PIPELINE TREATMENT OF A METAL MINE DRAINAGE CONTAINING COPPER AND ZINC[1]

Craig C. Hustwit[2] and Richard G. Sykes[3]

Abstract: A pipeline treatment system, previously used to treat coal mine drainage, was tested at pilot- and full-scale to determine its effectiveness in treating a copper-zinc bearing metal mine drainage in northern California. The 37.85 liters per minute (L/min) (10 gpm) system consisted of a jet pump and static mixer, arranged in series. Three alkaline reagents were each evaluated at four treatment pH values. An additional reagent mixture was evaluated at one treatment pH value. Initial copper, zinc, and cadmium concentrations were 100, 450, and 1.7 milligrams per liter (mg/L), respectively. Post-treatment concentrations for these metals were below detection limits for soluble metals using the inductively-coupled plasma spectroscopy (ICP) method, regardless of reagent used, when the treatment pH was in the 9.0 to 10.0 standard unit range. A full-scale version of the pipeline system was constructed and operated at 1,136 L/min (300 gpm) for approximately 5 months. Calcium hydroxide slurry was introduced at the jet pump to achieve a pH of 9.5 to 10.0 standard units. The system removed between 97% and 99% of copper, zinc, cadmium. Based on these studies, it was concluded that 1) pipeline treatment is a viable approach to metal mine drainage treatment, 2) establishing a treatment pH in the 9.0 to 10.0 standard unit range was critical for metals removal, and 3) treatment in the In-Line System (ILS) may involve coprecipitation mechanisms.

Additional Key Words: pyrite, acid mine drainage, heavy metals, treatment, ILS

Background

This study was undertaken as part of an effort led by East Bay Municipal Utility District (EBMUD) and the California Regional Water Quality Control Board (CRWQCB) to minimize the impacts of acidic drainage from the abandoned Penn Mine. EBMUD is a public utility that provides water and wastewater service to over 1 million people in Oakland, Berkeley, Alameda, and several other cities and communities east of the San Francisco Bay. The U. S. Bureau of Mines' (USBM) interests were in investigating metal mine drainage treatment options.

The purpose of this study was to evaluate the performance of an in-line treatment system (ILS) for treating metal mine drainage. While the chemical compositions of metal mine drainage vary, they are typified by elevated acidity and the presence of heavy metals and sulfates. They often constitute a threat to the environment if the water is not hydrologically isolated, diluted, and/or treated. The evaluation of ILS treatment is consistent with an EBMUD goal of protecting its water resources. Additionally, it is part of the USBM's ongoing effort to developing new technologies for protection and remediation of the environment.

The Penn Mine Site

This study was conducted at the Penn Mine in Calaveras County, CA. The site is located in a remote section of the western foothills of the Sierra Nevada mountains approximately 40 kilometers (km) east of Lodi, CA. Two watersheds converge on the site: Hinkley Run and Mine Run. The site is 79 meters (m) above mean

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[2] Craig C. Hustwit, Civil Enginner, U.S. Bureau of Mines, Pittsburgh Research Center, Pittsburgh, PA 15236.

[3] Richard G. Sykes, Senior Engineer, East Bay Municipal Utility District, Oakland, CA 94623-1055.

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sea level and lies approximately 152 m east of the Camanche Reservoir on the Mokelumne River (fig. 1).

The Penn Mine is one of several copper mines in this region. Chalcopyrite and sphalerite were discovered there in 1861 as adjacent land was being placer-mined for gold. Ore extraction of the copper began shortly thereafter, using the stope method. Mining continued intermittently until 1953, when the mine was finally closed. Remnants of various ore concentrator facilities are still present, including a copper cementation launder. The site is marred by numerous piles of waste rock, concentrator tailings, slag, and unprocessed ore. Many of these materials retain residual chemical reactivity (CRWQCB 1993).

