CHEMICAL STABILITY OF MANGANESE AND IRON IN MINE DRAINAGE TREATMENT SLUDGE: EFFECTS OF NEUTRALIZATION CHEMICAL, IRON CONCENTRATION, AND SLUDGE AGE[1]

by

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Abstract. The objective of this research was to determine how various factors influence the solubility of iron and manganese in mine drainage treatment sludge. Sludge samples from the field and laboratory-generated sludge samples were used for this study. The sludge collected in the field was subjected to lower pH conditions by sulfuric acid titration within one hour of precipitation and after one, two, four, and six months of aging. Two conditions were used for sludge aging: under the treated supernatant to simulate aging in a settling pond and in air to simulate aging in a drying pond or disposal on coal spoil. Additional tests were performed using untreated mine drainage collected in the field and treated in the laboratory with hydrated lime, sodium carbonate, or sodium hydroxide. Prior to alkaline treatment, iron in the form of ferric sulfate was added to portions of this water to represent various levels of iron. The results of these tests indicate: 1) sodium carbonate produced a less stable sludge than either lime or sodium hydroxide, 2) iron and manganese were less stable when iron was precipitated as ferrous as opposed to ferric hydroxide, 3) aging increased sludge stability, particularly aging in air, and 4) manganese was slightly more stable in sludge precipitated with high iron concentrations.

Additional key words: Acid mine drainage, acid mine drainage treatment sludge, metal hydroxide solubility.

Introduction

Chemical Treatment of Acid Mine Drainage

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 the addition of alkaline material, commonly lime (CaO or Ca(OH)$_2$), sodium hydroxide (NaOH), or sodium carbonate (Na$_2$CO$_3$); natural or mechanical aeration; and settling (U.S. Environmental Protection Agency 1983). When the pH of the drainage is raised to seven or eight, and there is sufficient time allowed for settling, most

mine water will meet the standards for pH, iron, and suspended solids. However, this treatment will rarely reduce manganese levels below effluent limits. 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 four years. Owens (1963) reported that a pH of at least 9.3 was necessary to remove over 50% manganese from solution using lime. In another study, pH values above 10 were necessary to reduce manganese concentrations below effluent limits for some mine drainage waters (Watzlaf 1985). At these 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 can be granted a variance that permits discharge of water with a pH greater than 9.0. The need to raise pH to these high levels can increase chemical treatment costs 20% to 100% over the costs to remove iron (Watzlaf 1985) and will increase the volume of acid mine drainage treatment sludge. 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.

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https://doi.org/10.21000/JASMR90010003

Table 1. Federal Effluent Limitations

Pollutant or Pollutant Property	Maximum for any 1 day	Average of daily values for 30 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

The sludge generated from the treatment of acid mine drainage (AMD) is typically (1) disposed of in underground coal mines, (2) disposed of with coal refuse or coal mine spoil, or (3) permanantly retained in ponds (Ackman 1982, Moss 1971). The fate of metals in the disposed sludge has not been examined. Underground disposal practices are receiving considerable attention due to pending regulation of class V injection wells by the U. S. Environmental Protection Agency. The problem of metal solubilization from AMD treatment sludge is potentially very significant. Millions of tons of mine drainage sludge have been and are being disposed. The solubilization of metals from this sludge could lead to significant increases in treatment costs as well as future liability to treat these metals.

Iron and Manganese Precipitates

Iron exists in acid mine drainage either in the ferrous (Fe^{2+}) or ferric (Fe^{3+}) form. Ferrous iron oxidation is dependent on pH and dissolved oxygen concentration of the water. At pH 7 and with ample supply of dissolved oxygen, ferrous iron oxidation proceeds very rapidly. Once iron is converted to the +3 state, ferric iron will hydrolyze to form ferric hydroxide. If the pH of mine drainage is raised above 8.3 and there is not enough oxygen available for ferrous iron oxidation, ferrous hydroxide can form (Stumm and Morgan 1981).

The precipitation and removal of manganese is more complex than that of iron. Soluble manganese is thought to exist in AMD mainly as Mn^{2+}, however, it can also exist in oxidation states of +3, +4, +6, and +7 (Sienko and Plane 1966, Morgan 1967). Initially, the average valence of manganese in an 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 of these minerals are eventually transformed into the more stable γ-MnOOH - manganite (Murray et al. 1985, Stumm and Giovanoli 1976). Stumm and Morgan (1981) present a schematic showing initial formation of amorphous $Mn(OH)_2$ followed by tranformation into hausmannite, feitknechtite, manganite, and pyrolusite (MnO_2) in the presence of oxygen.

