CHEMICAL STABILITY OF MANGANESE AND OTHER METALS IN ACID MINE DRAINAGE SLUDGE[1]

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Abstract.--Federal regulations require mine operators to reduce the average concentration of manganese in the effluent to 2 mg/L. To meet this standard, the majority of mine operators add an alkaline material, typically lime or sodium hydroxide, to raise the pH to about 10.0. Our laboratory tests using actual acid mine drainage (AMD) containing iron, manganese, nickel, copper, zinc, and chromium, have indicated that the high-pH precipitation method is effective at removing these metals. However, manganese, nickel, zinc, and copper in the precipitated sludge were susceptible to dissolution upon subsequent depression of pH. Up to 30 percent of the original manganese in the high-pH precipitated sludge dissolved at pH 7.5. At pH 6.0, this figure increased to 78 pct. Additionally, 30 percent of nickel, zinc, and copper redissolved at pH values of 6.8, 5.7, and 4.7, respectively. Iron and chromium were stable down to pH 3.5. No differences were found between the use of lime or sodium hydroxide regarding the stability of the precipitated sludge. In mine waters containing high concentrations of iron in relation to manganese and other metals, manganese and other metals were removed at lower pH values than in mine waters with less iron. However, manganese in the sludge precipitated from the high iron water was less stable. Aging also affected the stability of manganese in AMD sludge. After sludge had aged for three months, 50 percent less manganese was released upon depression of pH. The problem of manganese redissolution can be avoided by using an oxidizer such as sodium hypochlorite or potassium permanganate; however, these chemicals were ineffective at removing copper, nickel, and zinc. To reduce manganese below 2 mg/L, the use of sodium hypochlorite or potassium permanganate increased chemical treatment costs by factors of 2.3 and 2.6, respectively, over the chemical costs for sodium hydroxide treatment.

INTRODUCTION

Chemical Treatment for Manganese Removal

Federal legislation requires mine operators to adhere to specific effluent limits (U.S. Code of Federal Regulations 1985 a & b) (table 1). To meet these limits, treatment of acid mine drainage typically involves addition of alkaline material, commonly lime (CaO or $Ca(OH)_2$) or sodium hydroxide (NaOH); natural or mechanical aeration; and settling. When the pH of the drainage is raised to 7 or 8, and there is sufficient time allowed for settling, most mine drainage water will meet the

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Table 1.--Federal effluent limitations

Pollutant or pollutant property	Maximum for any 1 day	Average of daily values for 30 consecutive days
Iron, total *	7.0 mg/L	3.5 mg/L
Manganese, total	4.0 mg/L	2.0 mg/L
Total Suspended solids	70.0 mg/L	35.0 mg/L
pH	between 6.0 and 9.0	

*New source performance standards for total iron; daily maximum - 6.0 mg/L and 30-day average - 3.0 mg/L

standards for pH, iron, and suspended solids. However, this treatment will rarely reduce manganese levels below effluent limits because the oxidation rate of Mn^{2+} is pH-dependent and extremely slow below pH 8.5. Diem and Stumm (1984) found that dilute solutions of manganese nitrate ($Mn(NO_3)_2$), maintained at pH 8.4 in the presence of dissolved oxygen, showed virtually no oxidation for over 4 years. Owens (1963) reported that a pH of at least 9.4 was necessary to remove manganese. Our tests indicate pH values above 10 are necessary for some mine drainage waters. Therefore, to ensure adequate removal of manganese, many mine operators must add enough alkalinity to raise pH of the mine water to about 10. This increases chemical treatment costs 20 to 100 pct over the costs to remove iron (Watzlaf 1985) and generates a large volume of metalliferous sludge, up to 33 pct (by volume) of the treatment plant inflow (Holland et al. 1968). Nicholas and Foree (1979) found that increasing the treatment pH from 8 to 10 increases the required sedimentation basin area from 158 m^2 to 400 m^2 for NaOH, and from 200 m^2 to 316 m^2 for lime.