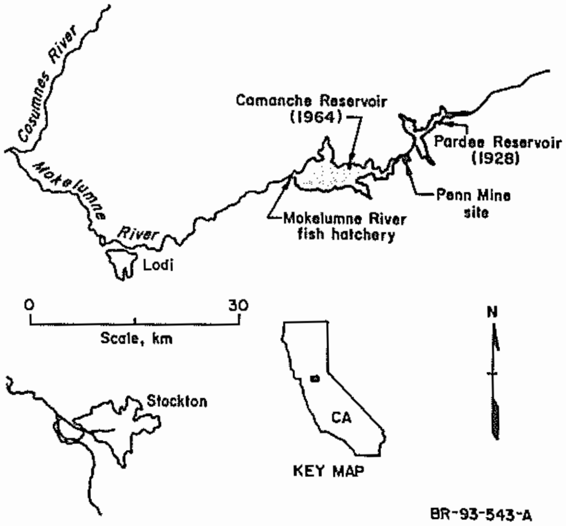


Figure 1. Area Map.

The historic and current reactivity of these materials has resulted in the production of classic metal mine drainage: acidified water with elevated concentration of soluble metals. Fish kills in the Molkumne River were first recorded in 1937 and occurred regularly following heavy rainstorms. During the 1960's, EBMUD constructed the Camanche Dam on the Molkumne River to increase their water storage capacity. The dam is located 12 kilometers downstream of the Penn Mine. A steelhead and salmon hatchery is located adjacent to the dam. In conjunction with this project, EBMUD purchased a narrow piece of the mine property that would be affected by the reservoir formation. After repeated administrative and legal efforts to force the owners of the Penn Mine to clean up the site and halt uncontrolled releases of mine drainage, the CRWQCB, EBMUD, and the California Department of Fish and Game embarked on a cooperative effort to install interim pollution control measures. In 1978, EBMUD constructed Mine Run Dam at the foot of the site and CRWQCB reconstructed six dams upstream on Mine and Hinkley Runs (fig. 2) These control measures eliminated the fish kills in the Camanche Reservoir and the Mokelumne River. However, during wetter than normal winters, the ponds' 67,849 cubic meters (m^3) (17,925,706 gal) capacity is exceeded, and controlled and uncontrolled releases have occurred. Evaporation is the principal method by which impounded water volumes are reduced each year.

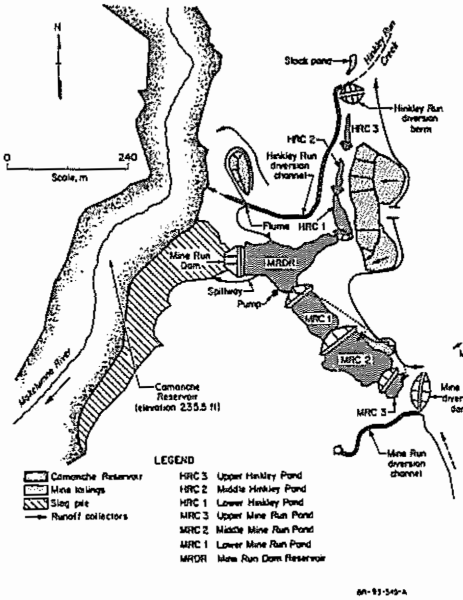


Figure 2. Site Map.

Mine Drainage Formation

The mineral pyrite, FeS_2, is the principal source of dissolved iron and acidity in the Penn Mine drainage. Pyrite is associated with the ore body and is subject to chemical weathering upon exposure to atmospheric oxygen and water. When this exposure occurs, pyrite releases soluble ferrous iron and sulfuric acid into the environment (Stumm and Morgan 1981). Pyrite's reaction with oxygen proceeds according to

$$FeS_{2(s)} + 7/2\ O_2 + H_2O \Rightarrow Fe^{2+} + 2S0_4^{-} + 2H^{+}.$$

Note that the iron released is initially in the reduced, ferrous form.

