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Pipeline Treatment of a Copper-Zinc Waste Stream: A Pilot-Scale Evaluation

UNITED STATES DEPARTMENT OF THE INTERIOR

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Pipeline Treatment of a Copper-Zinc Waste Stream: A Pilot-Scale Evaluation

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UNITED STATES DEPARTMENT OF THE INTERIOR
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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Metric Units

cm	centimeter	L/s	liter per second
kg/m^2	kilogram per square meter	m	meter
km	kilometer	mg/L	milligram per liter
km^2	square kilometer	min	minute
L	liter	m/s	meter per second
L/day	liter per day	mol/L	mole per liter
L/mol	liter per mole	μm	micrometer
L^2/mol^2	square liter per square mole	$\mu mho/cm^2$	micromho per square centimeter

U.S. Customary Units

ft	foot	MMgal	million gallon
fps	foot per second	pct	percent
gal	gallon	psi	pound per square inch
gpm	gallon per minute	s	second
in	inch		

PIPELINE TREATMENT OF A COPPER-ZINC WASTE STREAM: A PILOT-SCALE EVALUATION

By Craig C. Hustwit[1]

ABSTRACT

A pilot-scale treatment study was conducted on a copper-zinc bearing metal mine drainage using a pipeline treatment system called the In-Line System (ILS). The objective of this U.S. Bureau of Mines study was to determine whether the ILS could be extended from the treatment of coal mine drainages to the treatment of metal mine drainages. Hydrated lime ($Ca(OH)_2$), quick lime (CaO), and caustic soda ($NaOH$) were used to neutralize the drainage. A novel reagent slurry of $Ca(OH)_2$ and type C fly ash was also evaluated. Except for $Ca(OH)_2$-fly ash slurry, treatment performance was evaluated for all reagents at pH values of 7, 8, 9, and 10. The $Ca(OH)_2$-fly ash slurry was evaluated at a pH of 10. All reagents tested neutralized the metal mine drainage and substantially reduced the dissolved metal concentrations. It was concluded that the ILS could be useful in the treatment of metal mine drainages.

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INTRODUCTION

Metal ore mining frequently results in the formation of acidic drainages containing elevated concentrations of dissolved metals. The suite of contaminants in a metal mine drainage (MMD) is specific to the site geology; however, metal mines of the same type often have drainages with similar metal constituents. The maximum allowable metal concentrations in discharges from a minesite are established under Federal and State regulations. The regulations also require acidic waters to be neutralized. These requirements are customarily achieved by chemical neutralization. This treatment process consists of the addition of an alkaline reagent to neutralize acidity and precipitate metals, usually as metal hydroxides or oxides. Aeration is included in the process when ferrous iron is present. Conventional structures and equipment used include concrete, steel, or earthen basins and mechanical mixers and aerators. The basins, mixers, and aerators are expensive to purchase, install, and operate. Capital costs for a typical MMD treatment system installation can be about $1 million. Annual operating costs can range between $0.5 million and $1.5 million.

Coal mine drainage (CMD) is similar to MMD in that it is also often acidic and contains dissolved metals. CMD, however, usually contains lower concentrations of the more toxic dissolved metals. The treatment of CMD, therefore, uses the same treatment process, structures and equipment, and alkaline reagents that are used in MMD treatment. Consequently, the costs of CMD treatment systems are similar to that of MMD treatment systems, though disposal of the solid waste is simpler for CMD. System capacity, usually expressed as flow rate, is the principal capital cost variable with each type of treatment system.

In 1985, the U.S. Bureau of Mines (USBM) developed a treatment system called the In-Line System (ILS) to reduce the high capital costs associated with CMD treatment. The ILS replaces the basins, mechanical mixers, and aerators normally used in the chemical neutralization process with a jet pump and static mixer. Jet pumps and static mixers are off-the-shelf components and are significantly less expensive to purchase and install than the conventional treatment equipment.

In field studies, the performance of the ILS was evaluated at eight coal minesites *(1)*.[2] At each site, the ILS was successful in reducing metal concentrations and in neutralizing a split of the CMD. Additionally, the ILS consistently required less alkaline reagent to treat the CMD than the basin systems used at the testsites. Up to 30 pct reductions in reagent requirements were realized with the ILS. This is significant since reagent costs are the principal component of annual operating costs in mine drainage treatment.

The purpose of this study was to determine if the application of the ILS could be extended from CMD treatment to MMD treatment. The similar chemical character of CMD and MMD and the shared treatment process and alkaline reagents used suggested that ILS treatment of MMD should be possible. The study consisted of a series of pilot-scale treatments of an MMD from a copper and zinc mine. The principal metals at high concentrations in the untreated MMD were copper, zinc, iron, manganese, aluminum, and cadmium. The initial pH was 2.6. Three neutralizing reagents were evaluated at four treatment pH values. A fourth neutralizing reagent was evaluated at one treatment pH. Success in treating the MMD was judged by comparing the chemical properties of the treated water from each treatment to the standards cited in the Code of Federal Regulations, Chapter 40 Protection of the Environment: (1) Effluent Guideline and Standards; Ore Mining and Dressing Point Source Category; Copper, Lead, Zinc, Gold, Silver, and Molybdenum Ores Subcategory (40 CFR 440.102a); and (2) National Primary Drinking Water Regulations (NPDWR). No Federal or State permit existed at the study site when this study was conducted. Therefore, the data developed in this study had no bearing on permit compliance.

This study is part of the continuing mission of the USBM to develop more efficient and less expensive technologies for the remediation of liquid and solid wastes associated with the mining and mineral processing industries.

STUDY SITE

This study was conducted at the Penn Mine, Calaveras County, CA (figure 1). The Penn Mine is an abandoned underground copper and zinc mine and occupies about 0.57 km^2 (140 acres) (figure 2). Since mine closure in 1953, seven surface impoundments were constructed to collect MMD. Seasonally, between 15.6 million L (4.2 MMgal) and 34.4 million L (20 MMgal) of MMD are contained in the pond system. The semiarid climate results in substantial evaporation of MMD each year. In rainy years, however, the capacity of the ponds has been exceeded and uncontrolled spills of MMD have occurred.

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[2] Italic numbers in parentheses refer to items in the list of references at the end of this report.

The receiving stream is the Mokelumne River. The Mokelumne is a pristine river that provides drinking water for Oakland, CA, and serves as a trout and salmon fishery. Periodic MMD spills from the Penn Mine have caused fish kills in the Mokelumne River that date back to the turn of the century *(2)*.

The ILS was constructed on the dam that forms the impoundment designated Mine Run Creek (MRC 3) (figure 3). Water was pumped from MRC 3, through the ILS, and then discharged into impoundment Mine Run Creek (MRC 2). All dams and impoundments on the Mine Run Creek watershed were constructed using on-site materials, including a high percentage of reactive waste rock. There are two known sources of the water in MRC 3: surface runoff from adjacent disturbed areas and water pumped from the Mine Run Dam Reservoir on a periodic basis. Ground water recharge may also be occurring from the Mine Run Creek paleochannel underlying the ponds Mine Run Creek (MRC 1), MRC2, and MRC3 *(3)*.

MATERIALS AND METHODS

MATERIALS

Hydrated lime. Calcium hydroxide ($CaCO_3$), pulverized, American Society for Testing and Materials (ASTM) C911.

Quick lime. Calcium oxide (CaO), granular, ASTM C911.

Caustic soda. Sodium hydroxide (NaOH), 25% solution by volume.

Fly ash. Type C. ASTM C593.

Slurry water-dilution water. Untreated MMD from impoundment MRC3. Appendix A.

Process stream. Untreated MMD from impoundment MRC3. Appendix A.

METHODS

A 2.54-cm (1-in) polyvinyl chloride (PVC) jet pump was arranged in series with a 20-cm (8-in) static mixer that was 1.22 m (4 ft) long (figure 4). The suction port on the jet pump was open to the atmosphere. The polyethylene static mixer was packed with 2.54-cm (1-in) plastic trickling media. Sampling ports were located 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 delivered the alkaline reagents to the suction port of the jet pump. The feed unit consisted of a 208-L (55-gal) mixing tank equipped with a mixer and metering pump. A portable gasoline-powered generator provided electricity for the mixer and metering pump. Water from MRC3 was used to prepare the reagent slurries and solutions.

Drainage from MRC3 was pumped through the ILS with a gasoline-powered centrifugal pump. The pump pressure was 28,124 kg/m^2 (40 psi) at the entry to the ILS. The drainage flow rate was approximately 0.63 L/s (10 gpm). Treated drainage exiting the ILS was at atmospheric pressure and was directed by open channel flow into MRC2. No solid-liquid separation unit was included in the installation.