Manganese can also be removed by adsorption onto reactive surfaces. Ferric hydroxide ($Fe(OH)_3$) as well as 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. 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). If carbonates are present and oxygen is not readily available (low Eh), divalent iron and manganese can form $FeCO_3$ and $MnCO_3$, respectively (Stumm and Morgan 1981).

As an alternative to precipitation of manganese by the high-pH method, strong oxidizers (permanganate, chlorine dioxide, hypochlorite, or ozone) can be used. These chemicals oxidize manganese to pyrolusite (MnO_2) (Evangelou 1984, Clark et al. 1977). The use of chemical oxidants produces a stable manganese precipitate, however, treatment costs are greatly increased (Watzlaf 1985). 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 residual chlorine will dissipate before discharge. However, overtreatment and/or pond short-circuiting can result in discharge of high residual chlorine levels and subsequent 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. Because of these possible problems some state regulatory agencies discourage the use of these chemicals. Knocke et al. (1987) found that hydrogen peroxide was not effective for oxidizing manganese.

Experimental Methods

This paper discusses the results of various experiments to determine the effects of sludge aging, iron concentration, and alkaline treatment chemical on the stability of iron and manganese in AMD treatment sludge. The first series of tests consisted of collecting field samples and aging these samples in the laboratory for one, two, four, and six months. The second test series investigated the effects of iron concentration and treatment chemical in laboratory-generated sludge.

Aging of Field Samples

The first series of tests involved collecting AMD treatment sludge from five mine sites. These sites were selected based on manganese and iron concentration of the raw water and type of treatment chemical used. Table 2 shows the raw water quality and treatment chemical. Sites C, 7, M, and W treated seepage from reclaimed surface mines. Site S treated water from the pit of an active surface mine. Sites C and S both used sodium hydroxide with the In-line System (ILS), which is an aeration and mixing device developed by the Bureau of Mines (Ackman and Kleinmann 1985, Ackman and Place 1987). Site 7 added hydrated lime

utilizing a screw feeder. A gravity-fed hopper loaded with sodium carbonate briquettes was used at Site M. Sodium hydroxide was directly added to the raw water at Site W to raise pH to 11.6. Due to this high treatment pH, to the ferrous form of the iron, and to very little aeration, the sludge produced at Site W exhibited the typical green color of ferrous hydroxide. At Sites C, S, and 7, the treatment systems promoted aeration; therefore, sludge produced at these sites was a brownish-orange color indicating the precipitation of iron as ferric hydroxide.

At each site, three samples were collected immediately down stream of the point where the treatment chemical was added. These samples contained both treated water and resultant sludge. One of the three samples was used to determine stability of iron and manganese upon immediate pH depression by adding sulfuric acid to the stirred sludge/water mixture in the field. At a series of predetermined pH values, the stirring was stopped and the sample was permitted to settle. After 15 minutes, a 20 ml portion was withdrawn, filtered (0.45 μm), and acidified for subsequent metal analyses. The second sludge sample was aged while submerged under the treated supernatant water. Portions of these aged samples were tested for stability one, two, four, and six months after collection, using the sulfuric acid procedure outlined above. The third sample was filtered and aged in air and tested for stability after one, two, and four months of aging. Approximately 0.25 g of air-aged sludge was ground with mortar and pestle and added to 250 ml of distilled water. The mixture was stirred and sulfuric acid was added as outlined above.

Table 2. Raw water quality* and treatment chemical for the five sites used in sludge aging tests.

	C	S	7	M	W
pH	3.4	3.5	3.3	3.4	5.0
Acidity	330.	740.	460.	180.	680.
Sulfate	1830.	4350.	1980.	1400.	2980.
Ferrous Iron	NA	NA	37.0	NA	290.
Total Iron	12.6	208.	54.6	2.7	290.
Manganese	48.9	111.	94.0	62.0	117.
Chemical	NaOH	NaOH	Ca(OH)$_2$	Na$_2$CO$_3$	NaOH

* All concentrations in mg/L except pH in pH units. Acidity in mg/L as CaCO$_3$. NA = not analyzed.