The presence of a naturally occurring, acidophilic bacteria, *Thiobacillus ferrooxidans*, is known to accelerate the chemical weathering of pyrite by oxidizing the ferrous iron to ferric iron, which in turn reacts with pyrite:

$$FeS_2 + 14Fe^{3+} + 8H_2O \Rightarrow 15\ Fe^{2+} + 2SO_4^{2-} + H^{+}.$$

Additional acidity is also generated as Fe^{3+} that fails to react with pyrite, hydrolyzes, and forms ferric hydroxide.

Once an acidic environment is created, other less soluble sulfide minerals are chemically weathered, resulting in additional metals being mobilized. In the Penn Mine drainage, the metals of most environmental concern are copper, zinc, and cadmium.

Mine Drainage Treatment

The most common method of treating acidic mine drainage is the chemical precipitation process. In this process, an alkaline reagent, i.e., hydrated lime ($Ca(OH)_2$), quick lime (CaO), or caustic soda ($NaOH$), is added and mixed with the mine drainage. The added alkalinity removes free, excess acidity from the process stream and raises the ambient solution pH. Each metal precipitate has a pH at which its solubility is minimized. By adjusting the solution pH into the range of a metal's minimum solubility, the metal is substantially removed from solution through a hydrolysis precipitation process. However, the minimum solubility pH's for the metals are not concurrent. Since mine drainage typically contains multiple metals, the solution pH must be carefully selected. This is normally determined through bench-scale tests where the drainage is adjusted to different pH levels and the metal concentrations are evaluated.

Coprecipitation is a secondary metal removal mechanism that can occur during treatment. In coprecipitation, precipitation seeds (metal hydroxide particles, called floc) form and adsorb additional metals out of solution through a heterogeneous reaction.

Precipitation of metals in a conventional treatment system would normally take place in a basin or pond. While in the basin, the alkaline reagent would be added and mechanical mixers would provide sufficient agitation to thoroughly distribute the reagent and maintain the metal floc in suspension.

Following the precipitation of the metals, the metal floc must be separated from the water. A gravity separation method is normally employed for solid/liquid separation. In gravity separation the water-metal floc stream is directed to a quiescent pond or clarifier. Chemical additives, typically polyelectrolytic polymers, are sometimes added prior to solid/liquid separation to accelerate the settling rate. When the floc has separated, the clarified water can be drawn off. The metal floc, called sludge, from this process is a voluminous by-product with unstable chemical and physical properties. At present, the disposition of sludge is one of the most expensive components in metal mine drainage treatment. Although this study does not address sludge disposal issues a subsequent study is being conducted on a new method for chemically and physically stabilizing the Penn Mine metal sludge.

As an alternative to conventional mine drainage treatment systems that employ basins or ponds, the USBM invented the ILS. The ILS consists of two off-the-shelf components: a jet pump or eductor, and a static mixer. These are arranged in series in a pipeline carrying mine drainage. The drainage is pumped or gravity fed through the ILS at upstream pressures between 14,062 kilograms per square meter (kg/m^2) (20 psi) and

42,186 kg/m^2 (60 psi). An alkaline reagent is pulled in by the suction port of the jet pump and mixed with the drainage downstream in the static mixer. Atmospheric air is also introduced in the jet pump. The air bubbles assist in the mixing action and provide oxygen for the oxidation of any reduced metals present. The ILS replaces the basin-mixer unit where the chemical precipitation step occurs in conventional treatment systems.

Originally, the ILS was designed to treat coal mine drainage that contained acidity and dissolved metals (Ackman and Erickson 1986). The dissolved metals most common in coal mine drainage are iron, manganese, and sometimes aluminum. Currently, the ILS is being used at approximately 20 coal mines in the United States.