The study consisted of batch treatments of mine drainage using slurries made from (1) $Ca(OH)_2$, (2) CaO, and (3) $Ca(OH)_2$ with type C fly ash, and (4) NaOH solution. Slurries were prepared from the dry reagents and a dilute solution was prepared from the 25 pct stock NaOH. Each reagent, except for $Ca(OH)_2$-fly ash, was then evaluated at four treatment pH values: 7, 8, 9, and 10. Treatment pH values were measured at sampling port 2. Multiple treatment pH values with the $Ca(OH)_2$-fly ash were not possible because of an insufficient supply of fly ash. Each reagent, with this exception, was evaluated at all treatment pH values before proceeding to the next reagent. This was done by preparing a stock slurry or solution that was stoichiometrically calculated to provide a treatment pH of 6 at the lowest metering pump flow rate setting. The reagent stocks were formulated based on a treatment pH of 6 to ensure that the required pumping rate to establish a treatment pH of 7 did not fall outside the flow rate range of the metering pump.

For each batch treatment, the supply pump for the ILS and the metering pump for the chemical feed system were turned on. The metering pump flow controller was set to the lowest setting. After 2 min, the pH was measured at sampling port 2. Residence time in the ILS was approximately 35 s. If the treatment pH was not within plus or minus 0.2 standard units of the target pH, the flow controller of the metering pump was adjusted, and the procedure repeated. After the treatment, pH was established and maintained for a minimum of 1 min; three sample pairs were drawn at the ILS discharge. The solids in each sample bottle were permitted to settle, and the supernatants were filtered using 0.45 μm syringe filters. One sample from each pair was acidified with concentrated hydrochloric acid. All samples were placed on ice and delivered at the end of each day to the analytical laboratory. 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 metals by inductively-coupled plasma (ICP), spectroscopy *(4)*. The unacidified samples were analyzed for either acidity, alkalinity, or both *(5)*.

RESULTS

Samples of the untreated MMD were taken each day for a period of 3 days. During that period, the MMD had a minimum pH value of 2.6 and a maximum pH value of 2.7. The mean acidity was 4,141 mg/L as $CaCO_3$ with a standard deviation of plus or minus 42.4 mg/L as $CaCO_3$. Conductivity of the MMD had a mean of 6,855 μmho/cm_2 with a standard deviation of 96.6 μmho/cm_2. Figure 5 lists the mean concentrations of 5 metals of interest in the MMD. Metal concentrations reported here are for dissolved metals. In some cases, dissolved metals may be less than total metals. While dissolved metal concentrations cannot be used to evaluate regulatory compliance, they are legitimate for use in evaluating treatment performance for scientific purposes. In high ionic strength solutions, the activity coefficients for each metal will be significantly less than unity. The untreated MMD exceeded the maximum allowable discharge concentrations of 40 CFR 440.102a and/or the NPDWR for Cd, Cr, Cu, Pb, and Zn. No determination of total suspended solids (TSS) was made. Appendix A lists the mean concentrations with their standard deviations, and the maximum and minimum values of all chemical constituents of the MMD.

The concentration of Cu in the treated waters ranged from below the ICP detection limit of 0.002 to 0.010 mg/L (figure 6). Zinc concentrations ranged from below the ICP detection limit of 0.008 mg/L to a high of 1.57 mg/L (figure 7). All treatments resulted in Pb concentrations that were below the ICP detection limit of 0.04 mg/L (figure 8). The concentration of Cd had a maximum value of 0.108 mg/L and a minimum value of less than 0.008 mg/L (figure 9). All treatments, except one, reduced Cr to below the ICP detection limit of 0.005 mg/L (figure 10). The concentration of Cr in the test that did not fall beneath the analytical threshold was 0.047 mg/L. Manganese concentrations ranged from below 0.005 to 20.6 mg/L (figure 11). Iron concentrations were all below 0.02 mg/L (figure 12). Aluminum concentrations ranged from a minimum value of less than 0.02 mg/L to a maximum value of 5.29 mg/L (figure 13). Appendixes B through E present the concentrations of all chemical constituents in the treated waters arranged by treatment pH group.

DISCUSSION

The chemical neutralization treatment process consists of three reactions: (1) oxidation, (2) neutralization, and (3) hydrolysis. The external reactants necessary to support these reactions are atmospheric O_2 or a chemical oxidizing agent and an alkaline reagent to provide hydroxide. The oxidation reaction is only needed when there is Fe^{2+} in the drainage.

Many dissolved metals can be precipitated as hydroxides or oxides. The hydrolysis reaction responsible for this is usually pH-dependent (figure 14). The equilibrium concentrations for bivalent and trivalent metal ions in multiphase hydroxide and oxide systems are expressed in equations 1 and 2, respectively.

$$K_{eq} = \frac{[Me^{2+}]}{[H^+]^2} \text{ L/mol,} \qquad (1)$$

$$K_{eq} = \frac{[Me^{3+}]}{[H^+]^3} \text{ L}^2/\text{mol}^2. \qquad (2)$$

The equilibrium concentration of a dissolved metal at a specified pH can be predicted by equation 3.

$$\log [Me^{z+}] = \log K_{eq} - (z \times pH) \qquad (3)$$

where z is the charge of the metal cation.

Coprecipitation is a phenomenon known to occur to varying extents during MMD treatment. It is a physicochemical process in which soluble metal cations form weak electrochemical bonds with solid particles *(6-7)*. These solids may have a net electrochemical neutrality or may be charged. Neutral particles may serve as sites for coprecipitation when the geometry of their constituent charges result in locally charged surface zones. A soluble metal cation that comes within close proximity to a negatively charged surface zone can be drawn out of solution through a heterogeneous reaction. Because the bonds that form in coprecipitation are weak relative to ionic bonds e.g., hydrolysis, metals that are removed in this way are especially prone to redissolution. In MMD treatment, the solids that may serve as coprecipitation sites are sludge flocs and undissolved reagents, i.e., lime and fly ash.

Metal cations are also capable of reacting with chemical components in MMD other than the hydroxide ion (OH^-). The resulting metal complexes may have a net charge or be electrochemically neutral. Furthermore, these complexes may or may not be capable of participating in their own hydrolysis reactions. Analytical methods report total metal concentrations and do not differentiate between free metal cations in solution and cations that have been complexed. Therefore, there is no definitive means to evaluate if and to what extent complexation reactions have occurred. Nor is it possible to assess what fraction of removed metals were complexed prior to precipitation.

The success of the ILS in treating the MMD was evaluated using two Federal regulations: (1) 40 CFR 440.102a and (2) NPDWR. The water quality standards cited in these regulations are summarized in table 1. Although Mn, Fe, and Al are not regulated by either 40 CFR 440.102a or NPDWR, these metals can have detrimental effects on aquatic life. These metals were present in the untreated MMD in substantial concentrations, and the extent of their removal during treatment will also be discussed.

Table 1.—Summary of discharge water quality standards, mg/L

Parameter	Limit 1[1]	Limit 2[2]
Ag	NR	0.05
As	NR	0.05
Ba	NR	1.0
Cd	NR	0.010
Cr (VI)	NR	0.05
Cu	0.15	NR
Hg	0.001	0.002
Pb	0.3	0.05
Se	NR	0.01
Zn	0.75	NR
TSS	20	NR
pH	6.0-9.0	NR

NR Not regulated.
TSS Total suspended solids.
[1] 40 CRF 440.102a.
[2] 40 CFR 141.11 (NPDWR).
[3] Standard units.

The performance of the ILS in removing each of the regulated metals and Mn, Fe, and Al will be discussed separately. In figures 6 through 10, the regulatory limits for each metal are included. Figures 6 through 13, except for figure 10, also include plots of the predicted metal concentrations based on equation 3. No predicted concentration plot is included for Cr (figure 10) since Cr's K_{eq} value was not available in the literature. All soluble metal concentrations in figures 6 through 13 are expressed as the log of the metal concentration in mole per liter.

The mean Cu concentration in the MMD was 98.8 mg/L. Copper is regulated under 40 CFR 440.102a and should not exceed 0.15 mg/L. All reagents were successful in removing the Cu. Hydrated lime and CaO treatments at pH values of 7, 8, 9, and 10 reduced the Cu concentrations to below the ICP detection limit of 0.002 mg/L (figure 6). Caustic soda treatments at pH values of 7 and 8 also reduced Cu to below the ICP detection limit, as did the $Ca(OH)_2$-fly ash treatment at a pH value of 10. There were measurable quantities of Cu in the NaOH treatments at pH values of 9 and 10; however, they were still substantially below the regulatory limit. It was not possible to determine whether a relationship existed between the treatment pH and the Cu concentration because of the many instances of Cu concentrations falling below the ICP detection limit.

