2000 Billings Land Reclamation Symposium

SOURCE CONTROL - SURFACE WASTE PILE DEMONSTRATION PROJECT

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ABSTRACT

The Source Control - Surface Waste Pile Demonstration Project will demonstrate the feasibility of using an innovative source control technology for in situ stabilization of a surface waste pile at an abandoned mine. The work is being conducted under the Mine Waste Technology Program (MWTP), which is funded by the U.S. Environmental Protection Agency (EPA) and jointly administered by the EPA and the U.S. Department of Energy through an interagency agreement (IAG). The project addresses EPA=s technical issue of *Mobile Toxic Constituents B Water* by performing a field demonstration at a remote, inactive mine.

The source control technology(s) being demonstrated is designed to prevent the influx of water, whether precipitation or groundwater, through a surface waste pile, thus decreasing acid mine drainage (AMD) formation. Site characterization, materials testing/evaluation, and field emplacement were performed to define the optimal material and material application method for the demonstration. The alternate method used to seal the surface of the waste pile and inhibit infiltration of precipitation involved the spray application of a modified version of General Polymers 4994 KOBAthane grout directly onto the surface waste pile. A French drain that functions as a hydraulic barrier was constructed to divert the groundwater away from the surface waste pile.

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INTRODUCTION

Acid mine drainage typically results from sulfide-rich ore bodies and metal-sulfide mineral [particularly pyrite (iron disulfide)] coming into contact with oxygen and water. This reaction occurs in many surface waste piles resulting in increased acidity (lowered pH) of the water and increased metal mobility. Conventionally the surface waste pile at the mine is physically removed and deposited in a designated repository to prevent acid formation, heavy metal leachate, and suspended solids from entering the aquifer or adjacent surface water system. This solution can in some instances be very expensive, envasive to the environment, or not feasible due to the lack of a suitable repository location. The MWTP Source Control - Surface Waste Pile Demonstration Project was performed to find an alternate method(s) other than physical removal of the surface waste pile as a reclamation solution. Application of the MWTP source control technology was designed to provide a solution that could be applied in situ, be less envasive to the environment, be more cost effective than the removal option, and could be easily applied. This project was divided into three phases:

Phase I, Mine Site Selection/Site Characterization
Phase II, Materials Testing
Phase III, Field Emplacement

Phase I resulted in the selection of the Peerless Mine as the demonstration site. Prominent features resulting from historic mining activities include surface waste piles that were characterized as eroding, contaminated sediments, and two discharging adits. The water from the mine site flows into the East Fork of Banner Creek, which is part of the City of Helena, Montana=s water supply system. Additionally, AMD formed within the surface waste pile was affecting the surface water quality at the headwaters of Banner Creek. During Phase II, materials testing was performed at the MSE Technology Applications, Inc. (MSE) Testing Facility and IT Geotechnical Laboratories, Inc. (IT). During Phase III, the field emplacement consisted of the construction of a French drain system to hydraulically control the groundwater system and the application of the cap system using General Polymers 4994 KOBAthane grout reinforced with a woven jute material.

PHASE I, MINE SITE SELECTION/SITE CHARACTERIZATION

In 1998, the MWTP selected the Peerless Mine as a demonstration site for the field implementation and evaluation of the Source Control - Surface Waste Pile Technology Demonstration. Water discharging from the surface waste piles at the Peerless Mine was considered to be a main source of pollution to Banner Creek. The surface pile discharges range from 2.6 to 22.6 gallons per minute (gpm) and contained zinc, manganese, and cadmium at levels exceeding the National Drinking Water Maximum Contaminant Standards.

From these results, it was determined that the adit discharge from the Peerless Mine infiltrates into the downgradient surface piles and is the main source of groundwater flow, see Figure 1. However, other contributions to groundwater flow within the pile include the losing streams that flow on either side of the surface waste piles and infiltration by precipitation. Because surface water and groundwater both contribute to the AMD problems at the Peerless Mine, a multi-phase solution was considered for the field demonstration.

Rain water and water discharging from mine systems have a pH close to neutral and do not carry large percentages of heavy metals or suspended solids. When this water travels across the surface waste piles and becomes exposed to oxygen and sulfide ores, AMD is formed. To reduce and/or eliminate water from infiltrating the hydraulic connections/ voids in the surface waste piles, this demonstration proposed to place stabilization material(s) into the voids in the waste pile and hydraulic interconnections as an in situ stabilization technology forming an impervious barrier. This barrier will reduce or eliminate the amount of water infiltrating into the mine surface waste pile and decrease the generation of acidic and metal-laden waters.

PHASE II, MATERIALS TESTING

Phase II evaluated and compared the effectiveness of approximately 50 different stabilization materials under simulated field conditions. The objective of the materials testing was to provide a rational set of measurements and results by which decisions could be made regarding stabilization materials. Although many of these tests were site specific to the Peerless Mine, they could be generalized and modified for other applications. However, specific treatment requirements depend on the performance goals defined for a specific site. The initial feasibility of the potential stabilization materials was determined in the laboratory using the selected tests described in the *Site Characterization and Materials Testing Report*: *Surface Waste Piles Source Control Demonstration Project*.

The primary success criteria for the potential stabilization materials required that it 1) be environmentally benign; 2) achieve a hydraulic conductivity when mixed with the mine waste materials of 10-6 centimeters per second; 3) be able to withstand acidic mine water having a pH of 3 for an extended period of time; 4) be able to be applied for a field demonstration; and 5) be cost effective. The secondary success criteria for the potential stabilization materials were that the materials could withstand both wet-dry cycling and freeze-thaw cycling tests for 12 cycles maintaining less than 50% material loss over the duration of the testing. The stabilization materials were evaluated for performance, durability, applicability, and economics for the field demonstration. These tests were performed by MSE and at IT Laboratories. Each material was ranked as either passing or failing each test with three materials passing all tests. The three stabilization materials that passed all tests then underwent preliminary field testing to establish final application and cost parameters. After performing application testing and a cost analysis of the selected materials, the 4994 KOBAthane grout was selected as the final stabilization material.