Methods

Pilot-scale Study

Treatment Plant Description. A 2.54 cm (1 inch) PVC jet pump was arranged in series with an 20 cm (8 inch) x 1.22 m (4 foot) (diameter x length) static mixer. The static mixer was constructed of polyethylene pipe and packed with 2.54 cm (1 inch) trickling media. Sampling ports were provided immediately upstream of the jet pump and immediately downstream of the static mixer discharge. Pressure gauges were installed upstream and downstream of the jet pump. A chemical feed unit was used to deliver the alkaline reagents into the suction port of the jet pump. The feed unit consisted of a 208 L (55 gal) barrel equipped with a portable mixer and a metering pump with flow control. Water from MRC3 was used in the study to prepare the alkaline slurries. Figure 3 is a schematic of the ILS pilot system.

The pilot unit was positioned on the dam that forms MRC3. Drainage from MRC3 was pumped through the ILS with a gasoline-powered centrifugal pump and then discharged into MRC2. The pump was equipped with a foot valve and strainer and provided a nominal 28,124 kg/m^2 (40 psi) at the gauge upstream of the ILS. The flow rate of the drainage through the system was approximately .63 liters per second (L/s) (10 gpm).

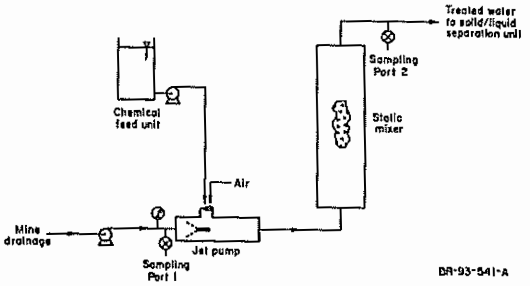


Figure 3. Schematic of the pilot-scale ILS.

Test Description. The study consisted of batch treatments of mine drainage using four alkaline reagents: hydrated lime, quick lime, caustic soda, and a mixture of hydrated lime and Type C fly ash. Slurries were prepared from the dry reagents and a dilute solution prepared from 50% caustic soda. Each reagent, with the exception of the hydrated lime/fly ash mix, was then evaluated at four effluent pH's: 7, 8, 9, and 10 standard units. A complete pH spectrum with the hydrated lime/fly ash was not possible due to an insufficient supply of the fly ash. With this exception, each reagent was evaluated at all treatment pH's before proceeding to the next reagent. After the desired effluent pH was established, three sample pairs were taken at the ILS discharge. All sample bottles were filled to the brim and tightly capped. The samples were then placed in an ice chest and delivered to the analytical laboratory. Each sample pair consisted of an acidified and unacidified sample. Acidified samples were filtered through a 0.45 micron filter prior to acidification. A similar sampling protocol was used on the inlet side of the ILS to establish the pretreatment water quality conditions.

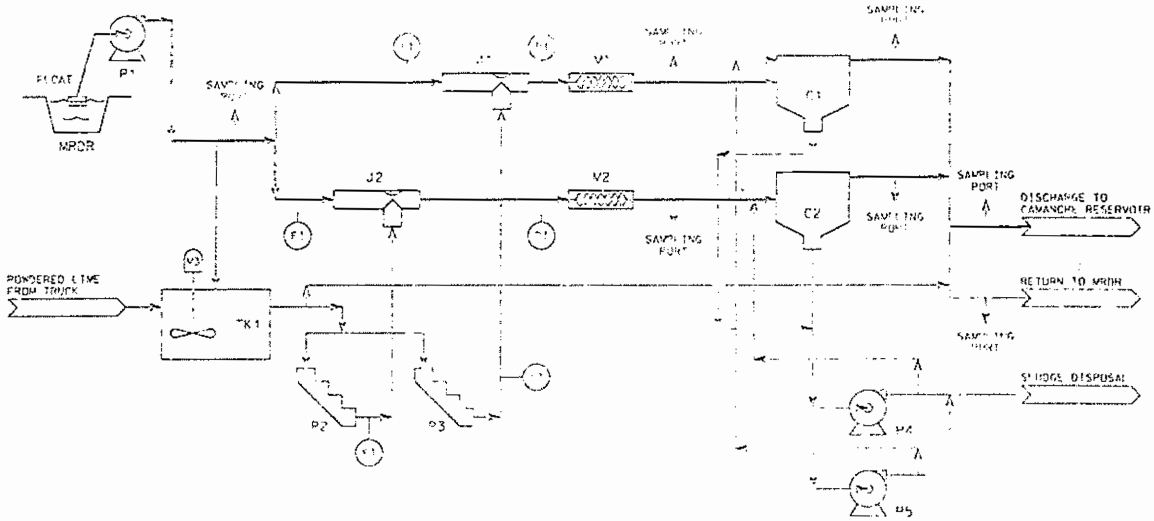
The acidified samples were analyzed for dissolved metals by inductively-coupled plasma (ICP) spectroscopy (American Public Health Association et al 1985). Determinations of acidity/alkalinity and pH were performed on the unacidified samples using Standard Methods 402 and 403 respectively.