The precipitation and removal of manganese in an aqueous system is complex. Manganese can exist in oxidation states of +2, +3, +4, +6, and +7 (Sienko and Plane 1966, Morgan 1967). Initially, the valence of manganese in the air-oxidized precipitate (removed at high pH) lies between 2.67 and 3.0 (Mn_3O_4 - hausmannite and β-MnOOH - feitknechtite, respectively) (Hem 1981, Murray et al. 1985). Both these minerals are eventually transformed into the more stable γ-MnOOH - manganite (Murray et al. 1985, Stumm and Giovanoli 1976). Manganese can also be removed by adsorption onto reactive surfaces. Ferric hydroxide ($Fe(OH)_3$) and manganese precipitates can provide surfaces for sorption of Mn^{2+}, which occurs at lower pH values than necessary for manganese removal as hydroxides (Morgan and Stumm 1964, Stumm and Morgan 1981, Collins and Buol 1970). Therefore, manganese in mine waters with high iron concentrations can usually be removed at lower pH values than manganese in mine water with lower iron levels. However, manganese precipitated with iron was found to go back into solution upon acidification (Collins and Buol 1970).

Additionally, manganese can exist in many different complexed and chelated forms (Martell and Calvin 1952, Clark et al. 1977, Evangelou 1984). The formation of manganese complexes depends on oxidation state, pH, bicarbonate-carbonate-hydroxide equilibria, and the presence of other materials (Nalco Chemical Company 1979). Organic complexes can hold manganese in solution to higher pH levels (Clark et al. 1977).

As an alternative to precipitation of manganese by the high-pH method, strong oxidizers, such as permanganate, chlorine dioxide, hypochlorite, or ozone can be used. These chemicals oxidize manganese to pyrolusite (MnO_2) (Evangelou 1984, Clark et al. 1977). Knocke et al. (1987) found that hydrogen pyroxide was not effective for oxidizing manganese.

In the process of removing manganese by the high-pH precipitation method, arsenic, chromium, copper, lead, mercury, nickel, selenium, and zinc should precipitate, principally, as hydroxides (Feitkecht and Schindler 1963). These metals may also be removed by sorption onto iron precipitates (Jones 1986, Mott et al. 1987, Slavek and Pickering 1986) and as with manganese, complexes and chelates may be formed (Martell and Calvin 1952). However, hydroxides of these metals may resolubilize if solution pH is changed (Peters and Ku 1985). Bogner (1983) found that for treated mine drainage, the order of extractability from the retention pond sediments was Mn > Ni, Zn, Co, > Cu, Cr > Fe, Al. Forbes et al. (1976) reported that 50% of Cd, Zn, Pb, and Cu was desorbed at pH 8, 7, 5.5, and 5, respectively, from synthetic iron oxide (goethite).

Regulation of Manganese

During the process of developing effluent limitation guidelines for the coal mining industry, the Environmental Protection Agency (EPA) found that certain metals, such as arsenic, chromium, copper, lead, mercury, nickel, selenium, and zinc, were occasionally present in the untreated mine water. Water treatment specifically to control iron (neutralization and aeration) reduced the concentrations of these toxic metals, but not consistently enough to provide effective control as required by the Clean Water Act of 1972.

Selection of a specific manganese standard was a result of a survey of 314 acid water sources (Weideman 1982). In their survey, EPA researchers found that the mine water treatment facilities were reducing manganese to approximately 2 mg/L, and therefore selected that value as the best available technology (BAT) effluent limit (U.S. Code of Federal Regulations 1985b). In addition, the eight toxic metals of concern (arsenic, chromium, copper, lead, mercury, nickel, selenium, and zinc) were reduced to acceptable levels whenever manganese was reduced to 2 mg/L. Therefore, limitations on these metals were not promulgated. In their survey of acid mine drainage sites, the EPA found average manganese concentrations in the untreated mine water of 4.9 mg/L at underground mines and 17.7mg/L at surface mines (Weideman 1982). The highest concentration of manganese was 63 mg/L at any surveyed site. However, a decade later, our work has found many sites at which manganese levels exceed those found by the EPA. The average manganese concentration from 23 sites with known manganese problems was 121 mg/L. Twenty of these sites had manganese levels over 63 mg/L (the maximum level in the EPA survey) and three sites exceeded 200 mg/L (Kleinmann and Watzlaf 1988).