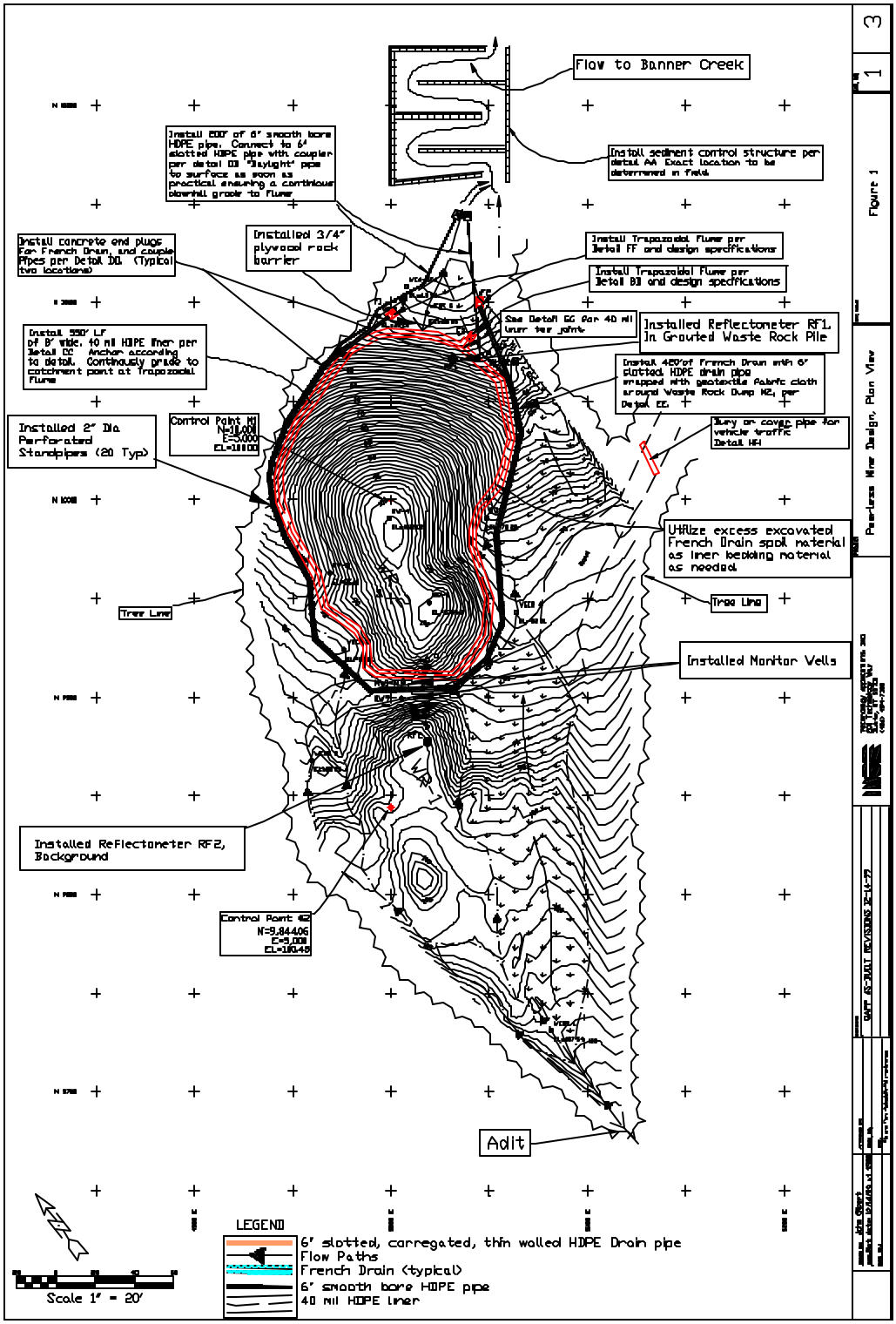

Figure 1. Peerless mine design.

PHASE III, FIELD EMPLACEMENT

Field emplacement was performed during October and November 1999. As part of the field emplacement, a French drain system was constructed to act as a hydraulic barrier to help eliminate the flow of groundwater through and beneath the surface waste pile, see Figure 2. In general, the French drain construction included: 1) excavating a 420-foot by 4-foot by 10-foot (on average) trench around the up-gradient perimeter of the surface waste pile; 2) installing 420 feet of 6-inch, slotted, high-density polyethylene (HDPE) pipe wrapped with geotextile filter cloth surrounded by 1½-inch minus washed gravel; 3) installing to surface grade, 6-inch minus, screened river-run, rip-rap over the previous smaller gravel; and 4) installing two concrete end plugs to anchor the wrapped pipe and to connect the slotted pipe to 200 additional feet of smooth bore HDPE drain pipe.

Once the French drain had been installed, a surface water collection channel was constructed on the inside perimeter of the drain. The collection channel, approximately 640 feet by 6 feet by 2 feet deep was lined with 40-mil HDPE liner and keyed into the surface waste pile. The collection channel was constructed to collect runoff from the surface waste pile.

To prevent infiltration of precipitation into the surface waste pile, General Polymers 4994 KOBAthane grout was spray applied. Approximately 930 gallons of 4994 KOBAthane grout (a two-component aromatic membrane urethane grout) was used to cover the 16,828 square feet of surface area. After applying the grout, the pile was covered with a heavy woven jute and burlap material. The surface waste pile is scheduled to be covered with soil and seeded in the summer of 2000.

Additional monitoring equipment (three large 60E trapezoidal flumes) was installed to monitor the flows from the French drain and collection channel and the flow from the toe of the surface waste pile. Reflectometers were installed to monitor the moisture content of the surface waste pile under the stabilized cap.

EMPLACEMENT OBSERVATIONS AND RESULTS

During the construction of the French drain system and the emplacement of the 4994 KOBAthane grout, visual observations and flow measurements were logged. The observations below were made.

1) The surface waste pile is very heterogeneous; the waste material contains a mixture of very fine silt to large 6- to 12-inch rocks. The pile was disturbed during the emplacement of the collection channel and during preparation of the surface waste pile for acceptance of the 4994 KOBAthane grout. The disturbed areas of the pile were difficult to spray because the fine, disturbed soil would dislodge or roll down the slope and follow preferential pathways down steeply sloped areas.

