

## **FEASIBILITY OF LIME TREATMENT AT THE LEVIATHAN MINE USING THE IN-LINE SYSTEM**

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### **ABSTRACT**

The In-Line System (ILS) was used in a pilot-scale water treatment study at the Leviathan Mine in California. The Leviathan Mine is a remote, abandoned, copper/sulfur mine. This study addressed two questions: (1) Can the severely polluted mine drainage at the Leviathan Mine be treated with lime to an acceptable quality? and (2) Can a neutralizing reagent formulation (using various ratios of lime, fly ash, and cement) be designed to improve the physical characteristics of the resulting sludge for disposal purposes? The primary pollutants of concern are arsenic, nickel, aluminum, iron, and sulfate.

Pilot-scale studies at the Leviathan Mine show that an in-line system (ILS) can be used to treat the severely polluted pond and adit water to meet the U.S. Environmental Protection Agency's National Ambient Water Quality for Freshwater Aquatic Life Protection (1-hour acute toxicity) criteria. Lime and lime-based admixtures were used to neutralize the adit and pond waters. The optimal treatment pH range was 6.9-7.9 for adit water, and 6.5- 8.0 for pond water. The ILS served as a neutralization and mixing system for treating both water sources, and also as an aeration system for treating the adit water. The ILS effectively oxidized nearly 900 mg/L of  $\text{Fe}^{+2}$  within 30 seconds of contact time when treating the adit water. Additional work is needed to evaluate sludge alternatives.

The simplicity, portability, flexibility, and economics of the ILS make it a prime candidate for remote treatment operations such as the Leviathan Mine. Furthermore, the ILS can operate by water power with elevational differences of 50 ft or greater. The need for permanent electrical power installation for water treatment can possibly be eliminated by coupling the ILS with a commercially available water-powered lime feed system.

### **INTRODUCTION**

The remote Leviathan Mine is a major source of pollution in Alpine County, CA. The primary pollutants associated with this State-owned abandoned mine site include arsenic, nickel, aluminum, and iron. A previous effort to passively address this pollution problem entailed the construction of evaporation ponds. The Lahontan Regional Water Quality Control Board (LRWQCB) is now considering acid mine drainage (AMD) treatment. This report discusses a pilot-scale water treatment study conducted to determine the feasibility of treating Leviathan Mine water using lime (calcium hydroxide) and the U.S. Department of Energy's In-Line System (ILS)(Ackman and Place, 1987). There were two sources of water. Adit water perennially flows out of the underground workings. The evaporation ponds receive flows from the adit and a subsurface drainage system. The primary differences associated with the water quality of the adit and ponds are that the concentration of metals is much greater in the evaporation pond water and the iron in the pond water is in the oxidized (ferric)

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form. The high levels of ferrous iron in the adit water require aeration as well as neutralization for effective removal. In contrast, the ferric iron in the pond water requires only neutralization (pH adjustment) for effective removal. The effectiveness of various concentrations of lime and lime-admixtures were evaluated for both water sources based on the lowest contaminant concentration achieved. Treated waters were then compared to the standards and criteria associated with agricultural irrigation, support of freshwater aquatic life, and drinking water.

In addition to water treatment, this cooperative effort also evaluated the modification of AMD sludge characteristics using lime-based admixtures, including various ratios and combinations of lime with fly ash and cement. The lime treatment established baseline information. Admixture treatment was an attempt to favorably modify chemical and physical characteristics of the sludge, as well as treating the water (Hustwit, 1995). Sludge samples were collected for leachate testing and volume measurements. The handling and disposal of the AMD sludge generated during treatment are critical economic aspects of most long-term water treatment operations. The California Waste Extraction Test (WET Test) (California Code of Regulations) was used in this study to determine if the lime/lime-admixture treatment sludge produced is hazardous according to California standards. This test was used in addition to EPA's toxicity characteristic leaching procedure (TCLP) test (U.S. Code of Federal Regulations, Title 40, EPA, 1994). If the sludge was found to be nonhazardous by the California WET test, on-site disposal could be considered. If the AMD sludge was found to be potentially hazardous, it would have to be hauled off-site to an approved waste disposal site. Due to the high costs typically associated with hazardous waste disposal and transportation, sludge volumes, in addition to chemical analysis, were important. Therefore, 30-min sludge settling tests were performed on all of the sludge samples.

### **LEVIATHAN MINE**

The Leviathan Mine is in Alpine County, California, approximately 3 mi from the Nevada border. This 500-acre copper/sulfur mine site, situated at an elevation of about 7,000 ft in the Sierra Nevada Mountains, was operated between 1863 and 1962 (Taxer et al., 1991). Accessibility to the site is limited during winter and early spring because of weather conditions. Since 1983, the State of California has owned the abandoned mine site and has actively pursued remediation measures.

Exposed ore and haphazard mining and tailing disposal practices has long had an adverse impact on downstream water quality. Surface runoff from snowmelt and precipitation became contaminated by contact with millions of tons of low-grade sulfur tailings. In addition, drainage (approximately 30 gallons/minute, (gpm)) from the underground mine adit, which is also highly polluted, provided a constant source of AMD to Leviathan Creek. The heavy metals of primary concern at this site include arsenic, nickel, aluminum, and iron (Taxer et al., 1991).

Leviathan and Aspen Creeks, which drain the mine site, are tributaries of Bryant Creek. Bryant Creek drains into the East Fork Carson River, which is a major western Nevada water supply source. These streams are a resource for agricultural irrigation, fish and wildlife habitats, and recreational use. Drainage from the Leviathan Mine has caused fish kills in Bryant Creek and a 10-mile segment of the Carson River.

Since assuming responsibility for the mine property, the LRWQCB has made significant environmental remediation efforts at the mine site. A channel approximately 1,900 long was constructed to prevent waste materials and polluted ground water seepage from contaminating stream

water. The open pit was filled and regraded. In addition, compacted terraced surfaces, subsurface drainage trenches, and open channels were constructed to carry surface runoff to the creek.

Five evaporation ponds, with a total area of 11 acres, were constructed on-site. These ponds were designed to receive water collected by the subsurface drainage channels in the mine pit and from the adit. Ideally, evaporation would equal or exceed recharge. The ponds were lined with heavy plastic membranes to prevent ground water degradation (Taxer et al., 1991).