Full-scale Study

In early February 1993, it appeared that the capacity of the Penn Mine storage ponds would soon be exceeded for the first time since May 1986. This was due to high rainfall levels during the winter months. In response to a potential overflow of acid mine drainage from the site, EBMUD wrote to the U. S. Environmental Protection Agency (EPA), Region IX, suggesting several measures to prevent or mitigate the impacts of a release. One of the measures was installation of an ILS treatment plant.

On February 11, 1993, EPA directed EBMUD to begin construction of an ILS plant. EPA set a treatment goal for the plant of 98% removal for heavy metals (measured as total metals for Al, Cd, Cu, Fe, Ni, Pb, and Zn). Using the data collected from the June 1992 pilot study, EBMUD designed a full-scale ILS plant. The plant was completed within 8 weeks and went into operation on April 13, 1993.

Treatment Plant Description. Figure 4 is a process flow diagram and a list of the major equipment used in the ILS plant. Mine drainage from Mine Run Dam Reservoir (MRDR) was pumped into two parallel treatment units. Each 9.46 L/s (150 gpm) capacity unit consisted of a 7.62 cm (3 inch) diameter jet pump, 7.62 cm (3 inch) diameter static mixer, and 79,500 L (21,000 gal) settling basin. The two clarifier overflow streams were recombined in a common outfall which discharged to Camanche Reservoir via the MRDR spillway. Two 3.16 L/s (50 gpm) sludge pumps drained the clarifiers. Sludge was disposed of in an arm of the MRDR upstream of a sediment curtain.



TK1	J1, J2	M1, M2	M3	C1, C2
Lime Mix Tank 24,600 L	Jet Pumps 7.62 cm 9.46 L s⁻¹ 3.52 kg cm⁻²	Static Mixer 7.62 cm x 55.9 cm	Mechanical Mixer	Clarification Tanks 79,500L

Figure 4. Schematic of the full-scale ILS.

Hydrated lime was selected as the pH adjustment reagent because it was the safest and easiest to use of the three reagents that were successful at the pilot plant level. The lime feed system consisted of a 24,600 L (6,500 gal) slurry tank and two chemical metering pumps. Lime slurry was injected into the jet pumps at a manually controlled rate to achieve a pH of between 9.5 and 10.0 units immediately following the static mixers. This range was originally selected based on the pilot studies and was reconfirmed as full-scale plant data became available.

Plant Operation. The ILS treatment plant was operated on 54 days between April 13 and September 17, 1993. For approximately half of these days, the plant discharged treated mine drainage to Camanche Reservoir. On the other days, the system was operated in a testing mode and treated water was returned to MRDR. In April, May, and June, EBMUD determined optimum system control parameters for metals removal and devised solutions to lime feed and scale formation problems. The system was shut down during July so that several minor modifications could be constructed. Plant operations resumed in August and continued through the third week of September.