Zinc was present in the untreated MMD at 416 mg/L. The regulatory limit for Zn under 40 CFR 440.102a is 0.75 mg/L. Only the NaOH treatment at a pH of 7 was unsuccessful in treating Zn (1.57 mg/L). Both lime treatments reduced Zn to beneath the ICP detection limit of 0.008 mg/L at treatment pH values of 9 and 10 (figure 7). In pH 7 and 8 treatments, Zn levels were only slightly higher than the detection limit with CaO, while Zn concentrations showed a steady decrease for $Ca(OH)_2$ in treatments at the same pH range. Caustic soda treatments at pH values of 8 and 10 resulted in Zn concentrations that were below the analytical detection limit with only a slightly higher value in the pH 9 treatment. The $Ca(OH)_2$-fly ash treatment at pH 10 had a Zn concentration of 0.010 mg/L. The Zn concentrations suggested a pH-dependency for $Ca(OH)_2$ and NaOH. No trend could be discerned for CaO.

The pretreatment Pb concentration was 0.196 mg/L. This value was below the maximum 0.3 mg/L allowed under 40 CFR 440.102a, but above the limit permitted under the NPDWR of 0.05 mg/L. All reagents at all treatment pH values evaluated were successful in lowering Pb to less than the more stringent NPDWR standard (figure 8). In fact, the Pb concentrations in each test were below the ICP detection limit of 0.04 mg/L. Because of this, no evaluation of pH versus Pb solubility was possible.

The mean Cd concentration in the MMD was 1.51 mg/L. Cadmium is regulated under the NPDWR at 0.01 mg/L. Treatment with NaOH at a pH of 7 resulted in a Cd level of 0.108 mg/L. Hydrated lime treatment at the same pH produced a Cd concentration of 0.027 mg/L (figure 9). These were the only two instances of unsuccessful treatment for Cd. At treatment pH values of 8, 9, and 10, both NaOH and $Ca(OH)_2$ reduced Cd concentrations to below the ICP detection limit of 0.008 mg/L. Quicklime reduced Cd concentrations to below the analytical detection limit at all pH values evaluated, while $Ca(OH)_2$-fly ash treatment produced a similar result at a treatment pH value of 10. A pH-solubility dependency was suggested by the NaOH and $Ca(OH)_2$. No evaluation could be made with the other reagents.

The concentration of Cr was 0.090 mg/L in the untreated MMD. No determination was made regarding the oxidation state of the Cr in the water. Under the NPDWR, Cr (VI) has a maximum permissible value of 0.05 mg/L. Assuming that the Cr was in the VI oxidation state, its concentration in the untreated water was only slightly higher than allowable. Chromium was reduced to concentrations below the detection limit of 0.005 mg/L by both lime and NaOH at all pH values evaluated (figure 10). With the $Ca(OH)_2$-fly ash treatment, the Cr level was 0.047 mg/L. Therefore, Cr treatment was uniformly successful in all tests. No evaluation could be made regarding the solubility of Cr and the treatment pH value.

The initial Mn concentration was 42.1 mg/L. Manganese was removed to below the analytical detection limit of 0.007 mg/L by $Ca(OH)_2$ at treatment pH values of 7 and 10, CaO at a treatment pH of 10, NaOH at treatment pH values of 9 and 10, and $Ca(OH)_2$-fly ash at a treatment pH of 10 (figure 11). All reagent-treatment pH combinations, except $Ca(OH)_2$ at a pH of 9, and NaOH at pH values of 7 and 8, resulted in Mn concentrations below 1 mg/L. For the exceptions cited, the respective Mn concentrations were 2.06, 20.6, and 2.35 mg/L, respectively. Manganese is relatively soluble until the pH has been increased to a value of approximately 9 and higher. The many instances of Mn reductions to levels below 1 mg/L at pH values of 7 and 8 are, therefore, significant and suggest that other metal removal mechanisms were operative.

Iron was present in the untreated MMD at a concentration of 127 mg/L. No speciation of the Fe forms was conducted. It was assumed that because the water was held in a shallow pond for an extended period, that most Fe was in the oxidized Fe^{3+} state. Iron was removed by all reagents at all pH values evaluated to below the analytical detection limit of 0.02 mg/L (figure 12). No evaluation could therefore be made regarding the sensitivity of the Fe removal to the treatment pH.

The initial Al concentration was 457 mg/L. Aluminum is noted for its propensity to redissolve under high pH conditions. For $Ca(OH)_2$ treatments, the Al concentration was below the detection limit of 0.02 mg/L at a treatment pH of 7, but rose to 0.216, 0.10, and 3.43 mg/L at treatment pH values of 8, 9, and 10, respectively (figure 13). For treatments with CaO, the Al concentrations were 0.225, 0.206, 1.08, and 4.41 mg/L at treatment pH values of 7, 8, 9, and 10, respectively. Similarly, with NaOH treatments, the Al concentrations began at below the detection limit at a treatment pH value of 7 and generally rose in succeeding treatments: 0.127 mg/L at pH = 8, 5.29 mg/L at pH = 9, and 3.72 mg/L at pH = 10. No explanation is offered for the modest decrease occurring at a pH of 10 with NaOH. The $Ca(OH)_2$-fly ash treatment at a pH of 10 resulted in an Al concentration below the detection limit. This suggests an alternative mode of removal.

For the regulated metals under 40 CFR 440.102a and/or NPDWR for which data were available, the optimum treatment pH appeared to lie at approximately 9. Slightly better treatment was achieved at a pH value of 10, but this value exceeds the maximum pH permitted under 40 CFR 440.102a. When Mn, Fe, and Al are considered with the regulated metals, there was no change in the optimum treatment pH. Since slight decreases, i.e., approximately 0.5 pH units, are often observed in treated MMD's over time, a treatment pH value somewhat above 9 may result in the best posttreatment water quality. Because no tests were conducted at fractional pH values, this cannot be corroborated.

There were few cases where metal concentrations could be directly compared with changes in the treatment pH value. This limitation was due to many metal concentrations falling below the analytical detection limits. In general, however, treatment performance as measured by the extent of metal removal improved as the pH was increased.

Test data presented in figures 6 through 13 are analytical concentrations. The K_{eq} values from the literature *(6,8)* used to plot the solubility curves in figure 14 were developed using low ionic strength solutions where the activity coefficients could be assumed to be equal to unity. No adjustment of K_{eq} values nor calculation of active metal concentrations was possible since many metal concentrations fell below, or in the case of sodium, above, the ICP detection limits.

In the cases of Mn and Zn, whose posttreatment concentrations were uniformly below their respective equilibrium concentrations in a hydrolysis system, an additional mechanism or mechanisms are suggested. Coprecipitation and/or a speculated very high transient pH zone within the ILS may be responsible. Data collection was not structured to verify either of these mechanisms.

The selection of reagent appeared to have little bearing on the removal of metals. This is not surprising, since from a strictly chemical perspective, each reagent is a source of the reactant OH^-. While some reagents are relatively stronger sources of OH^- on a unit mass basis, this difference was essentially eliminated by delivering the required quantity of each reagent to treat the MMD to a common set of treatment pH values. Therefore, all of the reagents can be regarded as sufficient and adequate for the successful treatment of the MMD used in this study. Other criteria, such as economics, can be used when a full-scale treatment of the MMD is considered.

SUMMARY AND CONCLUSIONS

The ILS was tested at pilot-scale on MMD whose principal chemical constituents were Cu, Zn, Fe, Mn, and Al. Trace amounts of Ag, Ba, Cd, Cr, and Pb were also present. The MMD was treated using the chemical neutralization process. This process is designed to remove acidity by the addition of an alkaline neutralizing reagent and to reduce concentrations by metal hydrolysis reactions. The neutralizing reagents used were $Ca(OH)_2$, CaO, NaOH, and a mixture of $Ca(OH)_2$ and fly ash. The treatment performance of each reagent, the $Ca(OH)_2$-fly ash slurry, was evaluated at pH values of 7, 8, 9, and 10. The $Ca(OH)_2$-fly ash slurry was evaluated at a treatment pH of 10.

This was the first comprehensive test of the ILS in treating a MMD. Previous work with this treatment system has been generally confined to CMD. While the suite of metals present in CMD is normally smaller than in MMD, the reactions used in CMD and MMD treatment are equivalent.