It is estimated that 8.1 million gal of AMD are produced annually by the adit and subsurface drains. The 11 acres of evaporation ponds cannot handle all of this drainage water without periodically overflowing. Storage capacity is further reduced by the buildup of metal precipitates. As a result, approximately three million gal are flushed from the evaporation ponds into Leviathan Creek during the average spring runoff (Taxer and others, 1991). The seasonal high flows of the creek help to dilute this discharge.

Effective treatment of the adit water, which is heavily polluted, is a challenge to any water treatment process. Coupled with water treatment is the handling and disposal of the resultant sludge. Limited laboratory testing by the University of California—Davis has indicated that conventionally treated lime sludge would be classified as hazardous by California Department of Health Services due to arsenic (California Code of Regulations). Sludge (waste) disposal would therefore be expensive, especially considering the remote location of the site.

## **TREATMENT SYSTEM**

### **Objectives**

A primary objective of this study was to treat all water so that it could be discharged from the site and used beneficially. Another objective was to evaluate the physical and leaching characteristics of the sludge. To meet these objectives, treated water and sludge must meet certain standards and criteria. Table 1 presents criteria for the protection of freshwater aquatic life. Sludge quality standards are presented in table 2, including EPA's TCLP and California's Waste Extraction Test (Wet Test), which includes the determinations of the Soluble Threshold Limit Concentration (STLC) and Total Threshold Limit Concentration (TTLC). The parameters associated with EPA's TCLP include silver, arsenic, barium, cadmium, chromium, lead, antimony, mercury, and selenium. The State criteria include the TCLP parameters, but also include beryllium, cobalt, chromium VI, copper, molybdenum, nickel, vanadium, zinc, thallium, and fluorine. Site-specific water quality standards are currently being established; thus, no effluent standards currently exist for the Leviathan Mine. Treated water was compared to criteria for freshwater aquatic life protection (Federal Register, 1992) in the absence of site-specific requirements. Only two samples were found to exceed the detection limit of 0.015 mg/L for selenium and antimony, and none exceeded 0.07 mg/L.

Table 1. Aquatic Standards		Table 2. Sludge Standards			
PARAMETERS (mg/L)	EPA AQUATIC STANDARDS <sup>1</sup>	Parameters (mg/L)	US EPA 40 CFR TCLP (mg/L)	CA DHS Threshold Limit Concentration	
pH	6.5 - 9.0			Soluble STLC (mg/L in extract)	Total TTLC (wet wt. mg/kg)
Alkalinity, as CaCO <sub>3</sub>	NA <sup>5</sup>	Silver, Ag	5.0	5	500
Acidity, as CaCO <sub>3</sub>	NA	Arsenic, As	5.0	5	500
Ferrous Iron, Fe <sup>2+</sup>	NA	Barium, Ba	100	100	10,000
Total Iron, Fe <sub>total</sub>	NA	Beryllium, Be	NA <sup>1</sup>	0.75	75
Calcium, Ca	NA	Cadmium, Cd	1.0	1	100
Magnesium, Mg	NA	Cobalt, Co	NA	80	8,000
Aluminum, Al	0.75	<sup>1</sup> Chromium (VI), Cr	NA	5	500
Sodium, Na	NA	Chromium, Cr	5.0	560	2,500
Manganese, Mn	NA	Copper, Cu	NA	25	2,500
Sulfate, SO <sub>4</sub>	NA	Molybdenum, Mo	NA	350	3,500
Potassium, K	NA	Nickel, Ni	NA	20	2,000
Arsenic, As	0.36	Lead, Pb	5.0	5	1,000
Barium, Ba	NA	Vanadium, V	NA	24	2,400
Beryllium, Be	NA	Zinc, Zn	NA	250	5,000
Cadmium, Cd	0.019*	Mercury, Hg	0.2	0.2	20
Cobalt, Co	NA	Selenium, Se	1.0	1	100
Chromium, Cr	5.404*	Thallium, Tl	NA	7	700
Copper, Cu	0.065	Fluorine	NA	180	18,000
Nickel, Ni	4.582*	<sup>1</sup> No standard applicable to parameter			
Lead, Pb	0.477*				
Antimony, Sb	0.088				
Selenium, Se	0.02				
Zinc, Zn	0.379*				
<sup>1</sup> reference					
<sup>2</sup> No standard applicable to parameter					
* Values based on a hardness of 400 mg/L as CaCO <sub>3</sub> , values directly proportional to hardness					

## In-line System (ILS)

The ILS is an alternative to conventional neutralization and mechanical aeration, and consists of two readily available in-line components: a jet pump aeration device and a static mixer (Ackman and Erickson, 1986; Ackman and Kleinmann, 1984). Jet pumps are simply nozzles that entrain air by venturi action. The jet pump used in this application was made of polyvinyl chloride (PVC) to resist corrosion. Water enters under pressure and is converted by the jet pump to a high-velocity stream, which passes through a suction chamber that is open to the atmosphere. When the system is being used for neutralization as well as aeration, the suction chamber also serves as the injection point for the alkaline material. After passing through the jet pump, the flow of air and liquid enters the static mixer to aid oxygen dissolution. Multiple jet pump units may be placed in parallel as long as water pressures of at least 20 psi per jet pump are maintained. Commercial installations containing up to 14 units are currently treating flows of 2000 gallons per minute of coal mine drainage.

The ILS used in this pilot-scale test consisted of a 1-inch-diam PVC jet pump and a vertical static mixer that contained trickling media (hollow plastic cylinders with internal baffles) (Ackman and Kleinmann, 1993). These media are used routinely in sewage and industrial waste treatment. Based on laboratory tests, they increase the mixing capacity and oxygen transfer of the ILS by enhancing bubble shear and by extending the air-water contact time (Hustwit et al., 1992). The static mixer was a 4-ft-long, 6-inch-diam PVC pipe with 1-inch-diam openings at both ends. The trickling media were 1-inch in diameter and 1-inch long.