Results

Pilot-scale Study

Untreated mine drainage from MRC3 had a pH of 2.6 standard units and an acidity of 4,100 mg/L as $CaCO_3$. Copper, zinc, and cadmium concentrations in MRC3 were 100, 450, and 1.7 mg/L, respectively. Table 1 shows the quality of untreated drainage from MRC3.

Table 1. Water quality from the pilot-scale study.

Conc.:[1]	Mine Drainage Quality	at pH = 7.0			at pH = 8.0			at pH = 9.0			at pH = 10.0			
Reagent:		Hydrated Lime	Quick Lime	Caustic Soda	Hydrated Lime	Quick Lime	Caustic Soda	Hydrated Lime	Quick Lime	Caustic Soda	Hydrated Lime	Quick Lime	Caustic Soda	Hydrated Lime/Fly Ash
pH, field, std. units[2]	2.6	7.0	7.0	7.0	8.0	8.0	8.0	9.0	9.0	9.0	10.0	10.0	10.0	10.0
pH, laboratory, std. units	2.6	5.0	3.3	4.0	6.1	3.9	NA[3]	3.4	4.5	9.1	3.1	5.4	9.8	9.8
Copper	100	<.002	<.002	<.002	<.002	<.002	<.002	<.002	<.002	.010	<.002	<.002	.006	<.002
Zinc	450	.590	.011	1.6	.061	.009	<.008	<.008	<.008	.010	<.008	<.008	<.008	1
Cadmium	1.7	.028	<.008	.110	<.008	<.008	<.008	<.008	<.008	<.008	<.008	<.008	<.008	<.008
Sulfate	8,600	2,900	2,400	7,300	2,800	2,400	7,100	2,100	1,700	1,500	1,500	1,500	7,100	1,800
Acidity, as $CaCO_3$	4,400	35	54	63	32	88	49	100	66	98	130	43	0	0
Alkalinity, as $CaCO_3$	0	4.8	0	0	10	0	0	0	0	110	0	0	91	29
Conductivity, umho cm^{-1}	8,400	3,540	3,180	9,410	3,390	3,150	9,880	2,950	2,400	NA	2,560	2,270	NA	2,530

[1] All units in mg/L unless noted. Metals data are for the dissolved fraction.

[2] +/- 0.2 standard units.

[3] NA indicates data is not available.

The pilot study indicated that, in general, the higher the treatment pH (up to 10 standard units) in the ILS, the greater the removal efficiency for metals. Metal concentrations in the ILS effluent were lower than would be expected based on the theoretical solubilities of metal hydroxides. This suggested that coprecipitation was occurring during treatment, although there was no direct confirmation of this. Additionally, there was no evaluation made of other metal removal mechanisms, such as insoluble carbonate formation. Table 1 also presents the post-treatment water quality results. Hydrated lime, quick lime, and caustic soda appeared to be suitable reagents for metals removal.

Cadmium removal clearly increased with increased treatment pH. At pH 7, cadmium removal ranged from 94% to 98%. Cadmium concentrations decreased to the ICP detection limit for all reagents at a pH of 8 or greater. At the ICP detection limits of .008 mg/L, the cadmium removal would be 99%. The minimum solubility of cadmium hydroxide ($Cd(OH)_2$) occurs at a pH of approximately 10.5. The significant reduction in cadmium at lower pH values may be attributable to coprecipitation or other unidentified removal mechanisms.

Virtually complete removal (>99.99%) of soluble copper was achieved for hydrated lime, quick lime, and caustic soda at all four pH ranges tested. The post-treatment copper concentration was two orders of magnitude less than the theoretical solubility of copper hydroxide for the hydrated lime, quick lime, and caustic soda reagents at pH 7. Coprecipitation is postulated as the explanation for this increased level of copper removal. Theoretical solubility and actual concentrations were not significantly different at the higher pH values.

