

Treatment of Mine Water to Remove Manganese

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Abstract. Typical acid mine water contains 1-8 mg/L Mn, but concentrations of 50-100 mg/L are not uncommon. At present, most mine operators with manganese problems use excess alkalinity to raise the pH of water to 10 or higher to facilitate manganese oxidation and precipitation. Excess alkalinity, although it increases treatment costs 20-100 pct, was determined by the Bureau of Mines to be less expensive than NaOCl and KMnO_4 (chemical oxidants). However, laboratory tests indicate that the manganese precipitated by excess alkalinity is easily resolubilized, while that produced by the oxidizing agents is relatively stable.

The Bureau also studied two novel approaches to the manganese problem. One was an inexpensive pipeline treatment system device known as the ILS, which was developed by the Bureau to aerate and neutralize mine water. At three mines with influent Mn concentrations of 10-68 mg/L, use of the ILS reduced Mn concentrations to less than 2 mg/L at pH values of only 6.8-7.3.

Another novel approach to mine water treatment is the construction of wetlands on mined sites. Results from ongoing tests indicate that this biological treatment can be engineered to optimize either iron or manganese removal. Moderate Mn concentrations (14-30 mg/L) have been reduced to 2-6 mg/L in constructed wetlands at four mine sites in western Pennsylvania.

Introduction

The oxidation of manganese (Mn) in aqueous systems is complex. Mn^{2+} can be oxidized to either Mn^{3+} or Mn^{4+} ; the valence of initially precipitated air-oxidized manganese minerals typically lies between 2.67 and 3.0 (Mn_3O_4 --hausmannite and β - MnOOH --feitknechtite, respectively).^{1,2} Hem¹ has shown that feitknechtite forms preferentially at low temperatures (10° C and below), while hausmannite is the dominant precipitate at 17° C and above. Both these minerals are eventually transformed into the more stable γ - MnOOH --manganite.^{2,3} The rate of Mn^{2+} oxidation is pH-dependent, and is extremely slow below pH 8.5. For example, dilute solutions of manganese nitrate ($\text{Mn}(\text{NO}_3)_2$) maintained in the presence of dissolved oxygen at pH 8.4 in the laboratory at 20° C showed virtually no oxidation for over 4 years.⁴ However, the oxidation process is catalyzed in nature by bacteria and by reactive surfaces. Included in the latter are Mn precipi-

tates themselves, so that Mn oxidation can be autocatalytic. Lewis found that manganese in the Susquehanna River was being removed from solution at near-neutral pH, with reaction half-times of a week at 50° C and about a day at 20° C.⁵

Typical acidic mine drainage contains 1 to 8 mg/L Mn, but concentrations of 50-100 mg/L are not uncommon.⁶ The Surface Mining Control and Reclamation Act of 1977 mandates that effluent water should not exceed 4.0 mg/L Mn and that the 30-day average should not exceed 2.0 mg/L.⁷ Although it is occasionally possible to meet this standard by raising the pH to 8.5-9.0, most mine operators with a significant Mn problem must add enough alkalinity to raise the pH to 10 or above.⁸ During the resultant precipitation of Mn, acidity is produced, lowering the pH. If the discharge pH remains above 9.0, the mine operator has two options: apply to the regulatory authority for a variance to discharge high-pH water, or reacidify the high-pH water.

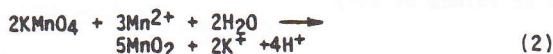
There are two problems with this approach to water treatment. The most obvious is the 20- to 100-pct increase in material costs for the excess alkalinity. Equally important, there is an environmental cost: the effect of the high pH discharge, even if legally acceptable, may be much more detrimental to the biota of a stream than the Mn would be. In this paper, the advantages and disadvantages of several alternative water treatment techniques are addressed.