Treated water can be discharged from the static mixer directly into a pond or clarifier at atmospheric conditions, rather than into a pipe. Atmospheric discharge prevents the buildup of back pressure on the discharge end of the jet pump, which significantly reduces the suction capacity.

Sludge handling and disposal at abandoned sites, rather than at active sites where AMD treatment and sludge disposal are regulated, present the greatest challenge for remote treatment technologies. The excellent mixing and aeration characteristics of the ILS, coupled with formulated neutralizing materials, presented an opportunity to engineer the characteristics (solidification and moisture content) of the sludge.

The pond water quality presented three problems for the initial treatment system: pH adjustment, scaling, and clogging. The adit water quality presented two problems: scaling and ferrous iron oxidation. A broad span of pH values could be obtained when treating adit water using a laboratory-scale chemical feed pump. However, the average acidity of the pond water was nearly 15 g/L, and the original chemical feed pump was unable to provide enough lime slurry to raise the pH above a circumneutral pH (7.2). Consequently, a 2-inch portable centrifugal pump was used. After this modification, feed rates were controlled by valves and pH measurements from a portable pH meter, rather than by the pH controller in the discharge line. Chemical feed adjustments using a manual ball valve were made relative to the intermittent pH measurements and targeted pH.

The high sulfate concentrations, more than 15.6 and 3.9 g/L in the pond and adit waters, respectively, caused significant scaling problems on the pH controller probe. Significant scaling on the pH probe was observed within 1 hour of operation for both the adit and pond waters when it was placed in-line of the static mixer discharge. When the probe was placed in-line of the tank 1 discharge, visible scaling was observed after four to six hours of operation. The in-line pH controller was therefore eliminated, and a constant feed lime slurry pump was installed and controlled with valves and a portable pH meter. All samples collected at the discharge of tank 1 were treated using the original chemical feed system, whereas all samples collected at the ILS discharge were treated using the modified system with the larger slurry pump.

The high metal content of the pond water (2.4 g/L of iron) generated large volumes of sludge. In the static mixer, the high sludge volumes, coupled with a rapid gypsum buildup on the trickling media, resulted in clogging and physical breaking of glued fittings during operation. The vertical 4-ft-long, 6-inch-diam PVC static mixer filled with trickling media, used for treating the pond water, was replaced with 4 ft of hollow 4-inch-diam PVC pipe. Because the iron content of the pond water was primarily in the ferric state, requiring pH adjustment and not oxygen transfer, the trickling media were not necessary. Clogging associated with the pond water was not a problem after the trickling media was removed. Clogging was also not a problem during the treatment of adit water, despite the presence of the trickling media, due to the lower concentrations of metals and sulfates.

### Chemical Feed System

Both a portable pH meter and pH controller were used to obtain accurate field pH measurements. Maintenance of the pH probes included daily acid baths and conditioning because of scaling problems. A field generator provided electrical power for the operation of the pH controller, a chemical metering pump, and paddle mixer. Sludge volumes were determined using Imhoff cones. Sludge volume measurements were taken every 5 min for 30 min. Extended settling times (approximately 24 hours) and the related volumes were recorded for several samples.

### Water Sampling Locations and Procedures

Treated water samples were collected in 2-gal buckets through in-line sampling ports located in the discharge lines of tank 1 (T) and the ILS (out of the static mixer) (S). A field pH was measured in a bucket for 60 seconds immediately after collection. Typically, a water sample was kept in a bucket for three to five hours prior to filtering and acid fixation. Pond samples, because of high sludge volumes, required this amount of time to provide an adequate amount of supernatant for sampling purposes. All treated water samples were removed from the buckets with a 60-cc syringe and placed in sample bottles after passing through either a 25- or 45-micron syringe filter. All buckets were scrubbed and rinsed after each sample with treated effluent water from storage tanks 2 and 3.

Three 175-mL bottles were collected for each sample. One bottle was water for laboratory pH, alkalinity, and sulfate determinations. One was acidified with hydrochloric acid for metals analysis using the Inductivity Coupled Plasma Spectrometer (ICP), and one was acidified with nitric acid for low-level metals detection using a Graphite Furnace Atomic Absorbption (GFAA).

Raw water was collected through a sampling port located upstream of the jet pump. These samples were collected directly into sample bottles and were not filtered. Raw water was sampled at least once per day, and was found to be relatively stable for both the adit and pond 1.

Targeted pH's ranged between circumneutral (6-8) and alkaline (8-9). Obtaining targeted pH values with reasonable accuracy was very difficult for the adit water because of the high concentration of  $\text{Fe}^{2+}$ . Iron oxidation and hydrolysis were still occurring during the collection of adit water samples. Hydrolysis generates acidity and results in a declining and unstable or transient pH until the reactions have been completed. To compensate for continued reactions and declining pH during sampling, a modification was made to raise the intermittent pH target by one to two pH units above the targeted pH value before sample collection. Consequently, the adit water pH measured immediately before and after sampling was higher than that of the recorded field, which was measured three to five hours after collection and before acid fixation.

## Sludge Sampling Locations and Procedures

Sludge samples collected for analytical purposes were drawn from the water sampling buckets. They were set aside for approximately three to five hours prior to volume testing. For volume testing, samples were thoroughly mixed and poured into a 1,000-mL Imhoff cone; for 30 min, levels of the sludge-water interface were recorded at 5-min intervals. Three 175-mL sample bottles were filled with sludge from one bucket (sample) using a 60-cc syringe for withdrawal from the bucket and delivery to the bottle.

Lime-based admixtures included mixtures of lime and fly ash, as well as lime and fly ash and cement. This ratio throughout this report uses the following format: lime:fly ash:cement. (In tables, this is abbreviated as L:F:C.) For example, a ratio of 1:0:0 indicates a lime-only slurry; a ratio of 1:4:0 indicates a slurry containing one part lime and four parts fly ash. Admixtures were based on a pound-per-gallon basis. Typically, whole-unit weights (e.g., 50-lb bag of lime, 80-lb bag of portland cement, or 37-lb can of fly ash) were initially placed in the mix tank. Occasionally, half-bags of lime and cement would be used. With one exception, all ratios presented in this report have been rounded to the nearest whole number. For example, a ratio of 1:4:0 actually contained 0.42 lb/gal lime, 1.72 lb/gal fly ash, and no cement (actual ratio was 1:4.1:0). Likewise, the ratio of 1:4:4 contained 0.25 lb/gal of lime, 1.0 lb/gal fly ash, and 0.92 lb/gal cement (actual ratio was 1:4.3:7). The ratios of admixtures used was based on limited laboratory testing.