In this study, the effluent limitations cited in 40 CFR 440.102a and the NPDWR were used as the criteria for evaluating effective treatment. The ILS was found to be effective in raising the pH value of the MMD to within an acceptable range of 6 to 9, while reducing metal concentrations to below the maximum permissible concentrations of all regulated metals. The ILS, therefore, has been demonstrated to be an effective treatment device for the specific MMD used in the study. More generally, it may be concluded that the ILS has an excellent potential for treating other MMD with different chemical profiles.

Circumstantial evidence suggests that additional metal removal mechanisms contributed to water treatment. The candidate mechanisms proposed were coprecipitation and an instantaneously very high pH zone within the ILS. No direct evidence was available to confirm or reject that either of these mechanisms actually occurred. Since both are beneficial to treatment, further study should be conducted to establish whether they are occurring in the ILS and, if so, to modify the equipment and/or treatment process to enhance their contributions to metal removal.

The successful treatment achieved with the $Ca(OH)_2$-fly ash slurry should also be studied further. The development of a beneficial use for a waste product from another industry is a desirable goal from an environmental perspective. Furthermore, the use of fly ash as a partial substitute for $Ca(OH)_2$ may result in decreased reagent costs. Finally, the pozzolonic properties of fly ash and the beneficial effect they may impart to the treatment sludge density and stability should be investigated.

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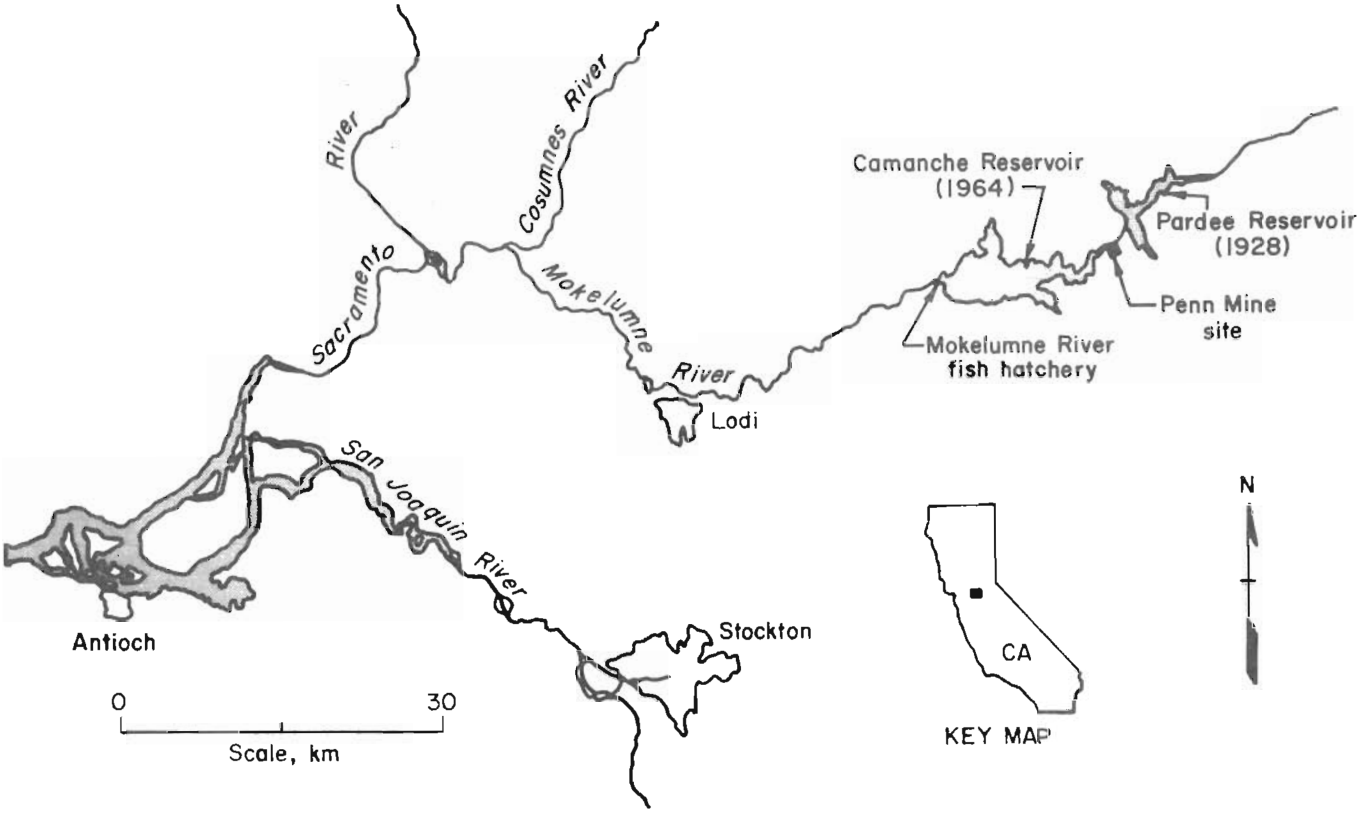
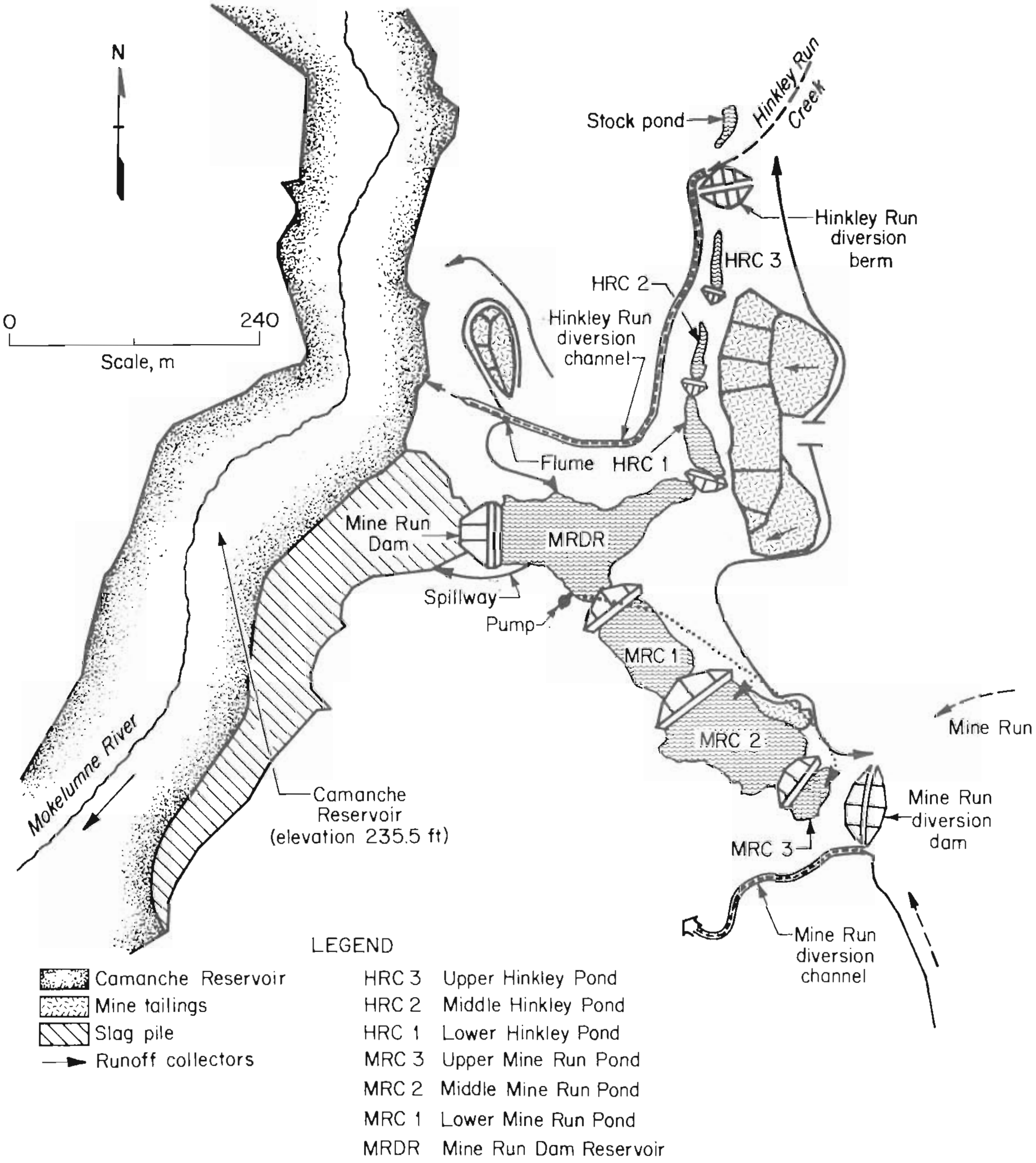
Figure 1