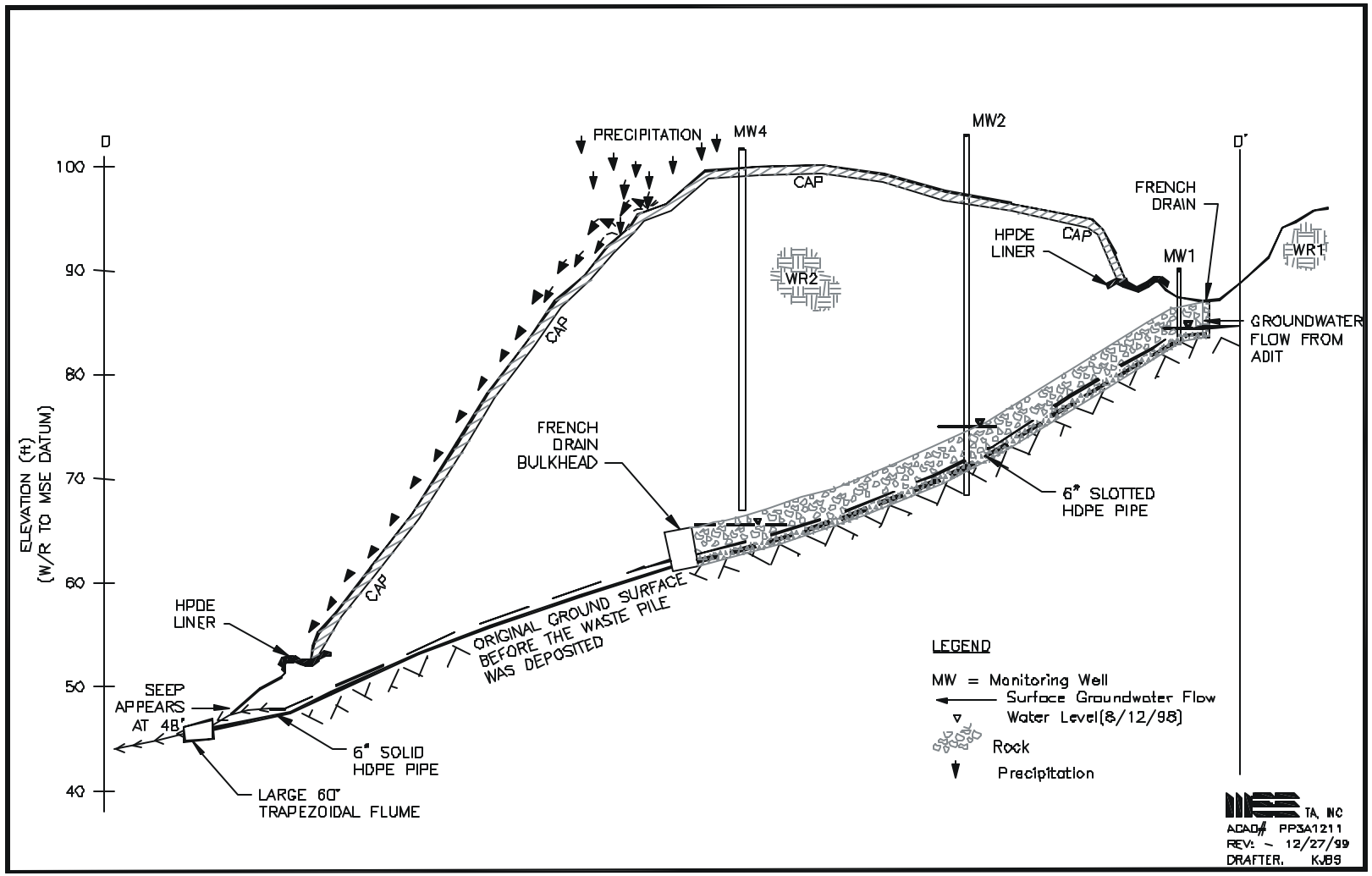

Figure 2. Peerless Mine cross section D-D' (not to scale).

2) In the steeply sloped portions of the pile, the 4994 KOBAthane grout followed the preferential pathways and sagged a great deal. This was partially due to the spray tip being too large and partially due to the lack of thixothropy in the grout product.

3) It was observed that 4994 KOBAthane grout applied directly to the surface waste pile was fairly successful. Many areas achieved a seal and served to stabilize the pile; however, voids could be observed around larger rocks.

4) In areas where the grout material was applied over areas of snow and ice, curdling occurred. In some areas the curdling effect caused the coating to be breached.

5) It was observed that after the 4994 KOBAthane grout had cured for at least 24 hours, people were able to walk on the stabilized surface. The binding of the 4994 KOBAthane grout to the surface waste pile material allows for precipitation to occur without erosional effects. The cap formed by the spray-applied 4994 KOBAthane grout over the surface waste pile provides erosion control in areas that are not accessible by motorized vehicle.

6) In some areas of the surface waste pile, the 4994 KOBAthane grout was sprayed onto the woven burlap and jute material instead of being sprayed onto just the surface waste pile. In those areas, less grout was required to cover the surface of the jute and burlap, and the final stabilized area produced an impermeable, continuous capped layer that bonded to the surface waste pile. The holes in the stabilized material applied directly to the surface waste pile were not present in areas with the jute and burlap.

7) Once the French drain was installed, the majority of the water flowing from the toe of the surface waste pile was reduced to only 2 gpm. However, once the water from the adit was placed back into its original flow regime, the flow at the toe of the surface waste pile increase to approximately 3 gpm, and flow was measured at .5 gpm at the large 60° trapezoidal flumes connected to the French drain system.

8) The pH before the demonstration was approximately 3.8; however, a month after the demonstration project was completed, the pH reading was 5.78. Two months after the demonstration project, the pH reading was 7.28. Long-term monitoring will determine whether the pH will remain at 7.28.

CONCLUSIONS AND RECOMMENDATIONS

The objective of the technology demonstration is to show the effectiveness and feasibility of using a source control technology to provide in situ stabilization/encapsulation to reduce and/or eliminate infiltration of surface and shallow groundwater into the surface waste pile. From the data taken to date, it appears that the placement of the French drain system and the 4994 KOBAthane grout cap have improved the quality of the water flowing from the toe of the

surface waste pile. This is apparent from the rise in pH levels from 3.8 to 7.28, the decrease in water temperature of approximately 2 degrees, and the change in the water quality at the toe of the surface waste pile.

It was also determined that if the jute and burlap material were applied to the surface waste pile before the 4994 KOBAthane grout was sprayed over the pile, most of the soil instability problem and the rock bridging would be solved. Also, less 4994 KOBAthane grout would be used to acquire the desired coverage of the surface waste pile because the grout binds in the woven fibers of the jute and burlap material, does not flow down the slope, and forms a smooth and consistent surface.

In areas where the slope was very steep, the grout should be made more thixotropic, allowing the grout to adhere to the soil on the area in which it was sprayed rather than flow down the slope in a preferential pathway.

For future applications, the spray equipment and tips should be optimized to determine which applicators would provide the best cover and still provide ease of application. By optimizing the equipment, this grout material could be applied at locations that are inaccessible by large earth-moving equipment.

From the work performed, it is apparent that the 4994 KOBAthane grout not only works as a capping material to reduce infiltration through the surface waste pile, but the grout was very effective at reducing and eliminating erosion of waste material into adjacent receiving surface waters.

ACKNOWLEDGMENTS

This work is being conducted as part of the Mine Waste Technology Program under an interagency agreement, IAG ID No. DDw89938513-01-0, between the U.S. EPA and the U.S. DOE, Contract Number DE-AC22-96EW96405.

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MSE Technology Applications, Inc., *Site Characterization and Materials Testing Report: Surface Waste Piles Source Control Demonstration Project,* Mine Waste Technology Program, Activity III, Project 10, MWTP-144, pg. 3-5.

MSE Technology Applications, Inc., *Test Plan-Surface Waste Piles Source Demonstration Project,* Mine Waste Technology Program, Activity III, Project 10, Phase 2, MWTP-108, pg. 11.

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CYANIDE HEAP BIOLOGICAL DETOXIFICATION

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ABSTRACT

A large-scale column test utilizing bacteria and a sulfide ore was conducted at McClelland Laboratories, Inc., in Sparks, Nevada, as part of the Mine Waste Technology Program (MWTP).

Through a Request for Proposal, four technology providers were subcontracted to provide their respective technology for participation in this demonstration. The sulfide ore, process effluent, and make-up water were provided by a Nevada mining company. A process effluent column and a hydrogen peroxide column, along with columns for each of the four biological technologies tested, were set side-by-side on a pad adjacent to the McClelland Laboratory building. The process effluent and hydrogen peroxide columns were used as experimental controls. The six, 4-foot outside diameter columns measuring 22 feet in height were constructed of high-density polyethylene pipe.

The project=s goal was to evaluate the viability and feasibility of the aforementioned biodegradation technologies to reduce weak acid dissociable cyanide concentration to the regulatory level of 0.2 parts per million (ppm) within an acceptable time and with low operational costs.

The MWTP is funded by the U.S. Environmental Protection Agency (EPA) and is jointly administered through an interagency agreement with the U.S. Department of Energy (DOE). This work was conducted through the DOE National Energy Technology Laboratory at the Western Environmental Technology Office under DOE contract Number DE-ACC22-96EW96405.