The primary objective of all slurries (lime and admixtures), from a treatment perspective, was to facilitate pH adjustments for the precipitation and removal of the various metals in solution. The primary objective of using admixture slurries was to modify sludge characteristics, in addition to pH adjustment. Although any of the admixture components (fly ash and cement) could be used individually as a means of pH adjustment, there are problems. The use of fly ash alone, due to its relatively low lime content, would require large amounts of fly ash and would generate enormous volumes of sludge. High costs prevent the use of only cement as a means of pH adjustment.

The calcium in lime and the silicates in fly ash generate pozzolanic or cementitious reactions, which in this study were directed toward solidifying/dewatering the AMD sludge. The addition of cement was intended to enhance this process. It was unknown whether the admixtures would aid in the removal of contaminants.

## ANALYTICAL TESTING

The standard water quality analysis included the following parameters: ferrous iron, total iron, calcium, magnesium, aluminum, sodium, manganese, sulfate, potassium, arsenic, barium, beryllium, cadmium, cobalt, chromium, copper, nickel, lead, antimony, selenium, and zinc. Laboratory pH and acidity-alkalinity values were also determined. In addition, selected metals, found to be below the level of detection of the ICP, were further analyzed using GFAA techniques. The metals selected for low-level detection include antimony, cadmium, copper, arsenic, and selenium. As previously discussed in the Water Sampling Locations and Procedures section, raw or untreated samples were not filtered to yield total concentrations and all the treated samples were filtered to yield dissolved concentrations.

### Raw Water

At least one raw water sample was collected for each water treatment event (see tables 3 and 4). Raw water data for both the adit and pond are summarized in table 5. The adit water, which

originates from a flooded underground mine, was consistent during the period of this study (September 20, 1994, to October 3, 1994).

Evaporation pond water quality is affected by seasonal changes. Relative to metals concentration and treatment of the pond water, the early fall time frame of this field study is considered to have been a worst-case scenario. The values shown for the pond water (table 6) depict a chemical composition of water that has experienced seven drought years of evaporation coupled with annual spring flushes. There was little variation in the pond's water quality during the time frame of this study. Table 6 lists the metals of concern (arsenic, nickel, aluminum, and iron) and several other parameters that illustrate that metal concentrations were significantly higher in the evaporation pond water than the adit water.

#### Treated Adit Water

Adit samples that met aquatic criteria all had treatment pH values in the 7 to 8 range, regardless of the slurry ratio. Aluminum concentrations started to exceed aquatic criteria (0.75 mg/L) at or above a pH of 8.5 due to resolubilization. It should be noted that this pH range of 7 to 8 was not obtained when using cement in the admixture (ratios 1:4:4 and 1:4:11). Manganese, although not an aquatic criteria parameter, reached its lowest concentration levels in approximately the same pH range (pH 8.5 and higher) in which aluminum resolubilizes. Sample S26 represents the best overall metal removal of the treated adit water, and is presented in table 8. The parameters for treated water sample S26 are compared to the raw water sample AA9, which was collected during the same treatment event, and the percent of metals removal for each parameter was determined. When compared to aquatic criteria, pH, acidity, and six elements were exceeded in the raw water. In the treated adit water, all of these parameters had acceptable values.

#### Treated Pond Water

Treated pond water that met or were borderline relative to aquatic criteria all had treatment pH values within the 6.3 to 8.6 range, regardless of the slurry ratio. Aluminum concentrations exceeded aquatic criteria at or above a pH of 8.2 due to resolubilization. However, water treated to a pH of 8.2 met the criteria. These data suggest that the highest treatment pH for an acceptable aluminum concentration in the pond water should be slightly less than 8.2 to avoid problems of Al resolubilization. Two samples suggest that the treatment pH for acceptable removal of metals can be as low as 6.3. With the exception that pH did not fall within the range of 6.5 to 9.0, all other parameters for these two samples met aquatic criteria, pH, acidity, and six elements were exceeded in the raw water. In the treated adit water, all of these parameters had acceptable values.



Table 3. Treated Adit Water Summary							
Raw Water		Treated Water					Sludge Analysis
		Date	#	Location	Ratio L:F:C	Field pH	
Date #	9/20 AA1-AA2	9/19	T0	Tank 1	1:0:0	6.8	
		9/20	T1	Tank 1	1:0:0	6.6	
		9/20	T2	Tank 1	1:0:0	6.4	
Date #	9/22 AA3-AA4	9/22	T3	Tank 1	1:0:0	6.5	
		9/22	T4	Tank 1	1:0:0	6.8	
		9/22	S1	ILS	1:0:0	6.7	
		9/22	S1A	ILS	1:0:0	6.6	
		9/22	S2	ILS	1:0:0	9.1	
Date #	9/23 AA5	9/23	T5	Tank 1	1:0:0	5.0	
		9/23	S3	ILS	1:0:0	5.8	
Date #	10/2 AA7	10/2	S19	ILS	1:0:0	9.5	□ ⊥
		10/2	S20	ILS	1:0:0	7.9	□ ⊙ ⊥
		10/2	S21	ILS	1:0:0	7.9	□ ★ ⊙ ⊥
Date #	10/2 AA8	10/2	S22	ILS	1:0:0	7.4	□ ⊙
		10/2	S23	ILS	1:0:0	8.7	□
		10/2	S24	ILS	1:0:0	7.0	□
Date #	10/2 AA9	10/2	S25	ILS	1:1:0	6.3	□ ⊥
		10/2	S26	ILS	1:1:0	7.7	□ ⊙ ⊥
		10/2	S27	ILS	1:1:0	6.4	□ ★ ⊙ ⊥
Date10/3 #AA10-AA11	10/3	S28	ILS	1:4:0	6.0	□ ⊥	
	10/3	S29	ILS	1:4:0	6.2	□ ⊥	
	10/3	S30	ILS	1:4:0	7.5	□ ★ ⊥	
	10/3	S31	ILS	1:4:4	6.5	□ ⊥	
	10/3	S32	ILS	1:4:4	6.1	□ ⊥	
	10/3	S33	ILS	1:4:4	8.5	□ ⊥	
	10/3	S34	ILS	1:4:11	6.4	□ ⊥	
	10/3	S35	ILS	1:4:11	9.1	□ ⊥	
	10/3	S36	ILS	1:4:11	6.7	□ ⊥	
*No static mixer, □ STLC, ★ TTLC, ⊙ TCLP, ⊥ Sludge settling & volume <i>Bold and italic - Best WO. Bold - Met WO Stds. Italic - Borderline WO</i>							