Effects of Iron Concentration and Treatment Chemical

In addition to the above tests using sludge samples collected at various treatment plants, laboratory experiments were conducted under more controlled conditions to examine the effects of iron concentration and treatment chemical on the solubility of iron and manganese precipitates. A large sample of mine water containing more manganese than iron was brought back to the laboratory. This water sample was split into three portions. Additional iron (ferric sulfate) was added to two of the portions to yield three levels

of iron, which will be referred to as low, medium, and high (Table 3). Each portion was treated with an alkaline substance to raise pH to approximately 10 in order to precipitate iron and manganese. The alkaline substances tested included hydrated lime, sodium hydroxide, and sodium carbonate. As in the previous tests, sulfuric acid was used to lower pH. At pH values of 10.0, 8.5, 7.0, 5.5, and 3.0, 20 ml were withdrawn, filtered (0.45 μm), and acidified for metal analysis.

Table 3. Raw water quality* of the low, medium, and high iron water used in laboratory tests.

	Low	Medium	High
Ferrous Iron	< 6	< 6	< 6
Total Iron	17.5	59.7	559
Manganese	69.3	70.1	71.7

* All concentrations in mg/L.

Chemical Analyses

For the unacidified samples of raw and treated mine water, acidity or alkalinity was determined by a fixed-end-point titration to pH 8.3 using sodium hydroxide or to pH 4.5 using sulfuric acid, respectively. Sulfate was analyzed by passing the sample through a cation-exchange resin and titrating with barium chloride using thorin (o-[2-hydroxy-3,6-disulfo-1-naphtyl)azo] benzenearsonic acid, disodium salt) as an indicator. For ferrous iron determinations, a potassium dichromate titration with a platinum redox electrode in the first derivative mode as an end-point indicator was used. Total iron and manganese were analyzed by inductively coupled argon plasma spectroscopy.

Results and Discussion

In all of the results, the solubilization of iron or manganese was expressed as a fraction of the total amount of the metal in the sample. For the air-aged sludge, the total metal content was calculated by dissolving a known weight of sludge in both concentrated hydrochloric and nitric acids. For all of the other tests, total metal content was based on the volume of water collected and the concentraion of metal in this raw, untreated water. The removal of 20 ml portions, acidification of these portions, and addition of sulfuric acid to the samples were acccounted for in the calculation of fraction of metal solubilized.

Aging of Field Samples

Freshly precipitated manganese began to solubilize at pH 8.5. At pH 7.0 and 3.0, respectively, 10% to 80% and 30% to 100% of the original manganese solubilized (figure 1a). Manganese became more stable after the sludge was aged for six months under water (Figure 1b). Four of the sites exhibited very similar trends of manganese solubilization; however, site M only showed a small increase in stability with 80% solubilizing at pH 3.0. This was the only site that used sodium carbonate for treatment.

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For the fresh precipitates, manganese in the sludge from Site W was the least stable (Figure 1a). At this site, 20% of the iron, which was precipitated as ferrous hydroxide, solubilized at pH 7 (Figure 2). Other sites, where iron was precipitated as ferric hydroxide, produced sludge in which iron was stable down to pH 3.5. As the sludge from Site W aged under water, its color changed from green to brownish orange indicating the coversion from ferrous to ferric hydroxide. During this aging, both iron and manganese became much more stable.

The majority of the increase in manganese stability was realized within the first month of aging for Sites S, C, and 7, which used lime or sodium hydroxide and precipitated iron as ferric hydroxide (Figure 3). Sludge from Site M, which used sodium carbonate, and Site W, which precipitated ferrous hydroxide, both showed increases in manganese stability throughout the six-month test (Figure 4).