Successful zinc removal (>99%) occurred at all four pH ranges tested for the lime and caustic soda treatments. Hydrated lime with fly ash achieved a 99.8% removal at a treatment pH of 10.0. In many cases of successful zinc removal, the actual concentrations of zinc were below the theoretical minimum concentration for the respective pH. Coprecipitation, again, is the suspected mechanism for the enhanced level of zinc removal.

Full-scale Study

Table 2 presents the ILS influent and effluent water quality data for cadmium, copper, and zinc. The data indicate the three distinct periods of system operation.

Table 2. Water quality from the full-scale study.

Period of Operation	1st			2nd			3rd		
Conc.:[1]	In	Out	% Removal	In	Out	% Removal	In	Out	% Removal
Copper, avg.	4.94	.612	87.6	15.3	.284	98.1	28	.129	99.5
Copper, min.	3.8	.52	86.3	7.4	.09	98.8	22	.02	99.9
Copper, max.	5.7	.69	87.9	20	1.2	94.0	30	.29	99.0
Zinc, avg.	27.6	7.04	74.5	72	3.03	95.8	156	1.48	99.1
Zinc, min.	23	5.9	74.4	35	.88	97.5	140	.17	99.9
Zinc, max.	31	9.1	70.7	100	16	84.0	170	2.9	98.3
Cadmium, avg.	.12	.064	46.7	.30	.026	91.3	.64	.012	98.1
Cadmium, min.	.1	.049	51.0	.15	.006	96.0	.56	.006	98.9
Cadmium, max.	.13	.085	34.6	.43	.11	74.4	.72	.019	97.4

[1] All concentration units in mg/L. Metals data are for the dissolved fraction.

First Operational Period. The first period, from April 14 to April 21, was the initial start-up period when the plant was operated to achieve an effluent pH of between 7.5 and 8.5 units. As predicted from the ILS pilot-scale study, metal removal during this period was limited, ranging from approximately 86% to 88% for copper, 71% to 74% for zinc, and 35% to 51% for cadmium.

Second Operational Period. During the second period of operation, from April 28 to June 24, the system was operated to achieve an effluent pH of between 9.5 and 10 units. The increased pH resulted in substantially improved metals removal. Copper removal averaged 98.1% with a range from 94.0% to 98.8%. Zinc removal averaged 95.8% with a range from 84.0% to 97.5%. Average removal of cadmium was 91.3% and ranged from 74.4% to 96.0%.

Third Operational Period. The third period of operation occurred from August 13 through September 17 and followed the completion of several plant modifications performed in July. The plant was operated to achieve a pH of between 9.5 and 10.0 units. During this operation period, the ILS effluent consistently met the EPA goal of 98% metals removal. Copper removal ranged from 99.0% to 99.9% with an average of 99.5% being removed from solution. The average reduction in zinc concentration was 99.1% with a range from 98.3% to 99.9%. The average cadmium reduction was 98.1% with a range from 97.4% to 98.9%.

Table 2 also shows that influent to the ILS plant was becoming more concentrated through the spring and summer owing to evaporation. This had no observable negative impact on ILS plant effluent quality; conversely, ILS effluent quality improved as the summer progressed.

Conclusions

Pilot-scale study of the ILS indicated that it was appropriate for treating metal mine drainage at the Penn Mine. Additionally, the pilot study permitted the selection of an optimum treatment pH and several acceptable reagents for pH adjustment. In many instances, metals removal in the pilot study was below theoretical solubility for metal hydroxides. This may have been the result of coprecipitation within the ILS.

Pilot study results were successfully used as a basis of design and operation of a full-scale ILS treatment plant. The ILS plant was designed, installed, and put in operation in a remote site within approximately 8 weeks. After approximately 30 days of operation, the full-scale plant was achieving the goal of removing 98% of influent heavy metals while a treatment pH range of 9.5 to 10.0 was maintained.

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