Table 4. Treated Pond Water Summary							
Raw Water		Treated Water					Sludge Analysis
		Date	#	Location	Ratio (L:F:C)	Field pH	
Date #	9/24 P1-P3	9/22	T9	Tank 1 Discharge	1:0:0	7.2	
		9/24	T6	Tank 1 Discharge	1:0:0	6.3	
		9/24	T7	Tank 1 Discharge	1:0:0	7.3	
		9/24	T8	Tank 1 Discharge	1:0:0	6.5	
Date #	9/25 P4	9/25	S4	ILS Discharge	1:0:0	7.3	⊙
Date #	9/27 P5	9/29	S5	ILS Discharge	1:0:0	9.1	□
Date #	9/30 P6-P7	9/30	S6	ILS Discharge	1:0:0	8.1	□★⊙⊥
		9/30	S7	ILS Discharge	2.5:1:0	7.2	□★⊙⊥
		9/30	S8	ILS Discharge	2.5:1:0	6.3	□⊥
		9/30	S9	ILS Discharge	2.5:1:0	4.4	□★⊙
Date #	10/1 P8	10/1	S10	ILS Discharge	1:1:0	9.3	□⊥
		10/1	S11	ILS Discharge	1:1:0	8.2	□⊥
		10/1	S12	ILS Discharge	1:1:0	8.6	□⊥
		10/1	S13	ILS Discharge	1:1:1	9.0	□★⊙⊥
		10/1	S14	ILS Discharge	1:1:1	9.8	□★⊙⊥
		10/1	S15	ILS Discharge	1:1:1	8.2	□★⊙⊥
Date	10/1	10/1	S16	ILS Discharge	1:1:3	9.3	□⊥
#	P9	10/1	S17	ILS Discharge	1:1:3	8.6	□⊥
		10/1	S18	ILS Discharge	1:1:3	7.8	□⊥
□ STLC      ★ TTLC      ⊙ TCLP      ⊥ Sludge settling & volume <i><b>Bold and italic - Best WQ</b></i> <i><b>Bold - Met WQ Stds</b></i> <i><b>Italic - Borderline WQ</b></i>							

Table 5. Comparison of Raw Water Metal Concentrations			
Parameter (mg/L)	Adit <sup>1</sup>	Pond <sup>1</sup>	Concentration Factor
As	14.3	49.9	3.5
Ni	6.0	25.7	4.3
Al	346	1540	4.5
Fe <sup>2+</sup>	863	135	(-6.4)
Fe <sub>tot</sub>	864	2449	2.8
Mn	8.9	43.2	4.8
Acidity	3589	14768	4.0
SO <sub>4</sub>	3899	15618	4.0
<sup>1</sup> Average metal concentrations.			

#### Adit Sludge

All parameters of the California STLC standards (table 5), except arsenic, were met by all of the adit sludge samples. Table 14 shows the arsenic values for the sludge samples. Samples S21 and S30 are considered to be borderline samples relative to the STLC standard.

TTLC sludge analysis was performed on three adit samples—two samples that correspond with treated water samples that met aquatic criteria (S21 and S30) and one that did not meet the criteria (S27). All TTLC sludge standards, except for arsenic, were met. This also held true for sample S27, which has a corresponding water sample that did not meet aquatic criteria. Generally, all reported concentrations are an order of magnitude or more below the established State TTLC standards, except for arsenic.

TCLP sludge analysis was performed on five evaporation pond water samples—three samples that

Table 6. Raw Pond Water Summary				
Parameter <sup>s</sup> (mg/L)	Average	Maximum	Minimum	Standard Deviation
Field pH	2.1	2.3	2.0	0.0016
pH	2.5	2.6	2.5	0.0003
Acidity	14768	15291	14430	341
Fe <sup>2+</sup>	135	201	89.7	37.6
Fe <sub>total</sub>	2449	2560	2367	55.8
Ca	490	510	470	11.8
Mg	203	211	197	4.26
Al	1540	1562	1509	16.9
Na	38.7	40.3	36.1	1.44
Mn	43.2	44.4	41.8	0.788
SO <sub>4</sub>	15618	16288	14941	403
K <sup>1</sup>	1.02	1.69	0.080	0.562
As	49.9	51.7	46.8	1.69
Ba	0.020	0.025	0.017	0.003
Be	0.060	0.070	0.050	0.005
Cd	0.290	0.320	0.220	0.039
Co	10.4	10.9	9.96	0.274
Cr	5.36	5.80	5.04	0.207
Cu	10.9	11.3	10.62	0.273
Ni	25.7	26.7	24.45	0.724
Pb	0.215	0.317	0.170	0.047
Sb <sup>2</sup>	0.165	0.165	0.165	ND
Se <sup>3</sup>	1.09	1.18	0.92	ND
Zn	4.80	7.01	4.29	0.792
<sup>1</sup> Seven out of nine samples measurable, all others below detection limit of 0.10 mg/L.				
<sup>2</sup> One out of nine samples measurable, all others below detection limit of 0.125 mg/L.				
<sup>3</sup> Three out of nine samples measurable, all other below				