Figure 1. Effect of pH depression on the solubilization of manganese from the sludge of five mine sites, (a) immediately after metal precipitation and (b) after six months of aging under water.
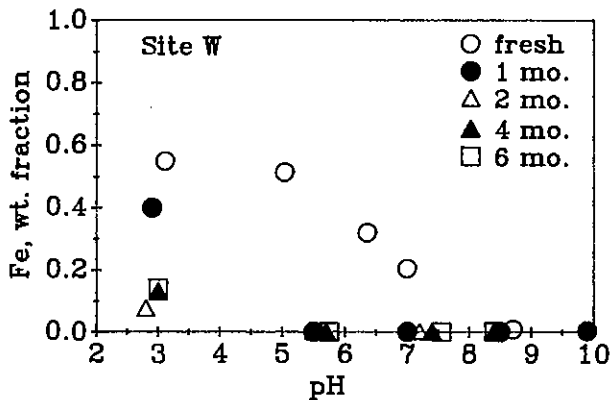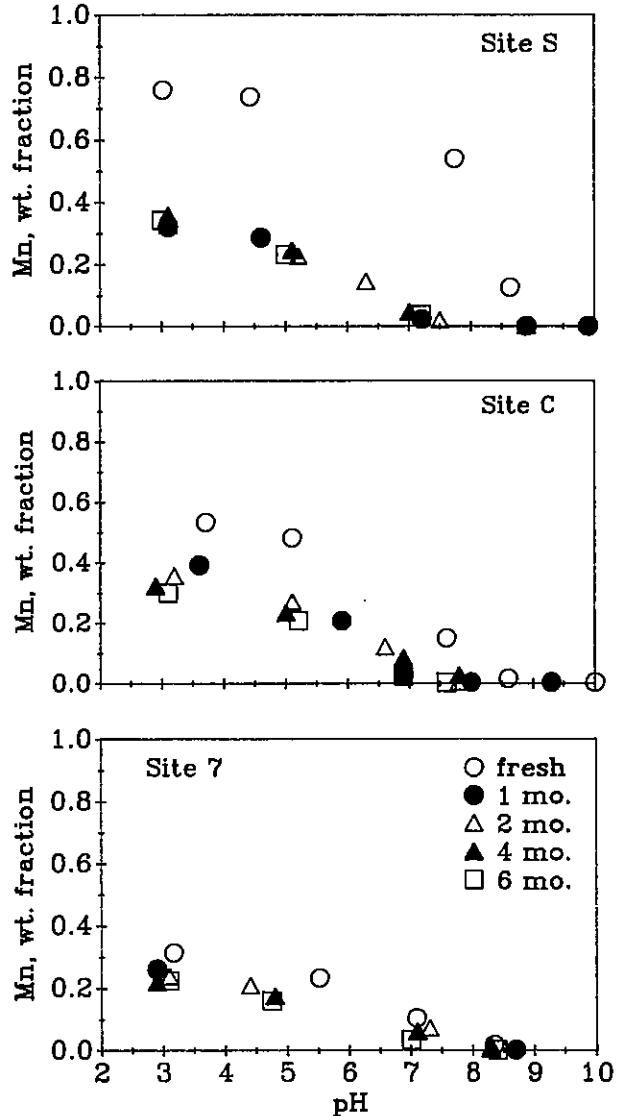

Figure 3. Effect of pH depression on the solubilization of manganese from sludge from Sites S, C, and 7 as it aged under water.

Figure 2. Effect of pH depression on the solubilization of iron from sludge of Site W as it aged under water.

At all sites, iron and manganese became more stable when the sludge was aged in air than when it was aged under water. Table 4 shows manganese and iron solubilization after one month of aging under water and in air for Sites C, W, and M. Sites S and 7 are not shown since they were very similar to Site C. Air aging had the greatest effect on Site W. At pH 2.9 or 3.0, 40% and 69% of the iron and manganese, respectively, solubilized from the sludge aged under water, compared to 1% and 3%, respectively, solubilized from the air-aged sludge.
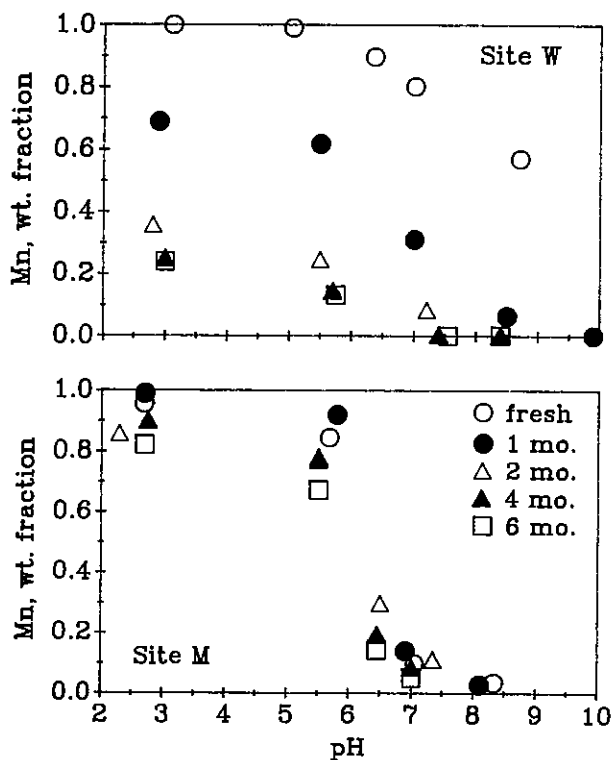
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Figure 4. Effect of pH depression on the solubilization of manganese from sludge from Sites W and M as it aged under water.