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INTRODUCTION

Cyanide is widely used in the mining industry to dissolve precious metals. Since certain cyanide species are hazardous to the environment, numerous cyanide detoxification processes have been developed. Most of these processes involve chemical oxidization and are expensive to construct and operate. Therefore, biological detoxification has been instituted as a replacement for chemical degradation.

The purpose of this demonstration was to obtain performance data and evaluate efficiencies of four biological technologies relative to a chemical rinse stage. Although biological detoxification technologies are commercially available, questions remain regarding efficiency, capital and operating costs, applicability to multiple ore types, and effects of biological treatment on related discharge parameters.

Principal cyanide heap neutralization rinsing data include: the extent and rate of weak acid dissociable (WAD) cyanide neutralization; decrease and rate of decrease in rinse effluent pH; and final rinse regulated contaminant concentrations.

TECHNOLOGY PROVIDERS

Four technology providers were selected to participate in this demonstration: 1) Applied Microbiology & Biotechnology Inc.; 2) Compliance Technology; 3) Little Bear Laboratories; and 4) Whitlock & Associates.

They were responsible for providing a bioreactor system, biological/bacteriological cultures, nutrients, and inoculation media.

TECHNOLOGY

Process water rinse is the simplest method of all the technologies as the process water is simply recirculated continually through the heap.

Hydrogen peroxide, frequently combined with a catalyst, is commonly used in the mining industry to detoxify heap leach solutions.

Biological cyanide detoxification is accomplished by introducing cyanide-metabolizing bacteria to a contaminated source or by stimulating indigenous bacteria through nutrient addition.

PROJECT OBJECTIVES

The primary objective of the project was to demonstrate if biological technologies are capable of reducing WAD cyanide concentration in the treated effluent to <0.2 milligrams per liter (mg/L) WAD cyanide.

Secondary objectives included:

- determining the effectiveness of the biological detoxification technologies in reducing heavy metals in the process solution;
- monitoring the variation in total metals in the treatment effluent over the test cycle; and
- determining cost in comparison to conventional technologies.

DEMONSTRATION

The demonstration took place at the McClelland Laboratories Inc. facility (MLI) in Sparks, Nevada. The demonstration consisted of six large-scale high-density polyethylene (HDPE) columns each measuring 22 feet in height with a 4-foot outside diameter. The columns were each loaded with approximately 9.1 tons of ore in November 1998. Cyanide-bearing process solution flowed to the columns at a rate of 0.004 gpm/ft^2 of column cross-sectional area and was recirculated for 2 weeks allowing finer particles to settle, thus, simulating actual heap conditions. On December 4, 1998, the four biological columns were inoculated, hydrogen peroxide solution was applied to the fifth column at a 5:1 stoichiometric ratio. The sixth column was the process water rinse.

RESULTS AND DISCUSSION

Operation of the columns began on December 4, 1998 and continued until May 17, 1999. The total solution applied to each column charge was equivalent to 4.3 tons solution per ton of solids (between 38 and 41 tons of solution per column). Parameters monitored during the test period included: WAD and total cyanide, heavy metal, and nitrate concentrations, pH and temperature.

WAD Cyanide

All six columns were effective in decreasing WAD cyanide concentration in the final rinse effluents to less than 1.3 mg/L. Over 99.9% of the WAD cyanide contained in the process water was neutralized by the rinsing processes. WAD cyanide concentration in the final rinse effluent from the chemical rinse and Whitlock & Associates were below the current drinking water maximum contaminant level (MCL) of 0.2 mg/L.

Effluent pH

Effluent pH decreased with all rinsing processes with the final effluent pH of the chemical rinse and Whitlock & Associates columns being within the MCL range. The process water rinse column required a longer rinse to meet the pH MCL.

CONSTITUENTS

Constituent analyses during the field demonstration included: arsenic; cadmium; cobalt; copper; iron; manganese; magnesium; mercury; nickel; selenium; silver; and zinc. With the exception of selenium, the six rinsing processes demonstrated were effective in decreasing process water constituent concentrations. Fluoride and magnesium concentrations, however, were below the secondary MCL. Manganese was mobilized in the hydrogen peroxide, Applied Microbiology and Whitlock & Associates columns. A decrease in manganese was noted in the process water, Compliance Technology and Little Bear Laboratories columns.

Copper

Copper values steadily dropped within the effluent for all six columns. The process water added to the columns contained soluble copper cyanide. In the hydrogen peroxide column, copper precipitated as a copper hydroxide or as cuproferro cyanide complex. This reduction of copper in the hydrogen peroxide rinse was dependent upon pH and available copper.

Biological technologies attack soluble copper cyanide causing the bond between copper and cyanide to break; copper is adsorbed or absorbed into the biomass where bacteria collect copper at the cell membrane. In the biological aerobic systems, copper deposited as a hydroxide is minimal.

Gold

Gold concentration in all six columns decreased as available cyanide concentration was reduced. Gold recovery decreased from 350 Fg/L to between 35 to 50 Fg/L within the first two to three weeks of the demonstration in all six columns. There was no significant difference in gold recovery between the simple water rinse, hydrogen peroxide rinse, and biological rinse columns.

Magnesium

The magnesium value from the six columns was low at startup and slowly decreased for approximately 107 days showing no significant variation among the six columns. On March 29, a significant increase in magnesium was noted in the hydrogen peroxide rinse column. The remaining five columns showed a slight and steady increase after 107 days of testing. This data trend corresponds with the trends in column discharge pH. As pH decreases, magnesium hydroxide dissolves from the ore causing an increase in effluent magnesium.

Nickel

The nickel value in the six column discharges decreased as the concentration of available cyanide was reduced. Nickel readily complexes with cyanide; in the absence of available cyanide, soluble nickel values decrease.

In the first two weeks of the demonstration, nickel values decreased from 2,500 Fg/L to approximately 1,000 Fg/L in all six columns. The soluble nickel stabilized for approximately six weeks, and then three of the six columns began to show a significant variation in nickel discharge.

During the first week of February, nickel values in the hydrogen peroxide rinse column decreased coinciding with the decrease in cyanide. The process water rinse column and the four biological columns remained slightly higher until cyanide concentrations approached low levels.

Nitrate/Nitrite-N

Nitrate discharge levels in the process water rinse, hydrogen peroxide rinse, Compliance Technology, Applied Microbiology and Little Bear Laboratories columns did not vary significantly. However, the Whitlock & Associates column showed a significant decrease in the nitrate discharge level. Permit nitrate discharge limits were low and it was necessary for the level to be reduced.

Selenium

Variations in selenium discharge levels for all six columns increased or decreased at the same rate.

Silver

Silver values in the six columns discharges decreased as the concentrations of available cyanide decreased. Silver readily complexes with cyanide; thus, in the absence of available cyanide, silver levels decrease rapidly.

Sulfate

During the first six weeks of the demonstration, all six columns produced similar sulfate levels. After 6 weeks, sulfate values began to increase slowly in the hydrogen peroxide rinse column. This trend continued until the demonstration ended. The biological columns showed a slow increase in sulfate discharge values with a slightly higher increase than the process water rinse column. The increased sulfate concentration is believed to be caused by the oxidizing nature of

hydrogen peroxide which converts sulfides to dissolvable sulfates. The increase in sulfates corresponded closely with the increase in hydrogen peroxide concentration.