Table 7 - Treated Adit Water					
Ratio (L:F:C)	SNo.	Lab pH	Field pH	Met WQ Criteria	Al (mg/l)
1:0:0	S3	4.60	5.80	no	
	T5	4.77	5.00	no	
	T3	5.58	6.55	no	
	S1	5.82	6.73	no	
	T1	5.94	6.57	no	
	S1A	6.12	6.59	no	
	T4	6.17	6.76	no	
	S24	6.22	7.0	no	
1:0:0	T2	6.80	6.42	no	
	S22	6.93	7.4	no	
	TO	7.09	6.80	no	
	S20	7.92	7.9	yes	
	S21	7.92	7.9	yes	
	S23	8.58	8.7	borderline	3.6
	S2	8.89	9.14	borderline	7.6
	S19	9.64	9.5	no	
1:1:0	S25	3.79	6.3	no	
	S27	3.79	6.4	no	
	S26	7.53	7.7	yes, best	
1:4:0	S28	3.67	6.0	no	
	S29	3.79	6.2	no	
	S30	7.54	7.5	yes, best	
1:4:4	S31	3.75	6.5	no	
	S32	3.84	6.1	no	
	S33	8.47	8.5	borderline	2.3
1:4:11	S34	3.71	6.4	no	
	S36	3.88	6.7	no	
	S35	8.84	9.1	borderline	5.1
<sup>1</sup> Borderline = exceeded aluminum standard only, 0.75					

Table 8 - Best-Case Adit Water				
Parameters	Raw	Sample S26	Aquatic	Percent
Field pH	2.9	7.7	6.5 - 9.0	NA
pH	2.6	7.5	6.5 - 9.0	NA
Acidity	3650	<10	NA	99.7
Alkalinity	0	67.7	NA	NA
Fe <sup>2+</sup>	887	0	NA	100
Fe <sub>total</sub>	887	0.14	NA	99.9
Ca	124	1458	NA	(-1075)
Mg	40.7	61.9	NA	(-67.4)
Al	353	0.21	0.75	99.9
Na	27.9	46.7	NA	(-167)
Mn	9.2	0.82	NA	91.1
SO <sub>4</sub>	4001	3657	NA	8.0
K	13.8	16.6	NA	(-20.2)
As	14.2	<0.021	0.36	>99.8**
Ba	0.02	0.194	NA	(-870)
Be	0.02	<0.005	NA	>75.0**
Cd	0.07	<0.001	0.019*	>98.6**
Co	2.42	0.022	NA	99.1
Cr	1.28	<0.015	5.404*	>98.8**
Cu	1.22	<0.002	0.065	>99.8**
Ni	6.07	0.063	4.582*	98.9
Pb	<0.125	<0.005	0.477*	***BDL
Sb	<0.125	<0.006	0.088	***BDL
Se	<0.5	<0.012	0.02	***BDL
Zn	1.07	<0.015	0.379*	>98.6**
<p>* Values based on a hardness of 400 mg/L as CaCO<sub>3</sub>, values proportional to hardness.</p> <p>** Values are approximate, numbers based on detection limits of analytical equipment.</p> <p>*** BDL - Below detection limit.</p>				

Table 9 - Best Case Pond Water				
Parameters (mg/L)	Raw Water P4	Sample S4 (1:0:0)	Aquatic Standards	Percent Metals Reduction
Field pH	2.3	7.2	6.5 - 9.0	NA
pH	2.6	7.9	6.5 - 9.0	NA
Acidity	15078	0	NA	100
Alkalinity	0	15.2	NA	NA
Fe <sup>2+</sup>	103	0	NA	100
Fe <sub>total</sub>	2431	0.10	NA	99.9
Ca	492	597	NA	(-20.7)
Mg	203	439	NA	(-116)
Al	1558	0.33	0.75	99.9
Na	40.0	46.0	NA	(-15)
Mn	4304	0.38	NA	99.9
SO <sub>4</sub>	15674	3217	NA	79.5
K	1.64	3.95	NA	(-140)
As	50.7	<0.025	0.36	99.9**
Ba	0.02	<0.015	NA	25**
Be	0.05	<0.005	NA	90.0**
Cd	0.32	<0.001	0.019*	99.7**
Co	10.5	<0.015	NA	99.9**
Cr	5.43	<0.015	5.404*	99.7**
Cu	11.3	<0.003	0.065	99.9**
Ni	26.0	<0.015	4.582*	99.9**
Pb	0.17	<0.005	0.477*	97.1**
Zn	4.62	<0.015	0.379*	99.7**
<p>* Values based on a hardness of 400 mg/L as CaCO<sub>3</sub>, values directly proportional to hardness.</p> <p>** Values are approximate, numbers are less than detection limits of analytical equipment.</p>				

Table 10. CA Wet Test - STLC Analysis - Pond Water Sludge		
SLURRY RATIOS	SAMPLE (pH) <sup>1</sup>	Arsenic <sup>2</sup> (mg/L)
1:0:0 (ILS DISCHARGE)	S6 (8.0)	5.7 <sup>3</sup>
2.5:1:0	S7 (7.2)	3.7
1:1:0	S11 (8.2)	8.7 <sup>3</sup>
<sup>1</sup> Field pH values. <sup>2</sup> Arsenic standard is 5.0 mg/L. <sup>3</sup> Sample is considered as borderline		

correspond with treated water samples that met the aquatic criteria (S21, S20, and S26) and two that did not meet the criteria (S22 and S27). All pond sludge samples, regardless of whether the corresponding water samples met aquatic criteria, were found to be nonhazardous according to EPA's TCLP.

#### Sludge Volume

Thirty-minute sludge settling tests were completed using 1,000-mL Imhoff cones. The following analysis will focus on only those sludge samples that correspond to the water samples that met the aquatic criteria. Several samples were monitored for periods longer than 30 min, and these data are also presented below.

The significantly (three to four times) higher metal concentrations associated with the pond water are reflected in significantly higher sludge volumes, as shown in table 13. Generally, the treated pond water produced approximately two to three times more sludge on a volumetric basis. The higher sulfate concentration and removal rate also contributes to this higher sludge volume.

Tables 13 and 14 show the 30-min sludge volume for the samples that correspond to the treated adit water samples that met the aquatic criteria. Sample S26 exhibited extended settling; after 1,020 minutes, the sludge volume was 170 mL. In 1,020 minutes, the volumes of samples S6 and S7 also decreased by one-third. Table 13 also provides the relevant slurry ratios and pH values.