EXPERIMENTAL PROCEDURES AND RESULTS

This paper summarizes research performed over the past 3 years. In these investigations, five mine waters with different chemical compositions were used (table 2). This section is divided into three subsections: manganese removal, manganese resolubilization, and behavior of other metals. In the following subsections, several experiments are discussed; and although similar procedures were used for each test, some modifications were necessary to account for the different water quality of individual mine waters. Therefore, for clarity, the experimental procedures are following immediately by the results of that particular test.

In all tests, pH was measured with an analog meter using a combination pH electrode. Acidity analysis consisted of a fixed endpoint titration to pH 8.3 using a 1N sodium hydroxide solution. Iron, manganese, aluminum, copper, nickel, zinc, and chromium concentrations were determined by inductively coupled argon plasma (ICAP) sprectroscopy. In all tests, immediately after a sample was collected for metal analyses, it was passed through a 0.45 µm membrane filter and acidified to less than pH 1.0 with concentrated hydrochloric acid. In all tests, concentrations have been corrected for dilution of all added solutions.

Table 2.--Water quality of mine waters

Water quality parameter	Concentration of untreated AMD*				
	I	II	III	IV	V
Iron	232	51.3	7.7	7300	39
Manganese	126	87.7	84.3	76.5	44
pH	5.3	3.1	3.1	2.0	5.0
Acidity	467	535	NA	18475	NA
Copper	NA**	NA	0.27	22.6	NA
Nickel	NA	NA	2.87	15.8	NA
Zinc	NA	NA	4.59	39.1	NA
Chromium	NA	NA	<0.04	1.82	NA
Aluminum	3.8	34.9	NA	NA	NA

*All concentraions in mg/L except pH in pH units. Acidity in mg/L as $CaCO_3$.
**NA = Not Analyzed.

Manganese Removal

Mine waters I and II were used to compare the treatment costs of three chemicals that were currently being used by the mining industry to remove manganese: sodium hydroxide (NaOH), sodium hypochloride (NaOCl), and potassium permanganate ($KMnO_4$). These three chemicals represent two basic treatment options for manganese; addition of enough alkaline material (NaOH or lime) to raise pH to approximately 10 or use of a chemical oxidant (NaOCl or $KMnO_4$) for direct manganese oxidation. Chemical treatment costs were calculated using the prices of the chemicals at the time of the study (1984) and as delivered to the mine: $0.28/gal and $0.80/gal, for bulk quantities of 20-pct-NaOH and 15-pct-NaOCl solutions, respectively, and $1.34/lb for granular $KMnO_4$. Bulk purchase price of $KMnO_4$ is about $1.08/lb, but a typical mine would not require such large quantities (minimum 20 metric tons).

For mine water I, 50 liters of raw water was collected and treated with a 20-pct solution of NaOH to raise pH to 7.5. This water was then aerated by pouring it from one container to another, causing iron to oxidize and precipitate and pH to decrease. The procedure of neutralization and aeration was repeated until pH stabilized at 7.5. Analysis showed that iron was reduced to approximately 4 mg/L and manganese to 95 mg/L. Addition of alkaline material prior to addition of the chemical oxidant is common practice since much of the iron can be easily removed and since discharge pH must be above 6.0. After settling for 30 minutes, twenty 400-ml samples of the supernatent water were collected in plastic bottles. Six of these bottles received incremental amounts of additional NaOH (5-pct solution) with pH raised to between 9.2 and 10.5. Six bottles received incremental amounts of a $KMnO_4$ solution (1 pct). Seven bottles received incremental amounts of NaOCl (8 pct available chlorine) and one bottle received no extra chemical addition. After settling for 23 hours at room temperature, a sample from each bottle was filtered, acidified, and analyzed. All three treatments were capable of reducing manganese below effluent limits, but sodium hydroxide was considerably less expensive than the chemical oxidants. Total chemical costs to treat 1,000 gal of mine water I (including $0.36 for the initial NaOH) averaged $1.02, $2.30, and $2.60 for NaOH, NaOCl, and $KMnO_4$, respectively (Watzlaf 1985).