Zinc

The zinc levels in the six columns discharges readily decreased as the concentration of the available cyanide decreased. Zinc readily complexes with cyanide. Therefore, in the absence of available cyanide, zinc levels rapidly decrease.

Zinc levels decreased from 60,000 Fg/L to approximately 6,000 Fg/L within the first month of the demonstration.

COST

A cost comparison of the demonstrated cyanide destruction technologies was based upon a previous study by MSE in November 1998. Detoxification of an abandoned heap would produce similar comparisons between technologies.

Process Water Rinse

The process water rinse requires the following capital costs: pumping systems; cyanide analyzer; piping and distribution systems; instrumentation; analytical equipment; sampling equipment; holding ponds; and a fixed or temporary facility. In addition operating funds include: personnel; analytical support; make-up water; and power.

Hydrogen Peroxide Rinse

The capital and operating costs of using hydrogen peroxide would require, in addition to the costs described for a process water rinse: holding tanks; mixing tanks; mixing equipment; process level control; storage area; procurement of the hydrogen peroxide; procurement of catalysts (if needed); additional equipment power; and additional labor.

Biological Rinse

Capital and operating cost requirements for a biological heap rinse operation, in addition to the costs of a process water rinse are: bioreactor tank(s); heaters (if necessary); clean water storage tank; live-culture holding tank; culture circulation pumps; process level control; air compressor; mixing and/or aeration equipment; additional piping; microbe isolation and/or procurement; nutrients; additional labor; and additional power.

Common Heap Rinse Costs

Depending on the technology used, costs for a common heap rinse vary. Labor rates associated with treatment system operation vary depending on the complexity of the treatment

system. Process water rinse labor costs are low due to simplicity. However, process water rinse requires longer retention time to reduce cyanide compared to hydrogen peroxide rinse and biological degradation. It is assumed that hydrogen peroxide rinse and biological degradation would require approximately the same amount of time. However, hydrogen peroxide costs are significantly higher than material costs associated with biological degradation. Hydrogen peroxide is copper catalyzed; therefore, more time and energy is expended with process control. Sludge produced by chemical systems can be an order of magnitude greater than biological systems.

Biological systems can utilize existing lined ponds or tanks. Microbe generation may be important for initial startup; however, biological growth is a self-sustaining process. Biological systems can be simplified to a greater degree than chemical systems and normally produce an effluent compatible with the environment. Biological systems will change with conditions; chemical rinse systems will not which can cause expensive upset conditions.

CONCLUSIONS

The hydrogen peroxide rinse column had the highest WAD cyanide degradation rate as the regulatory limit of <0.2 mg/L was reached in 36 days. This performance was expected as hydrogen peroxide is a strong oxidizer and readily degrades available cyanide. The process water rinse column showed a cyanide degradation curve of approximately one-third the rate of the hydrogen peroxide rinse column. All of the biological columns demonstrated had degradation rates higher than the process water rinse. Three of the biological columns were approaching the regulatory limit at the termination of the demonstration; however, one technology provider reached the regulatory limit in 151 days.

It is important to note that this was a demonstration of a difficult scenario for the biological technologies. Under optimal conditions, it is believed that the biological processes would have exhibited significantly higher rates of cyanide reduction. Several factors which added to the bio-difficulty of this demonstration were:

- The ore and process water used for this demonstration contained elevated cyanide concentrations far above the level normally associated with bio-destruction. Some strains of bacteria can tolerate cyanide levels above 250 mg/L; however, many strains of bacteria are severely inhibited at high concentrations.

- The extreme cold weather conditions greatly reduced the degradation rate of the biological columns. Low temperatures inhibit the growth rate of cyanide degrading bacteria.

- The ore type selected for this demonstration was a highly sulfidic, polymetallic ore.

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MICROBIAL CAPPING BARRIER FOR THE CONTROL OF ACID MINE DRAINAGE

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ABSTRACT

Acid mine drainage from mining wastes has been responsible for the degradation of surface and groundwater quality at many locations in Montana and throughout the world. Oxidation of sulfide minerals in mine tailings and waste-rock occurs when oxygenated water infiltrates tailings, resulting in acid generation and the solubilization of metals. Microbial capping technology involves the stimulation of beneficial bacteria at the surface of the tailings or waste-rock pile to remove oxygen from water infiltrating the waste, thereby, reducing acidic drainage and stabilizing dissolved metal ions. Laboratory-scale experiments were conducted using tailings collected from an abandoned hard rock mine and placed in six 0.3 m diameter columns that were 1.2 m long. Clean water was added to the top of the columns using a timer-controlled peristaltic pump. Effluent water from the columns was monitored for pH, oxidation-reduction potential, dissolved metals, and bacterial populations. Although field samples indicated acidic conditions, none of the six columns developed acidic effluents. Test columns received nutrient treatment applications to stimulate beneficial bacteria, while identical control columns were not treated. Nutrient treatments applied to the test columns were effective for stimulating the removal of oxygen from infiltrating water. The oxidation-reduction potential of treated columns was maintained below -250 mV, while the control columns remained in an oxidized-state. Populations of total bacteria and sulfate reducing bacteria showed a significant increase following the nutrient treatment. However, a measurable increase in the populations of heterotrophic bacteria in the treated columns was not observed. Overall, these results indicate that the nutrient treatments were effective for generating anaerobic conditions within the test columns. Column tests are currently being performed using tailings from an alternative site. This work is being conducted as part of the Mine Waste Technology Program under Interagency Agreement Number DW89938513-01-0 between the U.S. Environmental Protection Agency and the U.S. Department of Energy, Contract Number DE-AC22-96EW96405.

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INTRODUCTION

The oxidation of sulfide-containing minerals in mine tailings has resulted in acid production and the liberation of dissolved heavy metals to form acid mine drainage. Acidic drainage from mine tailings has been detrimental to surface and groundwater quality in current and former mining areas. Cost-effective treatments are required to stabilize mine tailings and prevent the formation of acidic drainage. Microbial capping barrier technology involves using nutrient treatments to stimulate beneficial bacteria within the tailings, creating a biologically active zone within the tailings that consumes oxygen and prevents the oxidation of sulfide mineral deposits.

Abiotic oxidation of sulfide-containing mine tailings occurs when oxygen-rich rainwater or surface water infiltrates tailings impoundments. Pyrite (FeS_2), a common constituent of mine tailings, undergoes the following reaction under these conditions:

$$4FeS_2 + 15O_2 + 2H_2O \rightarrow 4Fe^{3+} + 8SO_4^{2-} + 4H^+ \qquad (1)$$

Ferric iron produced in this reaction is a strong oxidant, which further abiotically oxidizes pyrite (or other mineral sulfides) as follows:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (2)$$

These reactions generate ferrous iron and large quantities of acid, which favor the growth of acidophillic, chemolithotrophic bacteria. The role of iron and sulfur-oxidizing bacteria (such as *Thiobacillus ferrooxidans*) in accelerating the production of acidic drainage from sulfide-containing mine tailings has been known for decades (Silverman and Lundgren, 1959). Populations of this or other naturally occurring and environmentally ubiquitous chemolithotrophs colonize open tailings after placement and accelerate acid production through the cycling of ferrous to ferric iron (Brierley and Brierley, 1996):

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \qquad (3)$$

Though this reaction consumes some acidity, the overall effect is the regeneration of ferric iron, which can then oxidize more pyrite and generate much more acidity (via reaction 2). It has been estimated that an active population of *T. ferrooxidans* increases the rate of pyrite oxidation up to 6 orders of magnitude over simple abiotic oxidation (Brierley, 1978). The acidity generated in these reactions further assists the growth and downward migration of *Thiobacilli* through the tailings column by providing the low pH conditions necessary for their growth.