The pond water with significantly higher metals and sulfate concentrations produced greater sludge volumes (in the 30-min settling test) than the adit water when both were treated with lime to meet aquatic criteria (figure 5). Sludge volumes that were generated with reagent mixtures were less than those generated with lime (see figures 5 and 6). Generally, sludge volume reductions were

Table 11 - STLC Analysis - Adit Water Sludge		
SLURRY RATIOS	SAMPLE (pH) <sup>1</sup>	Arsenic <sup>2</sup> (mg/L)
1:0:0 (ILS DISCHARGE)	S20 (7.9)	9.8
1:0:0 (ILS DISCHARGE)	S21 <sup>3</sup> (7.9)	6.5 <sup>4</sup>
1:0:0 (ILS DISCHARGE)	S22 (6.9)	10.0
1:1:0	S26 (7.5)	9.6
1:4:0	S30 <sup>3</sup> (7.5)	5.73 <sup>4</sup>
<sup>1</sup> Field pH values. <sup>2</sup> Arsenic standard is 5.0 mg/L. <sup>3</sup> Total threshold limit concentration (TTLC) determined. <sup>4</sup> Sample is considered as borderline.		

Table 12 -TTLC Analysis - Adit Water Sludge, mg/kg			
PARAMETER (Standard Concentration)	SLUDGE SAMPLE		
	S21 <sup>1</sup>	S27	S30 <sup>1</sup>
Ag (500)	ND	ND	ND
Al (NA)	42500	70600	67100
As (500)	1960	1590	975
Ba (10,000)	101	1110	59.9
Be (75)	<0.79	<0.65	<0.5
Bi (NA)	446	402	241
Ca (NA)	89300	87800	114000
Cd (100)	<2.8	<2.1	<1.9
Co (8,000)	344	268	131
Cr (2,500)	217	195	101
Cu (2,500)	190	184	90.9
Fe (NA)	93200	87300	46800
Hg (20)	ND	ND	ND
Mn (NA)	1310	888	757
Mo (3,500)	22.5	23.1	18.8
Na (NA)	6100	9460	8770
Ni (2,000)	837	661	334
P (NA)	425	2650	3480
Pb (1,000)	273	253	159
Se (100)	ND	ND	ND
Sr (NA)	119	578	928
Ti (NA)	167	1430	2160
Tl (700)	ND	ND	ND
V (2,400)	173	143	119
Zn (5,000)	250	105	<38
Fluorine (18,000)	ND	ND	ND
<sup>1</sup> Sample met aquatic criteria. ND = parameter not analyzed. NA = no standard applicable to parameter.			



Table 13 - Sludge Volume after 30 Min - Adit Water		
SLURRY RATIOS	SAMPLE (pH) <sup>1</sup>	VOLUME (mL)
1:0:0 (ILS DISCHARGE)	S20 (7.9)	260
1:0:0 (ILS DISCHARGE)	S21 (7.9)	375
1:0:0 (ILS DISCHARGE)	S22 (6.9)	350
1:1:0	S26 <sup>2</sup> (7.5)	240
1:4:0	S30 (7.5)	390
<sup>1</sup> Lab pH values. <sup>2</sup> Extended settling was observed		

Table 14. Sludge Volume After 30 Min - Pond Water		
SLURRY RATIOS	SAMPLE (pH) <sup>1</sup>	VOLUME (mL)
1:0:0 (ILS DISCHARGE)	S6 <sup>2</sup> (8.1)	910
2.5:1:0	S7 <sup>2</sup> (7.2)	910 <sup>2</sup>
1:1:0	S11 (8.2)	950
<sup>1</sup> Field pH values. <sup>2</sup> Extended settling was observed.		

minimal in the pond water sludge (approximately 10%). However, the volume of the adit water sludges was reduced by approximately 50% after 30 min of settling when an L/F/C reagent mixture was used (figure 6). Approximately 2 months after sludge sample collection, it was observed that several samples treated with L/F/C mixtures had hardened into a cementlike material. Apparently, further chemical reactions occurred within the sludge, resulting in hardening and further volume reductions. This is a research area that requires additional work.

### Conventional Sludge Dewatering

It is recognized that conventional sludge dewatering systems are available. However, the remote, powerless setting and limited access associated with the Leviathan Mine presents significant, expensive obstacles to overcome prior to the installation of conventional technology. Alternatively, a portable (conventional) system could be constructed for intermittent use at this site. Although the capital costs for conventional dewatering equipment are high, they are not prohibitive, especially in light of environmental compliance. There is, however, a major concern associated with the operation, maintenance, and continued effectiveness of conventional sludge dewatering equipment at this site due to the severe gypsum scaling observed in the pilot-scale study. It was demonstrated that the scaling problem can be reasonably managed with the ILS because of its lack of moving parts, simplicity, and polymer-based construction. It is questionable whether conventional sludge dewatering systems would be able to reasonably manage the scaling problem without a major increase in operation and maintenance costs.

## SUMMARY

### Water Treatment

The severely polluted Leviathan Mine drainage was successfully treated with lime and the ILS. The ILS was capable of treating both pond and adit water, so that water quality met EPA's national

ambient water quality criteria for protection of freshwater aquatic life. In the case of the pond water, the ILS simply served as a neutralization and mixing system. With regard to adit water, the ILS also served as an aeration system.

The optimal treatment pH range for adit water is between 7.5 and 8.0, and for pond water, 8.2. The use of lime-based admixtures had no apparent advantage relative to treated water quality for either the adit or pond. Water samples that met or approached aquatic criteria (tables 9 and 11) were generated by a variety of lime/fly ash admixtures, as well as simple lime slurry. The optimal pH ranges for either the adit or pond waters were not achieved when using lime/fly ash/cement mixtures; consequently, samples treated with these mixtures did not meet aquatic criteria.

The ILS effectively oxidized nearly 900 mg/L of  $\text{Fe}^{+2}$  after only 30 seconds of contact within the treatment system. Comparable Fe levels ( $<1$  mg/L) could be obtained with pH adjustments that differed by approximately 1 pH unit between the adit (pH 7.4) and pond (pH 6.3) waters. The different Fe species ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ), coupled with the aeration requirement associated with the treatment of  $\text{Fe}^{2+}$ , are believed to be responsible for this difference.

