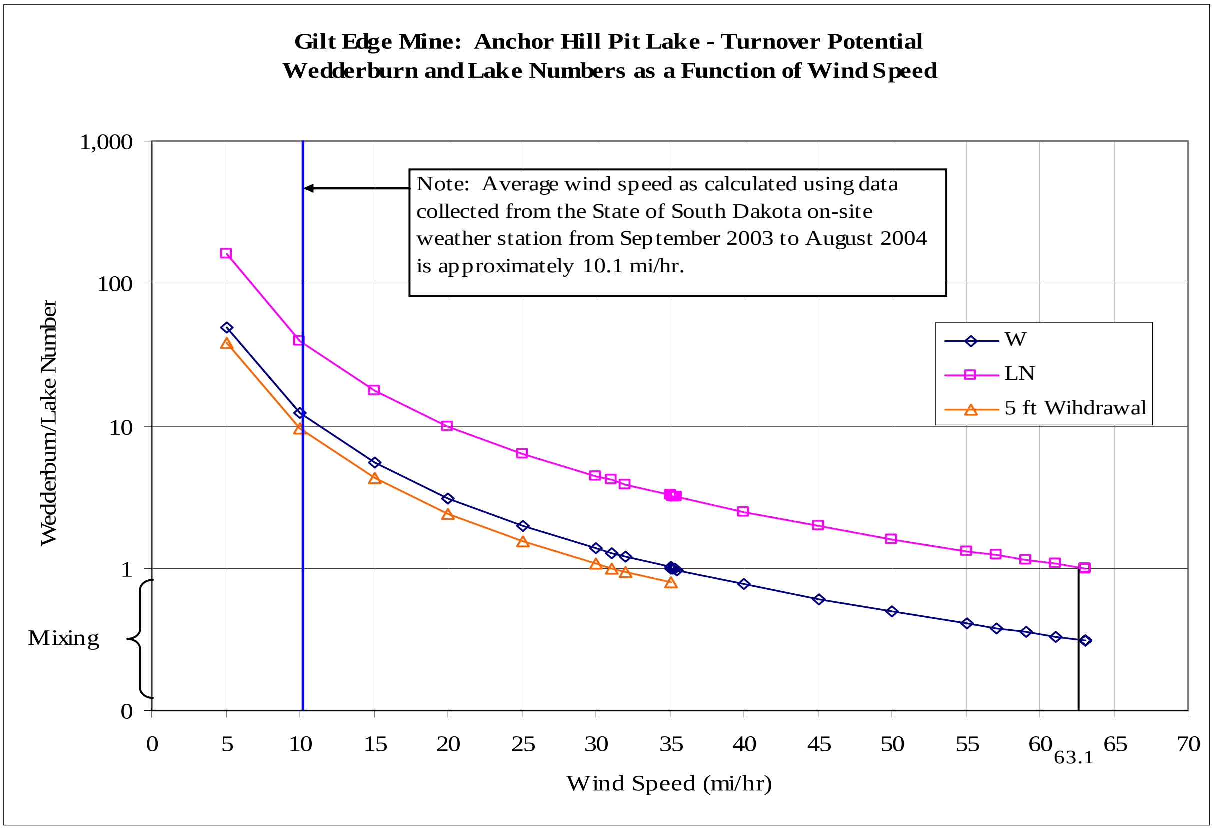

Figure 4.0. **Wedderburn and Lake Numbers as a Function of Wind Speed within Anchor Hill Pit Lake.**

Based on first-order lake hydrodynamic numbers lake turnover is highly unlikely to occur within AH Pit Lake. However, in the unlikely event that deep water mixing and/or turnover could occur, we also evaluated the resulting effects for the potential to release hydrogen sulfide (H_2S) due to off-gassing (i.e., volatization).

Volatization rate of hydrogen sulfide was calculated using the following relationship as defined by Watts (1998):

$$Q = \left(\frac{MKA \times (VP - P)}{RT} \right) \times X_{H_2S} \qquad \text{(Equation 7)}$$

Where: Q = Volatization rate (g/s)
M = Molecular weight of H_2S (i.e., 34.086 g/mol)
K = Mass transfer coefficient per area (m/s)
A = Area of AH Pit Lake (i.e., 17, 855 m^2 @ current water elevation)
VP = Vapor pressure (atm)
P = Partial pressure of H_2S in atmosphere (i.e., 0 at time = 0)
X_{H2S} = Mole fraction of H_2S in solution @ 55 mg/L
R = Ideal gas constant (i.e., 8.21×10^{-5} m^3·atm/mol·K)
T = Temperature (i.e., 8ºC)

The mass transfer coefficient and vapor pressure for H_2S were estimated using the following relationships (Watts, 1998):

$$K_1 = K_2 \left(\frac{M_2}{M_1} \right)^{1/3} \qquad \text{(Equation 8)}$$

Where: K_1 = Mass transfer coefficient for H_2S
K_2 = Mass transfer coefficient of water (i.e., 0.83 cm/s)
M_2 = Molecular weight of water (i.e., 18.02 g/mol)
M_1 = Molecular weight of H_2S (i.e., 34.086 g/mol)

$$VP = H \times S \qquad \text{(Equation 9)}$$

Where: H = Henry's constant (i.e., 8.56×10^{-3} atm·m^3/mol)
S = Solubility of H_2S (i.e., 398 g/100 g)

The average ambient air temperature of 8ºC was calculated from hourly data collected from the on-site meteorological station during the summer months of 2004. Data collected during the winter months were not considered for two reasons: 1) they would adversely bias the resulting average, and 2) due to the presence of ice cover turnover and/or lake mixing would not result from disturbing forces such as wind.

Applying Equation 7 to the AH Pit Lake, it was determined that the maximum H_2S concentration that could off-gas should a turnover event occur would be approximately 65 ppm. A summary of detailed calculations as generated using Excel are attached. The resulting maximum H_2S concentration that could evolve from AH Pit Lake in the unlikely event of a complete turnover is significantly less than the potentially fatal limit of 250 ppm (MSDS, Canadian Centre for Occupational Health and Safety).

We trust that the above information is sufficient at this time and look forward to hearing from you on this matter in the near future.

MEA/mea

Attachments (1)

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