Table 4. Fraction of Metal Solubilized After 1 Month of Aging in Air and Under Water.

Site	pH	Manganese		Iron	
		Water	Air	Water	Air
C	7.0	---	<0.01*	---	<0.01
	6.9	0.03	---	<0.02	---
	5.9	0.21	---	<0.02	---
	5.7	---	<0.01	---	<0.01
	5.0	---	0.03	---	<0.01
	3.6	0.39	---	0.10	---
	3.0	---	0.45	---	0.07
S	8.5	0.07	---	<0.01	---
	7.0	0.31	---	<0.01	---
	6.1	---	<0.01	---	<0.01
	5.5	0.62	---	<0.01	---
	4.3	---	<0.01	---	<0.01
	3.0	---	0.03	---	0.01
	2.9	0.69	---	0.40	---
M	8.1	0.03	---	<0.09	---
	7.1	---	0.08	---	<0.02
	6.9	0.14	---	<0.09	---
	5.8	0.92	---	<0.09	---
	4.2	---	0.65	---	<0.05
	2.7	1.00	---	0.35	---

* "<" indicates fraction solubilized was below detectable limits. These limits vary depending on dilution before analysis as well as total metal content in the sludge.

Effects of Iron Concentration and Treatment Chemical

For the laboratory-generated sludge, the chemical stability of manganese was the same for the sludges precipitated with lime or sodium hydroxide (Figure 5). However, sodium carbonate produced a sludge more prone to manganese solubilization. At almost all pH values and regardless of iron concentration, approximately twice as much manganese solubilized from the sodium carbonate-treated sludge than from the lime or sodium hydroxide sludges.

Figure 6 shows that manganese was more stable when it was precipitated with high iron concentrations with all three chemical treatments. This increase in stability was most prominent between pH 3.0 and 7.0 for the lime and sodium hydroxide treatments, and between pH 7.0 and 8.5 for the sodium carbonate treatment.
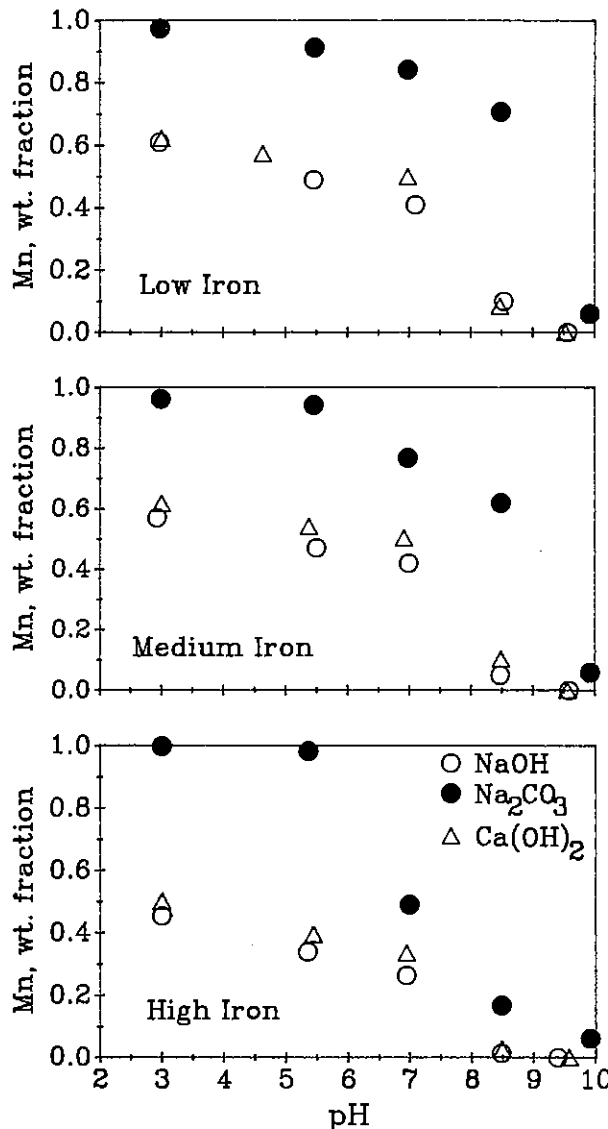