The percentage of sulfate removal resulting from treatment in the pond water was observed to be significantly higher (approximately 50% to 80%) than the treated adit water ( $<15\%$ ). However, the final concentrations of sulfates for both the pond and adit waters were essentially the same for those samples collected from the ILS discharge when a continuous alkaline slurry feed was used.

The highly corrosive water and heavy gypsum scaling were manageable with the ILS due to its lack of moving parts, simplicity, and polymer-based construction. The gypsum scaling problem at this site is considered to be significant and may prohibit the efficient, economical operation of more conventional treatment and sludge handling equipment.

Finally, the simplicity, portability, flexibility relative to flows, and low cost of the ILS make it a prime candidate for remote treatment operations such as the Leviathan Mine. The ILS can be operated by water power at sites with elevational differences of at least 50 ft. It appears that the need for permanent electrical power installation for water treatment could be eliminated by coupling the ILS with a commercially available water-powered lime feed system.

## Sludge

Fifty-three separate sludge analyses were completed. Except for arsenic, all sludge samples met, generally by at least an order of magnitude, all of California's STLC and TTLC standards. All 10 TCLP analyses found the sludges from both the pond and adit to be nonhazardous by EPA's definition. The 30-min sludge settling tests using lime and lime-based admixtures showed that significantly more sludge—approximately twice the volume—is generated from the treatment of the pond water. The greater sludge production is due to the higher concentrations of contaminants in the pond water. Lime-based admixtures were observed to further reduce sludge volumes in the 30-min settling test by approximately 10% and 50% in the pond and adit sludges, respectively. Also, 2 months after the tests were completed, several sludge samples were observed to harden. This observation has not been quantified and should be further investigated, as discussed below.

## RECOMMENDATIONS FOR FUTURE WORK

Additional sludge characterization data are essential to the development of a sound waste disposal plan. With water treatment capabilities apparently in hand, the key issue is the arsenic level in the sludge leachate and solids (California STLC and TTLC). The hazardous waste designation (by California standards, due to the high arsenic levels) of the generated sludge suggests that this waste material will require off-site transportation to an appropriate waste disposal facility. Thus, key issues that need to be further addressed are reducing sludge volumes and dewatering to minimize transportation costs. Coupled with the issue of sludge volume reduction is additional quantification of sludge characteristics, which includes chemical analysis, establishing the sludge settling rate, and longer-term sludge volume determinations (e.g., 48- or 72-hour settling tests). This information is needed to evaluate pond capacities and/or modifications that may be required for the installation of a treatment operation. This information can also be obtained in bench-scale tests. Also, x-ray diffraction analysis is recommended for sludge characterization. X-ray diffraction can identify mineralogical differences that may exist in the sludge relative to a particular lime-based admixture ratio (lime:fly ash:cement), and may provide insight into the hardening or dewatering process.

There are two alternatives to consider. The first is to continue with the approach described in this report using admixtures (e.g., lime, fly ash, and cement) during the neutralization process. The second is to modify the sludge after it has been generated by lime neutralization after liquid/solid separation of the lime sludge has been achieved. In actual field practice, the second path would entail using the same process described in this report, except that sludge would be pumped rather than mine water.

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## REFERENCES

Ackman, T. E. Sludge Disposal from Acid Mine Drainage Treatment. USBM RI 8672, 1982, 25 pp.

Ackman, T. E. and P. M. Erickson. In-Line Aeration and Neutralization (ILS)-Summary of Eight Field Tests. AIME/SME/TMS 115th Annual Meeting, New Orleans, LA, Mar. 2-6, 1986, 34 pp.

Ackman, T. E. and R. L. P. Kleinmann. In-Line Aeration and Treatment of Acid Mine Drainage. Paper in Proceedings, Symposium on Surface Mining, Hydrology, Sedimentology, and Reclamation (ed. by D. H. Graves). Univ. KY, Lexington, KY, Dec. 2-7, 1984, pp. 29-34.

Ackman, T. E. and R. L. P. Kleinmann. An In-Line System for Treatment of Mine Water. International Mine Waste Management, v. 1, No. 3, 1993, pp. 1-4.

Ackman, T.E. and J. M. Place. Acid Mine Water Aeration and Treatment System. U.S. Pat. No. 4,695,378, Sept. 22, 1987.

California Code of Regulations, Title 26, Division 22, Section 66261.24(a)(2)(A), Table II-List of Inorganic Persistent and Bioaccumulative Toxic Substances and Their Soluble Threshold Limit Concentration (STLC) and Total Threshold Limit Concentration Values (TTLC).

Federal Register. V. 57, No. 246, Rules and Regulations 6091, Dec. 22, 1992 (Freshwater Aquatic Life).

Greystone Environmental, Inc. Assessment - Leviathan Mine Site. Prepared for California Regional Water Quality Control Board, Lahontan Region, 1991.

Hustwit, C. C. Pipeline Treatment of a Copper-Zinc Waste Stream: A Pilot-Scale Evaluation. USBM RI, 9589, 1995, 19 pp.

The Use of Fly Ash and Portland Cement To Chemically Fix Metal Mine Drainage Treatment Sludges. Paper in Proceedings of the 50th Annual Purdue University Industrial Waste Conference, May 8-10, 1995, 57 pp.

Hustwit, C. C., T. E. Ackman, and P. M. Erickson. The Role of Oxygen Transfer in Acid Mine Drainage (AMD) Treatment. Water Envir. Res., v. 64, No. 6, 1992, pp. 817-823.

Taxer, E. J., J. J. Churchill, and R. S. Gill. A History of the Leviathan Mine Pollution Abatement Project, Alpine County, California. Prepared for California Regional Water Quality Control Board, Lahontan Region, 1991, 20 pp.

U.S. Code of Federal Regulations. Title 40—Protection of Environment; Chapter I—Environmental Protection Agency; Subchapter I—Solid Wastes; Part 261—Identification and Listing of Hazardous Waste; Appendix II—Method 1311 Toxicity Characteristic Leaching Procedure (TCLP); 1994.