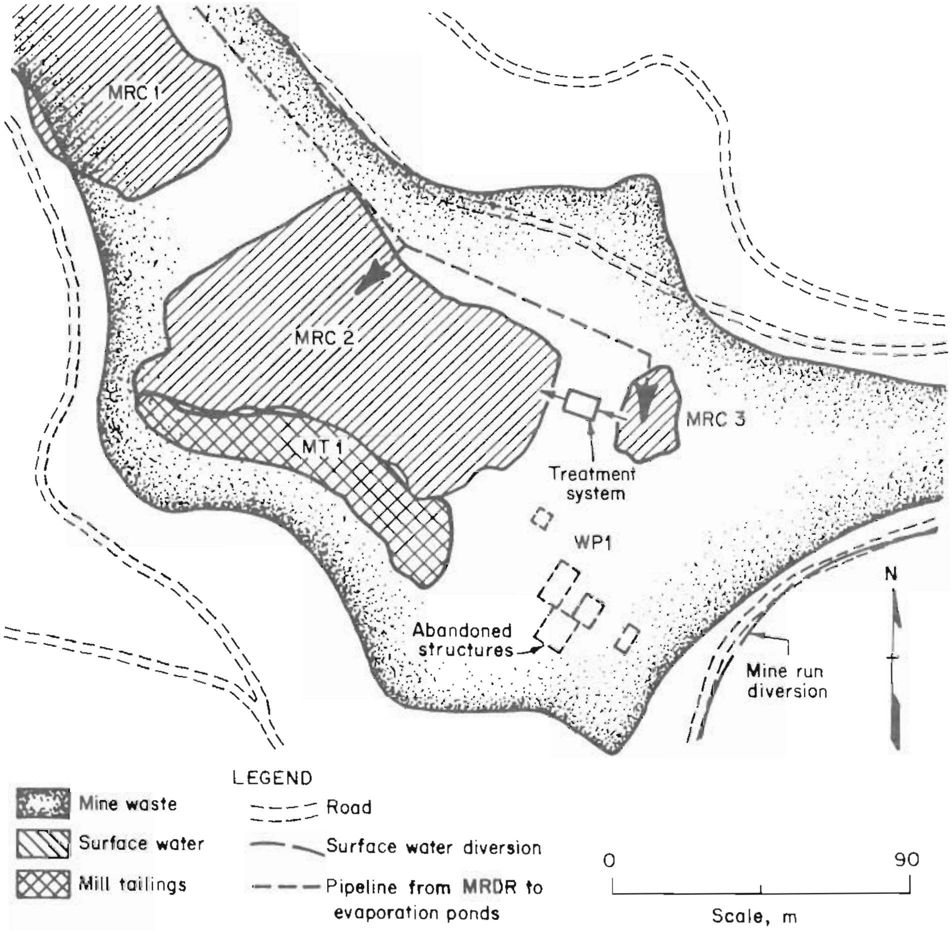
Area map.

Figure 2



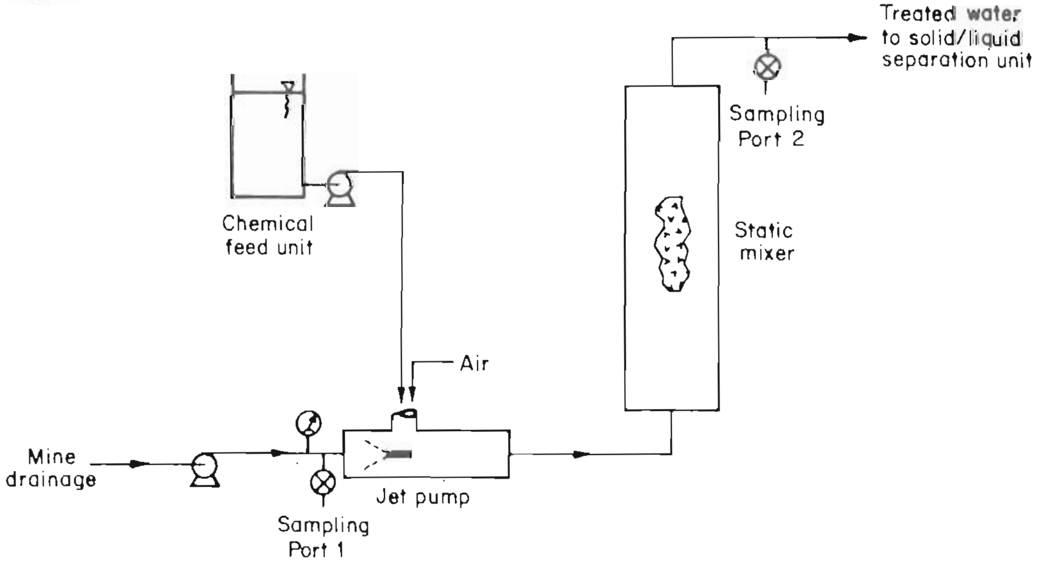
Minesite map.

Figure 3



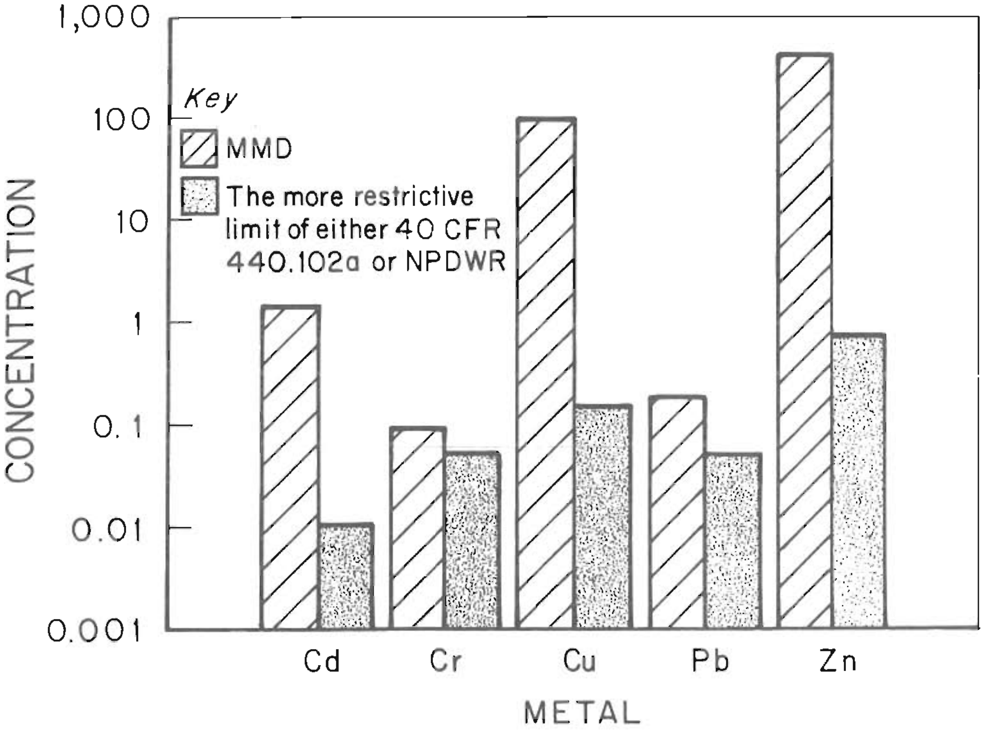
Testsite map.