The key to controlling the generation of acid mine drainage is preventing the initial oxidation of pyrite. Bound with iron, the sulfur in pyrite is unable to participate in the microbially catalyzed reactions that cause acid generation. Prevention of oxygen infiltration into tailings then is necessary to prevent oxidation of pyrite and subsequent acid generation. An innovative method to prevent oxygen transport into tailings is the

construction and maintenance of a biologically active barrier on the surface of the tailings.

The basis of biological capping barrier technology is the formation of a biologically active zone occupying the free pore space in the uppermost layer of the tailings. This zone consists of bacteria and other microorganisms enmeshed in a matrix of extracellular polymeric substances (EPS). The metabolism of aerobic and facultative microorganisms in the capping layer removes oxygen from infiltrating water resulting in a decrease in pyrite oxidation and subsequent acid generation and metal solubilization. Furthermore, the presence of the microorganisms and EPS may reduce the hydraulic conductivity of the tailings, thereby, decreasing the flux of water through the tailings. Stabilization of the tailings is also enhanced by the removal of oxygen and production of fermentation products by the capping layer, which promotes the growth of sulfate reducing bacteria (SRB) deeper within the tailings. The growth of SRB results in a pH increase due to carbonate production and precipitation of heavy metals as metal sulfides.

A previous laboratory study used small-scale tests with tailings columns and demonstrated that nutrient treatments to stimulate bacterial growth resulted in an increase in pH, reduction of permeability, and the generation of anaerobic conditions within the columns (Blenkinsopp *et al.*, 1992). This study reports the preliminary results of relatively large-scale column tests with tailings collected from a proposed demonstration site for the field-scale implementation of biological capping barrier technology. The goal of these experiments was to determine if nutrient additions could stimulate indigenous, aerobic bacteria in the soil columns, resulting in increased effluent pH and decreased metals mobility. Specific objectives were to: (1) determine the effects of nutrient addition on the oxidation-reduction potential (ORP), pH, and metals content of column effluent; (2) determine the longevity of these effects from a single nutrient addition; and (3) determine the effects of nutrient addition on the microbial consortia active in the columns.

A series of six columns were packed with tailings from an abandoned mine site and irrigated daily with clean water. After stabilization, four of the columns received nutrient treatments, while two served as untreated controls. The nutrient treatments resulted in a significant decrease in ORP and an increase in the populations of total bacteria and sulfate-reducing bacteria. However, neither the test nor control columns generated acidic effluent or significant concentrations of dissolved metals. Nonetheless, the results demonstrate the effectiveness of nutrient treatments for generating anaerobic conditions within the test columns.

MATERIALS AND METHODS

Tailings from an abandoned hardrock mine near Rimini, Montana, were studied for acid production potential and the applicability of a microbial capping barrier for mitigation of acid mine drainage. Field measurements of tailings surface water runoff indicated acidic conditions (pH under 4.0) and high concentrations of aluminum, iron, lead, and zinc. In October, 1998, approximately 1 cubic yard of tailings material was transported from the

mine site to laboratories at the Center for Biofilm Engineering at Montana State University in Bozeman, Montana. The tailings were packed into PVC columns (12 inches in diameter and 48 inches long). Six tailings columns were constructed and began operating in February 1999. In May 1999, after background conditions had been fully established for the columns, nutrient treatments were applied to four of the columns. Two control columns did not receive nutrient additions.

Each of the six PVC columns (C1–C6) was filled to a depth of 40 inches with tailings from the mine site. After placement in the columns, the tailings were flooded and drained twice to facilitate packing and allow close approximation of actual site permeability. After each flooding, columns were allowed to drain under gravity.

All six columns were operated in an unsaturated condition with dechlorinated tap water applied to the top of the column that was open to the atmosphere. Column influent was adjusted to a flowrate of 10 milliliters/minute for 60 minutes each day. Columns were allowed to drain freely under gravity. Drainage from the bottom of the columns was collected on a periodic basis for pH, ORP, heterotrophic plate counts (HPC), direct counts (DC) and SRB analyses.

The ORP and pH were measured with electrodes. The SRB were enumerated using Postgate B media and most-probable number (MPN) techniques. Direct counts were taken via microscopy, and HPC were enumerated on Difco R2A agar using serial dilution technique.

On May 10, after two months of operation, 10 liters of nutrient solution was added to columns 2, 3, 4, and 6. Columns 1 and 5 received an equal amount of unamended tap water. A second treatment of nutrient solution (5 liters) was added to the treated columns two weeks after the initial treatment.

RESULTS AND DISCUSSION

Although field samples indicated acidic conditions were present in ponded water atop the tailings pile, acidic effluent did not develop in any of the six tailings columns. Column effluent pH varied from 6.5 to 7.2 prior to the nutrient treatments. This range narrowed slightly, from 6.8 to 7.2 following treatment, but did not show significant change. Despite this lack of a critical measure of the treatment effectiveness, the test was continued to determine the effect of nutrient dosing on ORP and tailings microbiology.

As expected, the ORP dropped significantly in columns that received the nutrient treatment. Prior to adding nutrient solution, ORP in the columns varied from approximately –100 to +250 millivolts. Despite this high variability, ORP in all treated columns dropped significantly following treatment. Treated column ORP was generally in the range of –300 to –400 millivolts three weeks after the treatment occurred. The high variability in individual column response to the nutrient addition is attributed to natural variation in an unsaturated flow situation. The ORP in treated columns generally remained below –250 millivolts for at least 60 days following treatment.

Sulfate reducing bacterial (SRB) cell numbers were observed to increase over time in the effluent from columns receiving nutrient additions. Prior to nutrient addition, SRB were observed in column effluents at concentrations ranging from 1 to 10 cells/milliliter. Approximately two weeks following nutrient addition, test column effluents had SRB concentrations ranging from 10^2 to 10^4 cells/milliliter. Interestingly, one of the control columns remained at very low effluent SRB concentrations (column C5 at 10 cells/ milliliter) and one exhibited elevated levels (column C1 at 10^3 cells/milliliter). SRB growth would be expected to follow the onset of anaerobic conditions. Column C1 was observed to have a ORP indicative of slightly anaerobic conditions early in the experiments, while the ORP in column C5 was consistently in the aerobic range. The increase in SRB in the test columns is thought to result from the depletion of oxygen from infiltrating water by aerobic bacteria. This is a highly desirable result because SRB produce hydrogen sulfide (H_2S) as a product of metabolism. H_2S readily reacts with metals present in solution to form insoluble and immobile metal sulfide phases.