Similar tests were conducted on mine water II. A 50-liter sample of water was collected after being treated by the existing hydrated lime ($Ca(OH)_2$) treatment system. As in the above test, the mine water was manually aerated, after which the pH stabilized at 8.2. After 30 minutes of settling, iron was reduced to 2 mg/L and manganese to 70 mg/L. Based on previous lime use records, it was estimated that this treatment to pH 8.2 cost approximately $0.22 per 1000 gal of water. Twenty-seven 450-ml samples were taken from this treated water and incremental amounts of NaOH (5-pct solution), NOCl (8 pct available chlorine), or $KMnO_4$ (1-pct solution) were added to respective bottles. These bottles were mixed and left to settle for 90 minutes. Samples from each bottle were filtered, acidified, and analyzed. Total chemical costs per 1,000 gal to reduce manganese to 2 mg/L were $0.53, $0.95, and $1.70 for NaOH, NaOCl, and $KMnO_4$, respectively (Kleinmann et al. 1985).

In performing these and other tests (Ackman and Kleinmann 1985), it was observed that in the high-pH precipitation method, manganese was removed at lower pH values if the mine water contained higher concentrations of iron with respect to manganese. The next test used mine waters III and IV. Note that the iron to manganese concentration ratio in mine water III is 1:11, while in mine IV this ratio is 95:1. One liter of each mine water was stirred in a large beaker. A 5-pct solution of NaOH was incrementally added to the water. After addition each increment of NaOH, pH was measured and a 50-ml sample was taken from each beaker. Figure 1 shows the removal of iron and manganese as a function of pH. In the high iron water, manganese is removed at approximately 1.5 pH units lower than in the low iron water. Presumably, some manganese is removed during the precipitation of iron by adsorption on $Fe(OH)_3$ (Stumm and Morgan 1981).

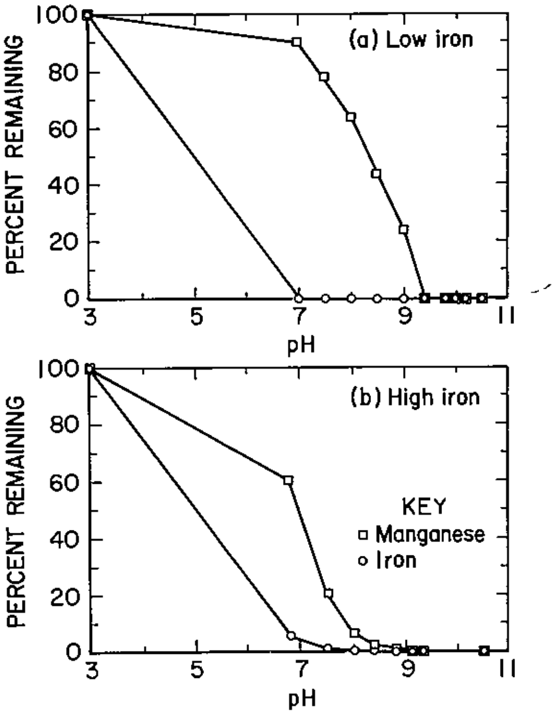

Figure 1.--Removal of iron and manganese from acid mine drainage containing (a) low (7.7 mg/L) and (b) high (7,300 mg/L) iron concentrations using the high-pH precipitation method (sodium hydroxide).

Manganese Resolubilization

From the above tests, it was observed that the high-pH precipitated manganese would resolubilized upon depression of pH. Approximately 800 ml of mine water V was placed in four beakers and slowly stirred. To the first beaker, a 5-pct solution of NaOH was added to raise pH to 10.5 to ensure complete manganese removal. To the second beaker, a hydrated lime ($Ca(OH)_2$) slurry was added to raise pH to 10.5. To the third and fourth beakers, a 5-pct-NaOH solution was added to raise pH to 7.2. The third beaker then received NaOCl treatment (2 pct available chlorine) and the fourth received a 1-pct solution of $KMnO_4$. The treated mine water was stirred for 15 minutes and 50-ml samples from each beaker were filtered and acidified. To each beaker incremental amounts of a dilute sulfuric acid (H_2SO_4) were added to lower pH. At various pH levels, 50-ml samples were taken. No differences in resolubilization of manganese were found between the two high-pH precipitation methods using lime or sodium hydroxide (figure 2). Approximately 50 pct of the precipitated manganese resolubilized after pH was lowered to 3.5. However, no manganese resolubilization of manganese occurred for the sludge precipitated with the chemical oxidants (NaOCl and $KMnO_4$).