Figure 4



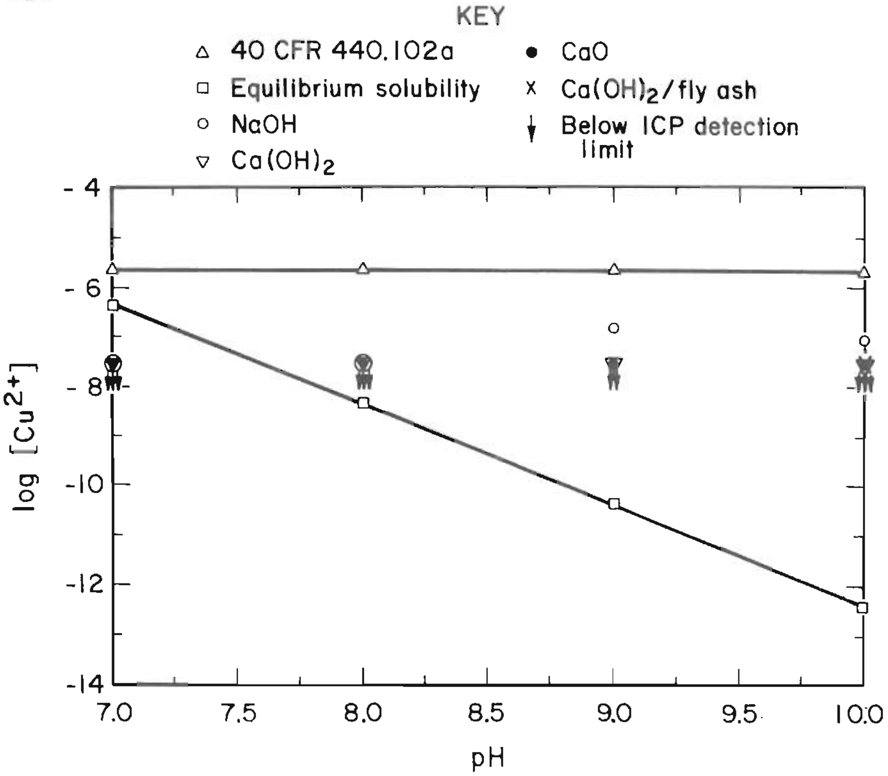
Schematic of In-Line System (ILS).

Figure 5



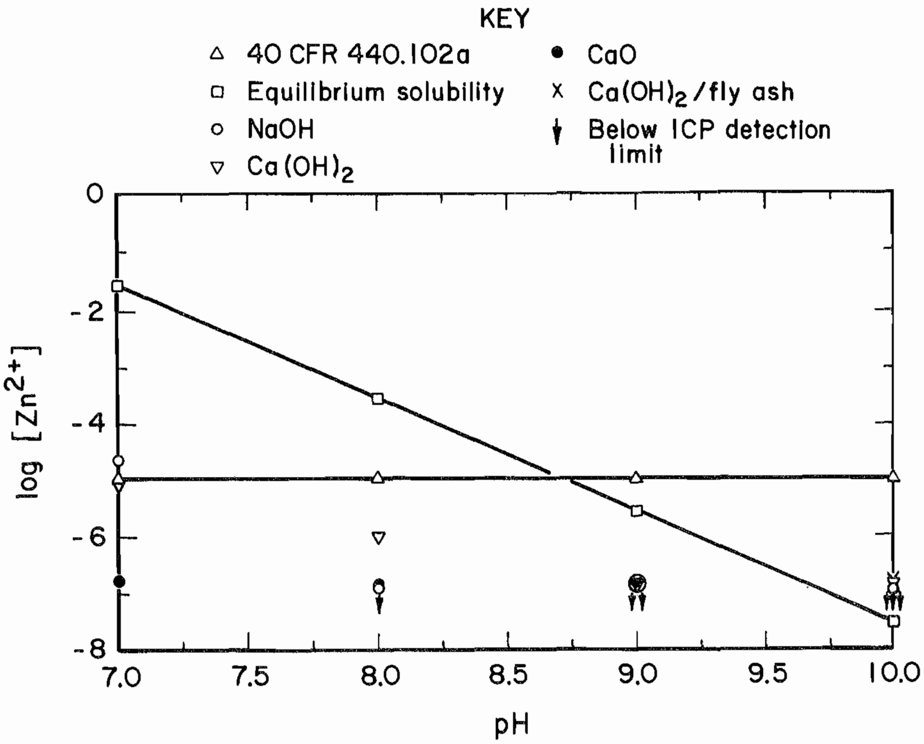
Pretreatment water quality of MMD.

Figure 6



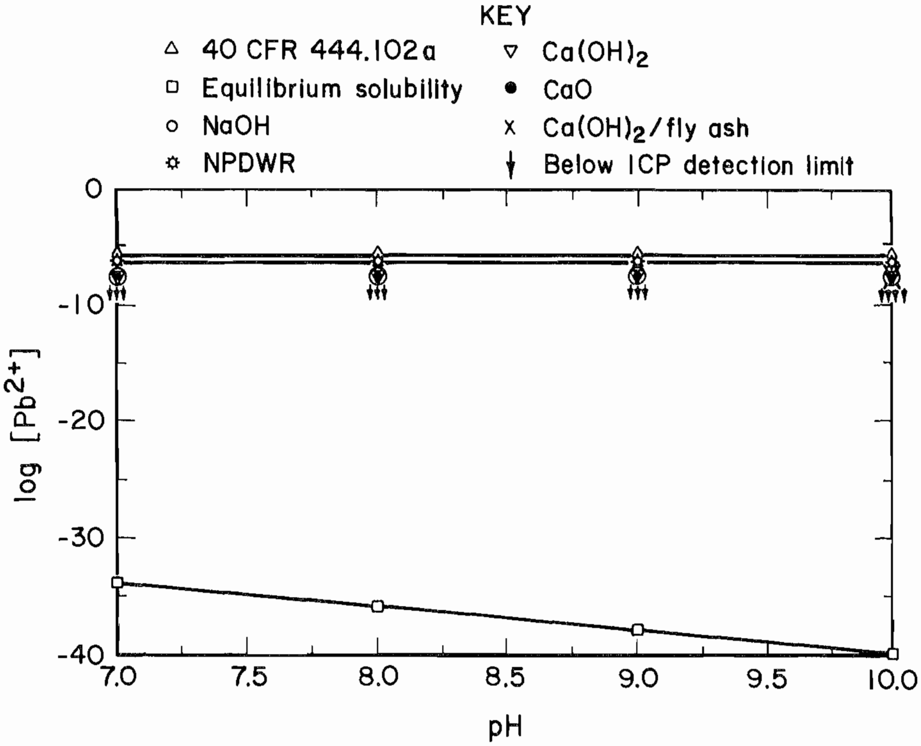
Posttreatment water quality - Copper.

Figure 7



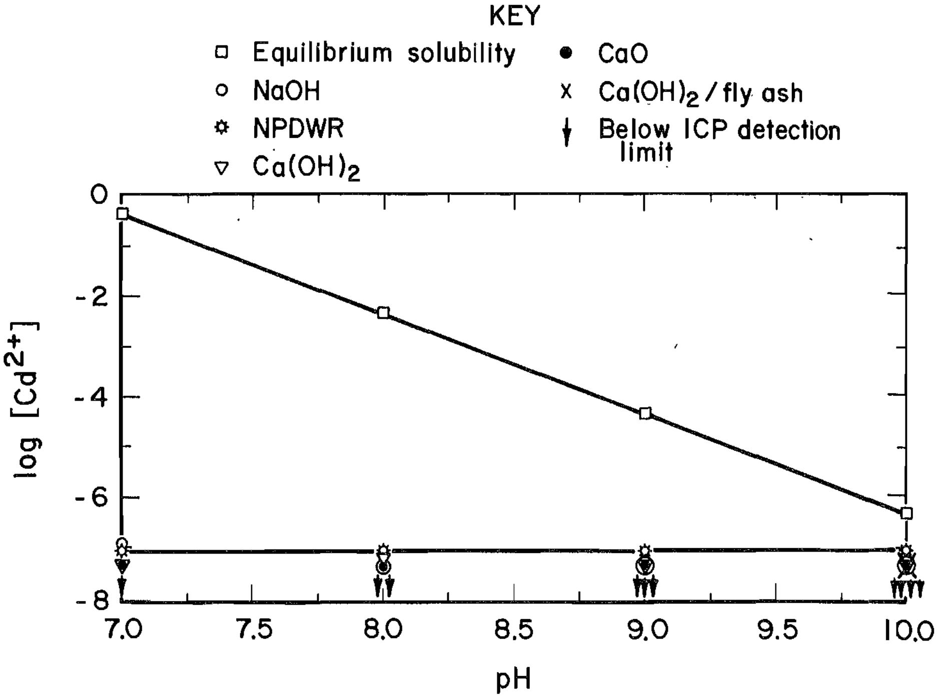
Posttreatment water quality - Zinc.