Heterotrophic plate counts from column effluents were not observed to have a significant response to adding nutrients to the tailings columns. The HPC is a measure of all the bacteria that are capable of growing on the nutrient agar under aerobic conditions. It was expected that adding nutrients would increase the total bacterial cell numbers growing in the column, hence, in the column effluent as well. The lack of measurable increase in HPC cell numbers in the effluents may have been due to the generation of anaerobic conditions throughout most of the test column length, which did not favor the proliferation of bacteria capable of aerobic growth. The population of aerobic heterotrophic bacteria was likely localized near the upper (inlet) sections of the columns.

Bacterial direct counts performed on column effluent indicated a slight increase in cells from test columns while showing mixed results from control columns. Direct counts are intended as a measure of all cells in a sample, living and dead. As such, it would be expected that DC results would be higher than HPC. This was found to be the case with DC levels in the range of 10^6 to 10^8 cells/milliliter for all samples. In comparing HPC and DC results, HPC levels were observed to drop in mid July (approximately 60 days following nutrient addition), while no such drop was observed in DC results. This could be due to the proliferation of anaerobic bacteria within the columns that were unable to grow under the aerobic conditions of the HPC assay.

Effluent from all columns was tested for dissolved metals (Al, As, Cd, Cu, Fe, Pb, Mn, Zn) on May 10, 1999. At that time, the columns had operated with declorinated tap water influent for approximately 10 weeks, yet no nutrient additions had yet been made. Results from this sampling indicate the absence of elevated concentrations of any of the eight analytes. In many cases, concentrations of target metal analytes were below detection limits.

CONCLUSIONS

Because column pH remained in the neutral range and metals were not mobilized from the columns, the abandoned mine from which the tailings were collected was deemed an

inappropriate site for demonstration of this technology. The data collected does demonstrate several useful facts, however:

1. Dosing 15 liters of nutrient solution effectively reduced the ORP in mine tailings columns for a period of at least 60 days.

2. The effects of nutrient addition on HPC were not observable in column effluents, but nutrient addition significantly increased SRB in column effluents, suggesting the potential to precipitate dissolved metals as metal-sulfide complexes.

3. Adequate populations of SRB and HPC bacteria exist in these mine tailings such that bacterial additions to the columns were unnecessary. Simply adding a nutrient solution was adequate to provide for sustained, measurable populations of these organisms.

An alternative site for demonstration of this technology has been selected and column studies using tailings from this site is currently being performed.

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ARSENIC REMOVAL AND LONG-TERM STABILIZATION FOR SOLIDS

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ABSTRACT

Three technologies were demonstrated and evaluated for arsenic removal and stabilization of arsenic by-products. Each technology was evaluated treating two separate industrial waste water streams. The baseline technology was ferrihydrite precipitation with concurrent adsorption of arsenic onto the ferrihydrite surface. The two innovative technologies demonstrated were: 1) an integrated adsorption membrane filtration process that used activated alumina and micro filtration; and 2) a process called mineral-like precipitation. Each of the technologies were evaluated for arsenic removal capabilities, long-term stabilities of by-products produced, and process costs. The overall results will be presented and discussed. MSE Technology Applications, Inc., managed the project and demonstrated these technologies through the U.S. Department of Energy (DOE) and U.S. Environmental Protection Agency's Mine Waste Technology Program under Interagency Agreement Number DW89938513-01-0. Work was conducted through the DOE National Energy Technology Laboratory at the Western Environmental Technology Office under DOE Contract Number DE-AC22-96EW96405.

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INTRODUCTION

Project Management

This paper describes the research that was conducted and summarizes the technical results that were obtained by the Arsenic Removal Demonstration Project The Arsenic Removal Demonstration Project was performed for the U.S. Environmental Protection Agency's (EPA) Mine Waste Technology Program (MWTP). MSE Technology Applications, Inc. (MSE) implements the MWTP and owns/operates the MSE Testing Facility in Butte, Montana. The Arsenic Removal Demonstration Project was funded by the U.S. EPA MWTP.

Project Purpose

The purpose of the Arsenic Removal Demonstration Project was to demonstrate alternative water treatment technologies capable of effectively removing arsenic. Two innovative technologies, mineral-like precipitation and alumina adsorption with microfiltration, and one conventional technology, ferrihydrite adsorption, were chosen to be evaluated under the Arsenic Removal Demonstration Project.

Scope of Problem

Acidic, metal-bearing water draining from remote, abandoned mines has been identified by the EPA as a significant environmental/ health hazard in the Western United States (U.S. EPA).

Arsenic compounds and solutions are frequently an unwanted byproduct of the mining and metallurgical extraction of metals such as copper, gold, lead, and nickel. Arsenic waste problems will continue to grow as high-grade ores with low-arsenic content are depleted, and the processing of sulfide ores with high arsenic content becomes increasingly common. An example of arsenic-bearing solid wastes from the processing of gold and base metal ores is the flue dust produced from roasting and smelting unit operations. The flue dust is often concentrated in arsenic, and the arsenic is usually present as arsenic trioxide. Large quantities of flue dust from past and current mineral-processing operations are being kept in temporary storage pending the development of safe disposal methods.

Dissolved arsenic has two common valence states (III and V). Generally, arsenic in the arsenite state (III) is more soluble than arsenic in the arsenate state (V). Due to this chemical trait, arsenic is generally removed more effectively from solutions in the oxidized or arsenate state (Robins, 1983).

The U.S. National Drinking Water Standard for arsenic is 50 parts per billion (ppb). Due to concerns for cancer risk associated with arsenic, the World Health Organization recently revised the guideline for arsenic in drinking water from 50 to 10 ppb in 1993 (Rosengrant and Fargo, 1990).

Statement of Project Objectives

The primary objective of the field demonstration project was to assess the effectiveness of the chosen processes for removing arsenic from solution. Another objective of the project was to evaluate the products formed from each process to determine if they are environmentally stable. More specifically, the project objectives are:

- Reduction of the concentration of dissolved arsenic in the effluent waters to a level less than the National Primary Drinking Water Regulation Limit for arsenic established by the EPA of 50 ppb, or reduce the concentration of dissolved arsenic by 50% if the influent concentration was less than 50 ppb.

- Production of the concentrated arsenic-bearing solids from the processes that are environmentally stable by demonstrating that arsenic results using toxicity characteristic leachate procedure (TCLP) will be below the maximum concentration for toxicity of 5.0 milligrams per liter.

TECHNOLOGY DESCRIPTIONS

The three arsenic removal technologies demonstrated during the Arsenic Removal Demonstration Project were 1) mineral-like precipitation; 2) alumina adsorption with microfiltration; and 3) ferrihydrite adsorption.

Mineral-Like Precipitation

Mineral-like precipitation has been extensively investigated on bench-scale by Dr. Larry Twidwell, a Montana Tech of the University of Montana (Montana Tech) professor. The research has been performed over 10 years on several different arsenic-bearing waters.

The objective of the mineral-like precipitation technology is to strip arsenic from solutions in a way so as to produce mineral-like precipitated products that are stable for long-term storage in outdoor pond environments. Arsenic is incorporated into a mineral matrix that is stable against atmospheric reagents such as carbon dioxide. The precipitation of the mineral-like products can remove arsenic from solution to well below the U.S. Environmental Protection Agency (EPA) regulatory discharge standard as well as remove other heavy metals.