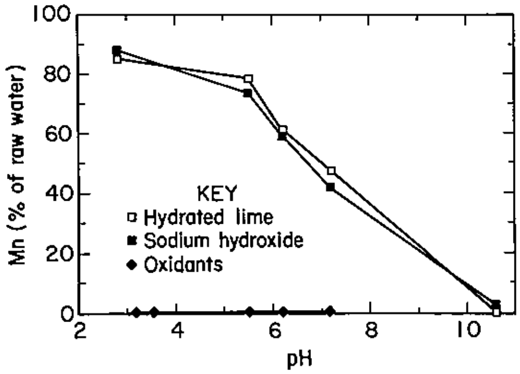

Figure 2.--Comparison of manganese resolubilization from acid mine drainage sludge precipitated with sodium hydroxide and hydrated lime (high-pH method) and with chemical oxidants (Sodium hypochlorite and potassium permanganate).

Although an elevated iron to manganese ratio facilitated manganese removal, it also resulted in a less stable sludge. Mine waters III and IV were treated with a 5-pct solution of NaOH to pH 10.5. Dilute sulfuric acid was added to each mine water and samples were taken at various pH levels as in the previous test. Figure 3 shows the removal and resolubilization of manganese for mine waters III and IV, which have iron to manganese ratios of 95:1 and 1:11, respectively. For the high-iron AMD, the removal and resolubilization curve follow the same path. Presumably, this indicates that much of the manganese was removed by adsorption to ferric hydroxide, and subsequently desorbed with depression of pH. For the low-iron water, the manganese in the sludge was more stable.

The other factor that influenced the stability of manganese in AMD sludge was the age of the sludge. Mine water V was treated with NaOH (20-pct solution) to pH 10.5 and the water-sludge mixture was stored in a loosely covered container. After aging for three months, the mixture was stirred and H_2SO_4 was added to lower the pH. Figure 4 shows that the manganese in AMD sludge becomes more stable as it ages.

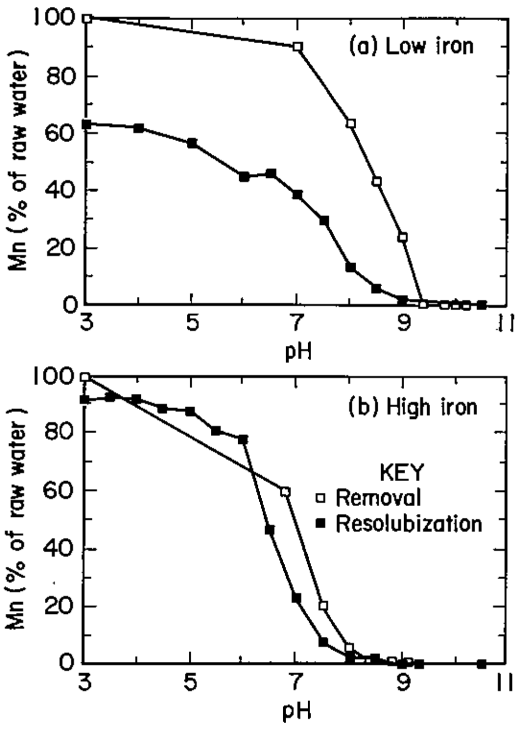

Figure 3.--Removal and resolubilization of manganese. Untreated acid mine drainage contained (a) low (7.7 mg/L) or (b) high (7,3000 mg/L) iron concentrations. Sludge was precipitated with the high-pH method using sodium hydroxide.

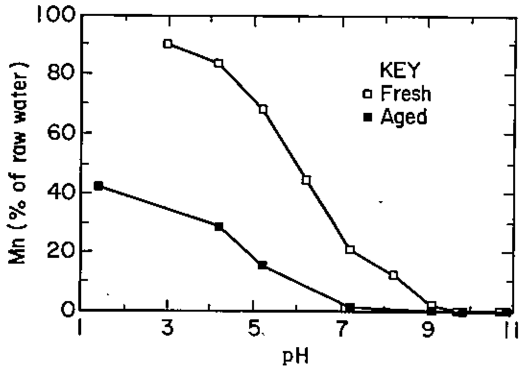

Figure 4.--Comparison of manganese resolubilization from freshly precipitated acid mine drainage sludge and sludge aged 3 months. Sludge was precipitated with the high-pH method using sodium hydroxide.