Figure 8



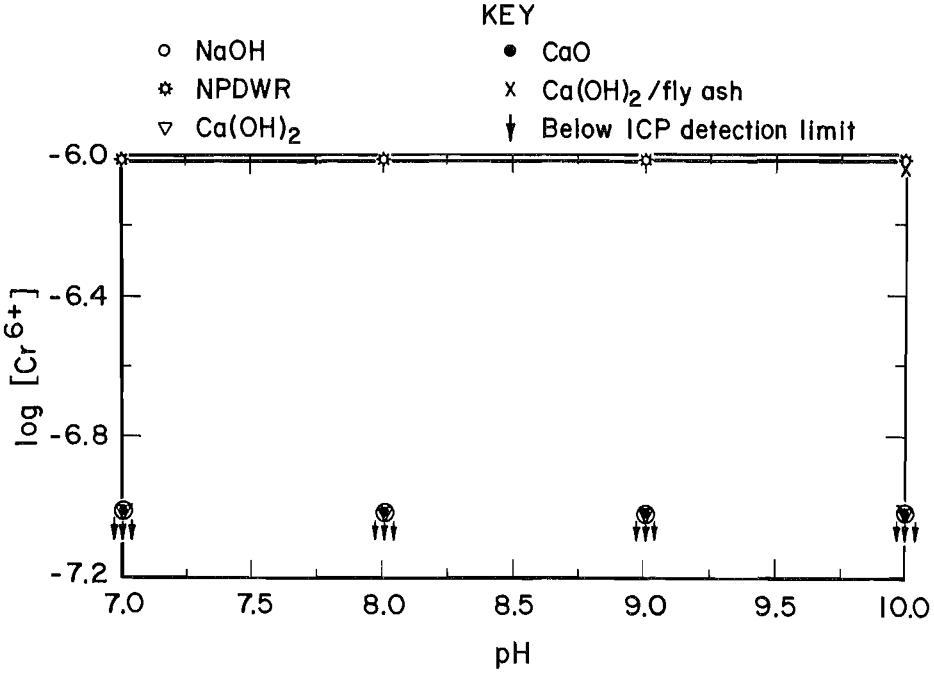
Posttreatment water quality - Lead.

Figure 9



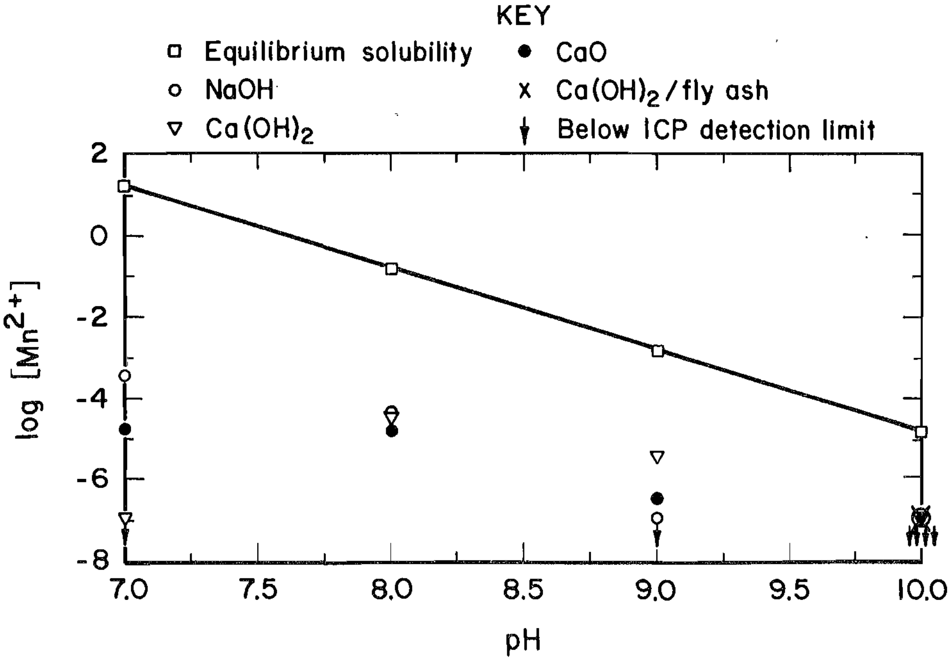
Posttreatment water quality - Cadmium.

Figure 10



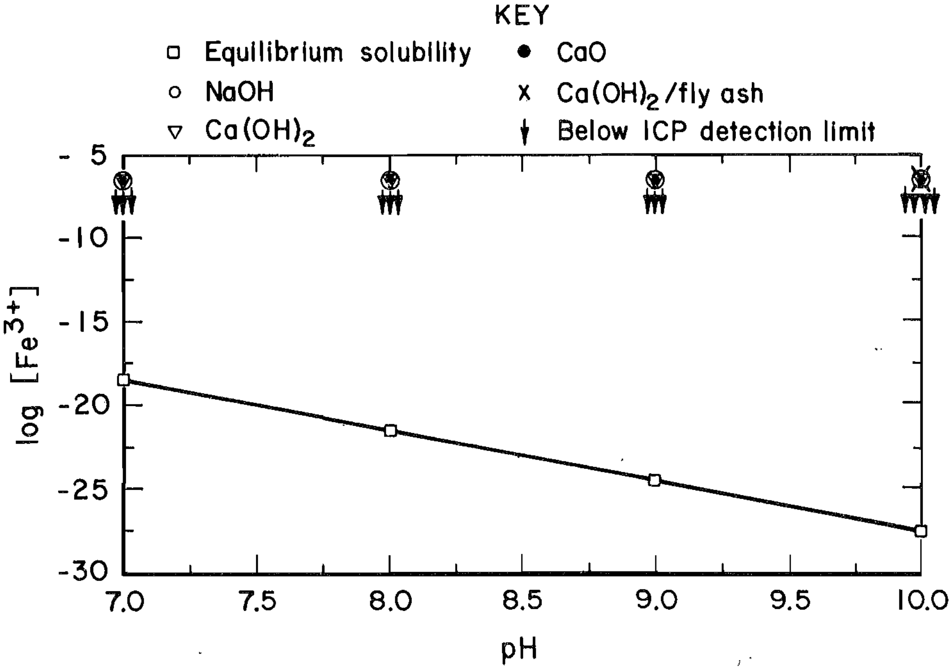
Posttreatment water quality - Chromium.

Figure 11



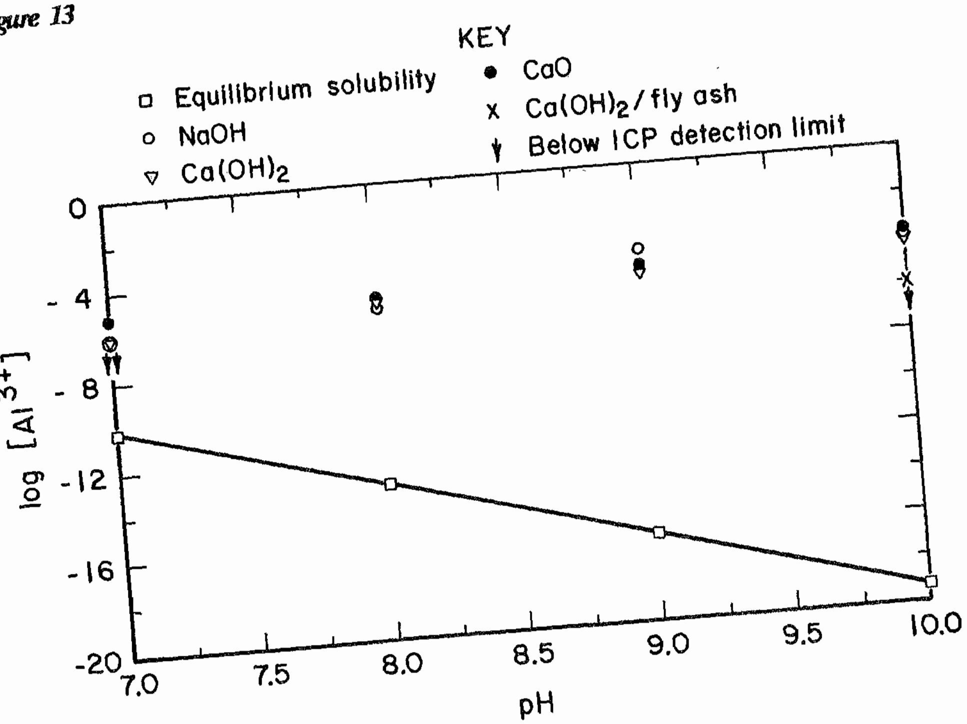
Posttreatment water quality - Manganese.