Alumina Adsorption with Microfiltration

Alumina adsorption is a widely recognized technology for removing arsenic from water. An innovative approach using alumina adsorption combined with microfiltration has been developed by ZENON Environmental Inc. (ZENON) of Canada.

Ferrihydrite Adsorption

The ferrihydrite adsorption process is EPA's Best Demonstrated Available Technology to remove arsenic from industrial waters. This technology was used as the baseline technology for comparative purposes to the innovative technologies of alumina adsorption with microfiltration and mineral-like precipitation.

DESCRIPTIONS OF TREATED WATERS

The pilot-scale demonstrations were performed on three waters: 1) scrubber blowdown water, and/or 2) thickener overflow water from the gas cleaning system prior to entering an acid plant of a lead smelter, and 3) an abandoned mine water. Chemical profiles of these waters is presented in Table 1.

Table 1. Constituents of treated waters.

Constituent	Dissolved Species micrograms/liter (F/L)[1]
Scrubber Blowdown Water	
As(III)	3,913,000
As(V)	702,000
Thickener Overflow Water	
As(III)	4,060
As(Total)	5,810
Abandoned Mine Water	
As(V)	366
As(Total)	362 (range was 366–670)
[1]Dissolved concentrations (i.e., sample filter through a 0.2 micron high-density polyethylene filter disk).	

Field testing of these processes was conducted by MSE, Montana Tech, and ZENON personnel. Monitoring of pH, E_H, and flow rates were performed at both sites.

Inorganic chemical analyses for samples collected at both sites were conducted at the MSE-HKM Analytical Laboratory, which is located in Butte, Montana. Long-term stability tests are being conducted on the solids produced from the ferrihydrite process and the mineral-like precipitation process at Montana Tech.

DEMONSTRATION RESULTS

Mineral-Like Precipitation

Scrubber Blowdown Water Analytical Results

Removing arsenic from the scrubber blowdown water by the mineral-like precipitation technology was very effective. The effluent water from the settler (after 24-hours continuous operation) contained <10 ppb arsenic [the goal was to remove the arsenic to below 50 parts per billion (ppb)]. The influent and effluent experimental results are summarized in Table 2.

Table 2. Mineral-like precipitation analytical results.

	Influent Arsenic (ppb)	**Effluent Arsenic (ppb)**
Scrubber Blowdown Water	3,300,000	<10
Thickener Overflow Water	5,800	<15
Abandoned Mine Water	420	<10

Thickener Overflow Water Analytical Results

Removing arsenic from the thickener overflow water by the mineral-like precipitation technology was very effective [e.g., the effluent water from the settler (after 8-hours continuous operation) was <15 ppb arsenic (the goal was to remove the arsenic to below 50 ppb)]. The influent and effluent experimental results are summarized in Table 2.

Abandoned Mine Water Analytical Results

Removing arsenic from the abandoned mine water by the mineral-like precipitation technology was very effective [e.g., the effluent water from the settler (after only 1 hour of continuous operation) was <10 ppb (one sample was 25 Fmg/L, the goal was to remove the arsenic to below 50 ppb)]. The influent and effluent experimental results are summarized in Table 2.

Toxicity Characteristic Leachate Procedure (TCLP)

The TCLP was performed on the composite solids produced at the end of each demonstration. The product solids produced from the demonstration on each passed the TCLP test; therefore, these solids are considered to be nonhazardous with respect to handling and land disposal.

Long-Term Stability

The solids that are produced by other technologies (lime precipitation and ferrihydrite adsorption) may not be stable for long-term outdoor storage. The mineral-like precipitation technology solves the storage problem because the product is thermodynamically stable against conversion to calcium carbonate by carbon dioxide in atmospheric air.

To validate that the mineral-like product is indeed stable, long-term stability testing was initiated and will be continued for 2 years. Test slurries of the solids produced from the Arsenic Removal Demonstration Project were prepared and set up so air could be sparged into the slurries. Solution pH, Eh, and temperature are monitored monthly. The solubility of the solids will be determined after 1 and 2 years of exposure.

Alumina Adsorption with Microfiltration Results

Four tests were conducted treating thickener overflow water and one test treating abandoned mine water. A summary of the analytical results is presented in Table 3. High concentrations of sulfate [up to 2,500 parts per million (ppm)] in the thickener overflow were competing with arsenic for adsorption sites on activated alumina.

Table 3. Alumina adsorption with microfiltration analytical results.

	Initial Arsenic (ppb)	**Final Arsenic (ppb)**
Thickener Overflow Water	5,800	180–1,420
Abandoned Mine Water	420	< 20

Ferrihydrite Adsorption

Thickener Overflow Water Analytical Results

For removing arsenic in thickener overflow water, two separate parameters were used. An iron to arsenic mole ratio of both 8 and 10 was used for ferrihydrite adsorption. The removal of arsenic from thickener overflow water is dependent on the amount of iron inputted into the system. Ferrihydrite adsorption technology was performed at the lead smelter site using their existing facility.

<u>Low Iron Demonstration</u>

Using an iron to arsenic mole ratio of 8, arsenic concentrations were lowered from 5.8 ppm to 100 ppb at a pH of 7. Ferrihydrite absorption was effective for arsenic removal; however, the established drinking water standard of 50 ppb was never achieved at this iron to arsenic mole ratio. The analytical results can be observed in Table 4.

Table 4. Ferrihydrite adsorption analytical results.

	Influent Arsenic (ppb)	Effluent Arsenic (ppb)
Thickener Overflow Water (Fe/As ratio = 8)	5,800	100
Thickener Overflow Water (Fe/As ratio = 10)	5,800	<20
Abandoned Mine Water (Fe/As ratio = 10)	420	<20

High Iron Demonstration

Increasing the iron content was very effective for removing arsenic from the thickener overflow water. Concentrations were lowered from 5.8 ppm to less than 20 ppb. The influent and the effluent water analytical results are summarized in Table 4.

Abandoned Mine Water Analytical Results

Removing arsenic using abandoned mine water by ferrihydrite adsorption was very effective. Results indicate arsenic concentrations were lowered from 420 ppb to less than the drinking water standard of 50 ppb. The arsenic to iron mole ratio used for this demonstration was 10, which proved to be sufficient. Analytical results are summarized in Table 4.

ECONOMIC ANALYSIS

One objective of this study was to perform a first order cost estimate for each of the treatment flow sheets. The cost estimate presented here is not a detailed engineering cost analysis; it is a first order cost estimate that should be within ±30%.

The three different technologies, mineral-like precipitation, alumina adsorption with microfiltration, and ferrihydrite adsorption, were economically evaluated for a system that contained 0.5 ppb arsenic at a flowrate of 300 gallons per minute. The comparative results can be seen in Table 5.

Table 5. Economic evaluation for selected technologies.

	Mineral-Like Precipitation	**Alumina Adsorption**	**Ferrihydrite Adsorption**
Capital	$250,000 ±$75,000	$396,000 ±$118, 800	$250,000 ±75, 000
Operations and Maintenance per Year	$41,080	$130,700	$78,904
Operations and Maintenance per 1,000 gallons treated	$0.30 ± 0.09	$0.70 ± 0.30	$0.55 ± 0.16

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