Behavior of Other Metals

Regulation of manganese was based partly on the fact that it acted as a surrogate for removal of other potentially more toxic metals. Therefore, concurrent with the test on mine waters III and IV outlined above, the removal and resolubilization of other metals were also investigated. Figure 5 shows the removal of the other metals from mine waters III and IV. The ratios of iron concentration to the sum of the concentrations of other metals (manganese, copper, nickel, zinc, and chromium) were 1:12 and 47:1 for mine waters III and IV, respectively. Like manganese, these metals were removed at lower pH values in the high-iron mine water presumably by adsorption to ferric hydroxide. The resolubilization of these metals was also influenced by the concentration of iron in the mine water (figure 6). These metals were more soluble in sludge precipitated from the high iron mine water.

We also investigated the ability to permanganate and hypochloride to remove copper, nickel, zinc and chromium. NaOH (5-pct solution) was added to 1 liter of mine water IV to raise pH to 6.0 and was left to settle for 3 days. This partially neutralized, water-sludge mixture was split into three equal portions and sampled. One portion was treated with a 5-pct-NaOH solution to pH 10.4, another portion was treated with a 1.5-pct solution of potassium permanganate, and the remaining portion treated with an 8-pct available chlorine solution of hypochlorite. Analyses showed that the initial neutralization to pH 6.0 removed all of the chromium and some of the nickel, zinc, copper and manganese. Treatment with NaOH removed the remaining amounts of these metals. However, the oxidants, while effectively removing manganese, were unable to remove nickel, zinc, or copper.

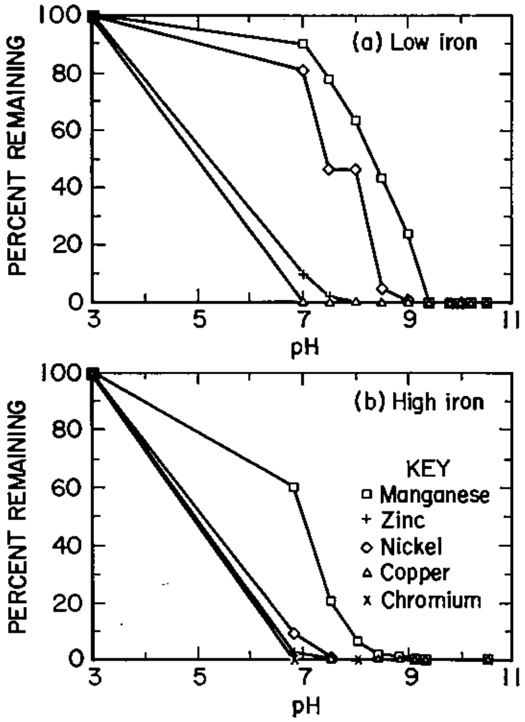

Figure 5.--pH required to remove manganese, zinc, nickel, copper, and chromium from acid mine drainage containing (a) low (7.7 mg/L) and (b) high (7,300 mg/L) iron concentrations using the high-pH precipitation method (sodium hydroxide).