Figure 12



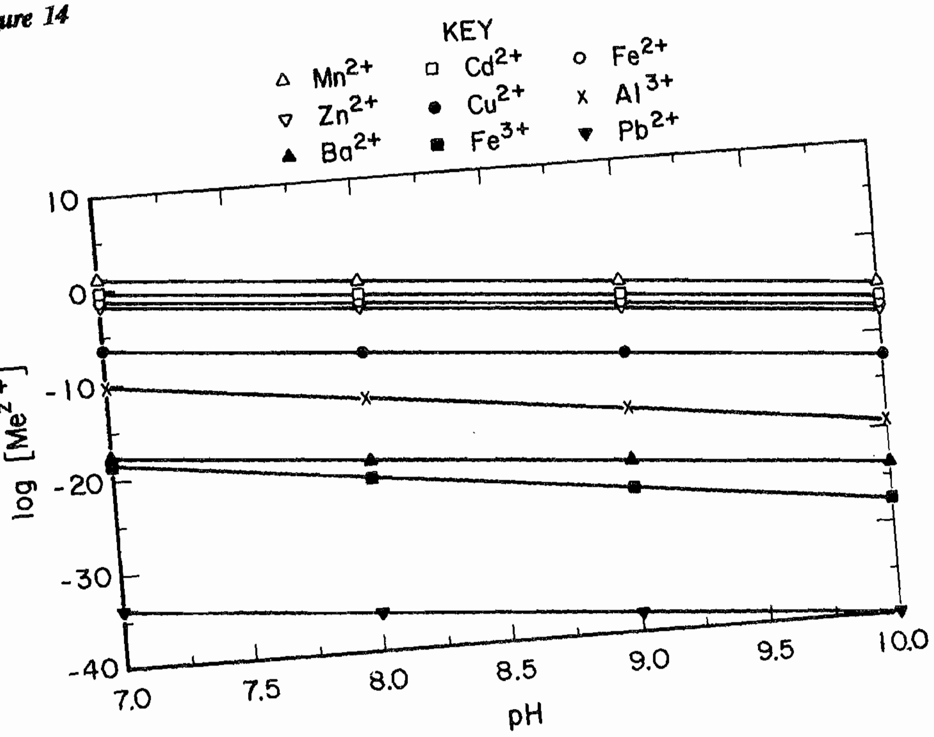
Posttreatment water quality - Iron.

Figure 13



Posttreatment water quality - Aluminum.

Figure 14



Metal solubilities under equilibrium conditions.

APPENDIX.—WATER QUALITY OF MMD

Table A-1.—Pretreatment, mg/L

Parameter	Mean	Standard deviation	Maximum	Minimum
Ag	NC	NC	0.020	NC
Al	457	7.84	470	451
B	2.11	0.049	2.16	2.06
Ba	NC	NC	0.008	NC
Ca	466	18.2	500	451
Cd	1.51	0.08	1.67	1.47
Co	0.909	0.008	0.92	0.90
Cr	0.09	0.014	0.108	0.069
Cu	98.8	8.00	108	88.2
Fe, tot	127	0	127	127
K	12.7	9.70	19.6	NC
Li	0.421	0.01	0.431	0.412
Mg	664	16.9	696	647
Mn	42.1	1.52	45.1	41.2
Na	59.4	1.18	60.8	57.8
Ni	0.74	0.04	0.78	0.69
Pb	NC	NC	0.196	NC
Sc	0.184	0.004	0.186	0.176
Sr	1.76	0	1.76	1.76
Ti	NC	NC	0.05	NC
Zn	416	13.3	441	402
SO_4	8,134	152	8,428	8,036
pH	2.6[1]	NC	NC	NC
Cl	37.0	1.75	39.2	34.3
Acidity[2]	4,141	42.4	4,214	4,018
Conductivity[3]	6,855	96.6	8,232	6,752

NC Not calculated.

[1] Standard units.

[2] As $CaCO_3$.

[3] μmho/cm_2.

Table A-2.—Treated at pH = 7, mg/L

Parameter	$Ca(OH)_2$	CaO	NaOH
Ag	<0.009	<0.009	<0.009
Al	<0.02	0.225	<0.02
B	0.892	0.843	0.902
Ba	0.011	0.011	0.004
Ca	431	470	343
Cd	0.027	<0.008	0.108
Co	0.007	<0.005	0.013
Cr	<0.005	<0.005	<0.005
Cu	<0.002	<0.002	<0.002
Fe, total	<0.02	<0.02	NA
K	0.157	<1.00	<1.00
Li	0.323	0.084	0.07742
Mg	323	225	402
Mn	<0.007	0.980	20.6
Na	49.0	52.9	>500
Ni	<0.04	<0.01	<0.01
Pb	<0.04	<0.04	<0.04
Sc	NA	0.006	NA
Sr	<0.002	0.823	1.18
Ti	NA	<0.002	NA
Zn	0.578	0.011	1.57
SO_4	2,842	2,352	7,154
Cl	43.1	43.1	103
Conductivity[1]	3,469	3,116	9,222

NA Not analyzed.

[1] μmho/cm$_2$.

Table A-3.—Treated at pH = 8, mg/L

Parameter	$Ca(OH)_2$	CaO	NaOH
Ag	<0.009	<0.009	<0.009
Al	0.216	0.206	0.127
B	0.980	0.755	1.18
Ba	0.014	0.010	0.006
Ca	480	431	382
Cd	<0.008	<0.008	<0.008
Co	<0.005	<0.005	<0.005
Cr	<0.005	<0.005	<0.005
Cu	<0.002	<0.002	<0.002
Fe, total	<0.02	<0.02	<0.02
K	3.92	0.980	0.980
Li	0.157	0.074	0.108
Mg	323	196	265
Mn	2.06	0.872	2.35
Na	58.8	45.1	>500
Ni	<0.01	<0.01	<0.01
Pb	<0.04	<0.04	<0.04
Sc	0.005	0.007	0.005
Sr	0.813	0.696	1.47
Ti	<0.002	<0.002	<0.002
Zn	0.060	0.009	<0.008
SO_4	2,744	2,352	6,958
Cl	35.3	35.3	103
Conductivity[1]	3,322	3,087	9,682

[1] μmho/cm^2.

Table A-4.—Treated at pH = 9, mg/L

Parameter	$Ca(OH)_2$	CaO	NaOH
Ag	<0.009	<0.009	<0.009
Al	0.510	1.08	5.29
B	0.725	0.676	1.47
Ba	0.012	0.012	0.003
Ca	470	549	284
Cd	<0.008	<0.008	<0.008
Co	<0.005	<0.005	<0.005
Cr	<0.005	<0.005	<0.005
Cu	<0.002	<0.002	0.010
Fe, total	<0.02	<0.02	<0.02
K	<1.00	<1.00	2.94
Li	0.098	0.088	0.323
Mg	127	29.4	<0.03
Mn	0.225	0.021	<0.007
Na	49.0	57.8	>500
Ni	<0.01	<0.01	<0.01
Pb	<0.04	<0.04	<0.04
Sc	0.006	0.005	0.003
Sr	0.686	0.853	1.37
Ti	<0.002	<0.002	<0.002
Zn	<0.008	<0.008	<0.010
SO_4	2,058	1,666	6,958
Cl	59.8	45.1	113
Conductivity[1]	2,891	2,352	10,780

[1] μmho/cm^2.

Table A-5.—Treated at pH = 10, mg/L

Parameter	$Ca(OH)_2$	CaO	NaOH	$Ca(OH)_2$/ fly ash
Ag	<0.009	<0.009	<0.009	<0.009
Al	3.43	4.41	3.72	<0.02
B	0.666	0.412	1.27	0.196
Ba	0.015	0.012	0.004	0.033
Ca	559	519	284	392
Cd	<0.008	<0.008	<0.008	<0.008
Co	<0.005	<0.005	0.006	<0.005
Cr	<0.005	<0.005	<0.005	0.047
Cu	<0.002	<0.002	0.006	<0.002
Fe, total	<0.02	<0.02	<0.02	<0.02
K	<1.00	0.980	6.86	50.0
Li	0.108	0.118	0.274	0.066
Mg	0.921	<0.03	<0.03	29.4
Mn	<0.007	<0.007	<0.007	<0.007
Na	59.8	51.0	>500	44.1
Ni	<0.01	<0.01	<0.01	<0.01
Pb	<0.04	<0.04	<0.04	<0.04
Sc	0.003	0.0049	0.004	0.007
Sr	0.853	0.784	1.27	2.25
Ti	<0.002	<0.002	<0.002	<0.002
Zn	<0.008	<0.008	<0.008	0.010
SO_4	1,470	1,470	6,958	1,764
Cl	84.3	40.2	103	30.4
Conductivity[1]	2,509	2,225	9,800	2,479

[1] μmho/cm^2.

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