Figure 5. Effect of pH depression on the solubilization of manganese from unaged, laboratory-generated sludge. To show differences between treatment chemicals; sodium hydroxide, sodium carbonate, and lime treatments are plotted together for each concentration of iron in the raw water.
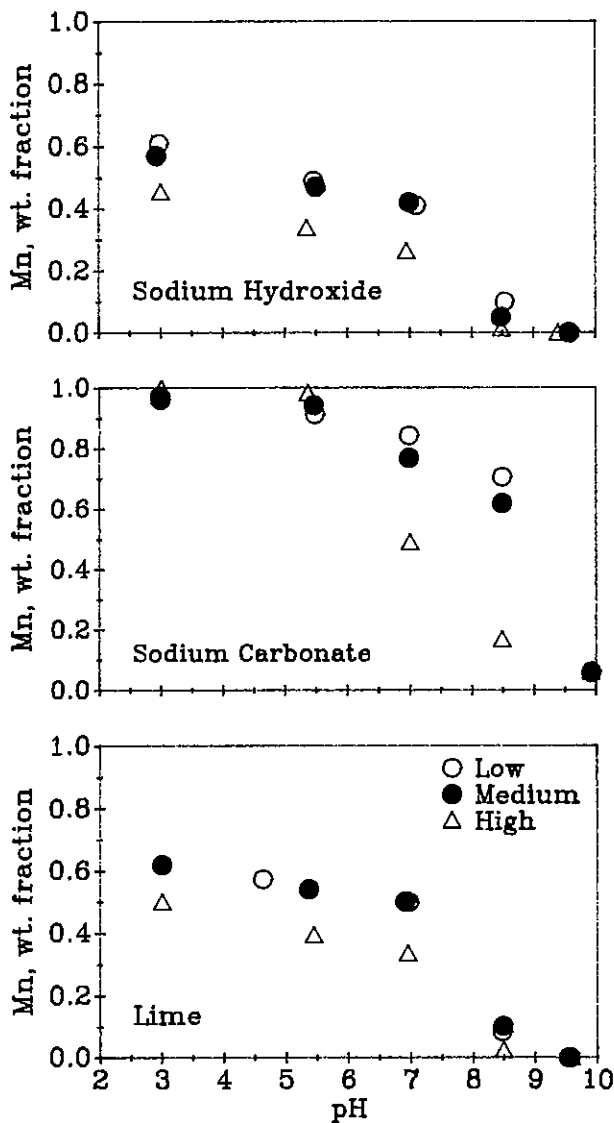
Figure 6. Effect of pH depression on the solubilization of manganese from unaged, laboratory-generated sludge. To show differences between iron concentrations; low, medium, and high iron concentrations are plotted together for each treatment chemical.

In all of the tests, iron remained insoluble at all pH values ≥ 5.5. At pH 3, the most iron solubilized from the sludge resulting from sodium carbonate treatment (Table 5).

Table 5. Fraction of iron solubilized at pH 3 from sludge treated with the listed chemical.

IRON LEVEL	Na_2CO_3	NaOH	$Ca(OH)_2$
Low	0.58	0.12	0.11
Medium	0.69	0.09	0.16
High	0.13	0.04	0.04

CONCLUSIONS

Based on the results of laboratory studies and analysis of field samples the following conclusions can be made:

1. Iron and manganese were more stable in sludges precipitated with lime or sodium hydroxide than in sludge precipitated with sodium carbonate.

2. Iron and manganese were less stable if the iron was precipitated as ferrous hydroxide than if precipitated as ferric hydroxide.

3. Generally, iron and manganese were more stable in air-aged sludge than in sludge aged under water.

4. The largest increase in stability occurred in the first month of aging.

5. Manganese was more stable if precipitated with high iron concentrations.

SUMMARY

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. Chemical oxidants are very rarely used due to their high costs and/or to their restriction by state regulatory agencies. A major concern of the high-pH method is the instability of manganese in the sludge it produces. Although we found that the manganese in the sludge becomes somewhat more stable as it ages, significant amounts of manganese may solubilize if the pH is not kept high. If hydrated lime or sodium hydroxide is used, 20% of the original manganese may solubilize at pH values between 5 to 7, even after six months of aging under water. If aged in air for four months, 10% to 20% of the manganese can solubilize at pH 4. If sodium carbonate is used, 75% and 65% of the manganese can solubilize at pH 4 from sludge aged for six months under water and sludge aged four months in air, respectively. If the sludge is disposed in or on surface mine backfill, any manganese that solubilizes 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. Additional research is needed to determine the fate of metals at actual sludge disposal sites in the field.

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