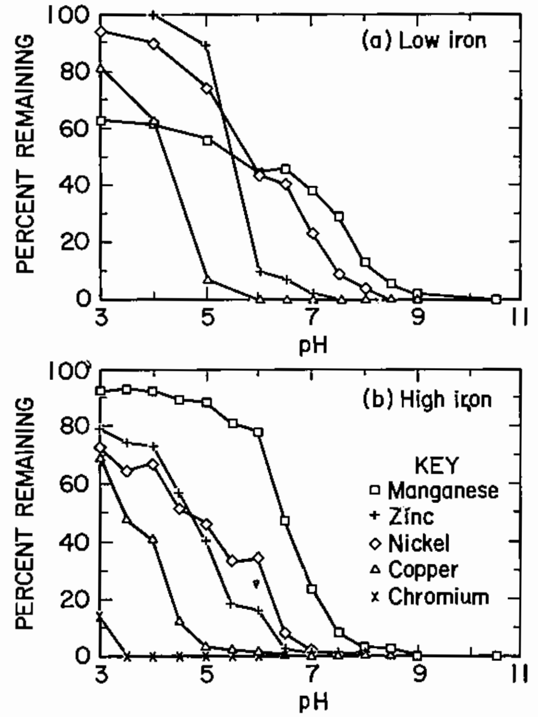

Figure 6.--Resolubilization of manganese, zinc, nickel, copper, and chromium from sludge precipitated from acid mine drainage containing (a) low (7.7 mg/L) and (b) high (7,300 mg/L) iron concentrations. Sludge was precipitated with the high-pH method using sodium hydroxide.

DISCUSSION

In order to comply with effluent limits for manganese, mine operators have two main treatment options: use of alkaline materials for high-pH removal or use of chemical oxidants. The principal advantage of the high-pH method is cost. Chemical costs for this method are two to three times less than for the chemical oxidants. However, at some sites, the reduction of manganese to 2 mg/L may necessitate discharging water with a pH higher than the effluent limit of 9.0. A mine operator in this situation is commonly granted a variance that permits a high-pH discharge, which may be deleterious to the environment (Kleinmann and Watzlaf 1986). Another disadvantage of the high-pH method is the instability of the sludge it produces. Although we found that the manganese in the sludge becomes somewhat more stable after three months, up to 30 percent can resolubilize at pH 4.2. The effects of longer aging periods are not known. If the sludge is disposed of in or on the backfill, any manganese that resolubilizes may need to be retreated. The same may be true of underground disposal. This cycle of treatment, precipitation, sludge disposal, resolubilization, and retreatment may be repeated indefinitely at great expense to the operator. In fact, the high manganese concentrations currently found in some mine drainage may be due to sludge resolubilization.

The use of chemical oxidants produces a stable manganese precipitate, however, treatment costs are greatly increased. These chemicals also require very accurate control of dose rate. In order for hypochlorite to be effective, enough chemical must be added to produce a chlorine residual. With adequate detention time and proper chemical dosage, this chlorine residual will dissipate before discharge. However, overtreatment and pond short-circuiting could result in discharge of high residual chlorine levels and damage to the environment. Similarly, the dosage of permanganate needs precise control. Too much permanganate will result in excess MnO_4^-, which will place the effluent in violation of the manganese limit. Also, although very effective at removing manganese, these chemicals do not remove nickel, zinc, or copper.

The problem of resolubilization of manganese and other metals from acid mine drainage sludge is potentially very significant. Millions of tons of AMD sludge have been and are being disposed of with little or no concern to potential metal resolubilization. The resolubilization of this sludge could cause mining companies significant increases in treatment costs or, if released to the environment, substantial environmental damage. Additional research is needed to determine the effects of long-term aging on AMD sludge in the treatment pond and after disposal. Other factors involved in removal and resolubilization need to be delineated in order to evaluate current treatment and disposal practices.

CONCLUSIONS

Tests using five different mine waters investigated the removal and resolubilization of manganese as well as other metals from AMD using various chemical techniques. The major conclusions of this study are:

1. When sodium hydroxide or lime was used, minimum pH values necessary to reduce manganese below 2.0 mg/L ranged from 8.4 to 10.2.

2. The pH necessary to remove manganese from mine water with an iron:manganese ratio of 95:1 was approximately 1.5 pH units less than from a mine water with an iron:manganese ratio of 1:11.

3. In the high-iron mine water (7,300 mg/L), 50% of manganese, nickel, zinc, and copper resolubilized at pH 6.6, 5.8, 5.6, and 3.5, respectively.

4. In the low-iron mine water (7.7 mg/L), 50% of manganese, nickel, zinc, and copper resolubilized at pH 5.6, 4.5, 4.7, and 4.3, respectively.

5. Manganese was stable to pH 3.5 in the sludges generated with permanganate or hypochlorite.

6. The high-pH method using sodium hydroxide significantly reduced concentrations of nickel, zinc, and copper; however, permanganate and hypochlorite did not.

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