Chemical Treatment

Background

One alternative to the use of excess alkalinity is the use of a chemical oxidant to remove Mn at near-neutral pH. Oxidizing agents used for conventional water treatment include chlorine, sodium hypochlorite, calcium hypochlorite, potassium permanganate, hydrogen peroxide, and ozone.⁶ While any of these could be used, sodium hypochlorite (NaOCl) and potassium permanganate (KMnO₄) were chosen for comparison with the excess alkalinity method using sodium hydroxide (NaOH). The selection of these three chemical treatments was based on ease of use, availability, effectiveness, and likelihood of acceptance by the mining industry.

The manganese-oxidizing reactions for sodium hypochlorite (equation 1) and potassium permanganate (equation 2) are shown below. Note that the oxidizing agents produce Mn⁴⁺, as opposed to air oxidation (discussed earlier), which produces Mn³⁺. MnO₂ is thermodynamically more stable than the less-oxidized Mn precipitates.⁹



Field Tests

The intent of the field tests was to determine the most economic chemical treatment that would successfully reduce Mn concentrations below 2 mg/L. Testing was conducted at two surface mine sites in Greene and Venango Counties, PA.

The Greene County site is an active surface mine with over half the site mined and reclaimed. The 40-gal/min flow of raw water (pH 4.5) was being treated with NaOH to pH 8.0, followed by settling in two ponds (fig. 1). Our treatment chemicals were added to the effluent of pond 1 (point B) where the ferrous iron (Fe²⁺) and Mn concentrations averaged 88 mg/L and 78 mg/L, respectively. Water samples were collected at point C and left to settle for 1 day, after which the supernatant liquid was analyzed.

All of the chemicals proved to be suitable for reducing Mn levels to less than 2 mg/L.⁷ Excess alkalinity was the most cost effective method. Chemical costs per 1,000 gal to reduce Mn concentrations to 2 mg/L were \$0.97, \$1.92, and \$2.26 for NaOH, NaOCl, and KMnO₄, respectively. This is based on prices of chemicals as delivered to the mine: \$0.28/gal and \$0.80/gal, for bulk quantities of 20-pct-NaOH and 15-pct-NaOCl

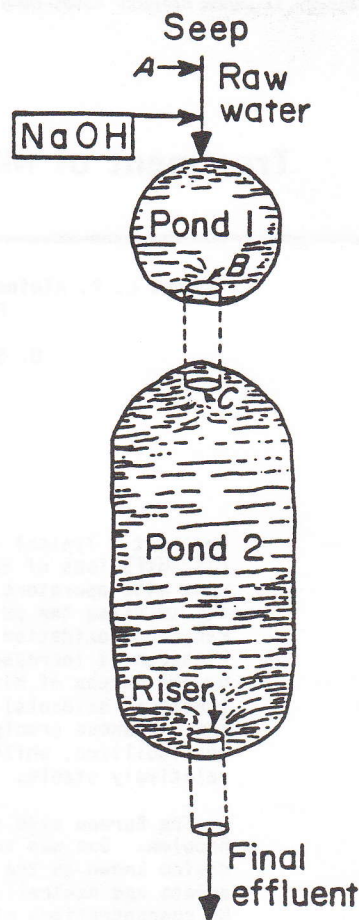


Figure 1. Water treatment system at Greene County field site.

solutions, respectively, and \$1.34/lb for granular KMnO₄. Bulk purchase price of KMnO₄ is about \$1.08/lb, but a typical mine would not require such large quantities (minimum 20 metric tons).

Since the high Fe²⁺ concentrations may have increased the demand for NaOCl and KMnO₄, additional testing was conducted to determine the effects of Fe²⁺ concentrations on chemical requirements. In these additional tests, raw water was collected at the seep (point A of figure 1). NaOH was added to the raw water to raise the pH to 7.5. This water was then aerated by pouring it from one bucket 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 and Fe²⁺ concentrations were reduced to below 1 mg/L. Treatment chemicals were then added to this water, which was low in Fe²⁺ and high in Mn (95 mg/L).

The samples were left to settle for 1 day, after which the supernatant liquid was sampled and analyzed. Figure 2 shows the relative performance of the three chemicals: excess alkalinity again proved to be the least expensive method to reduce

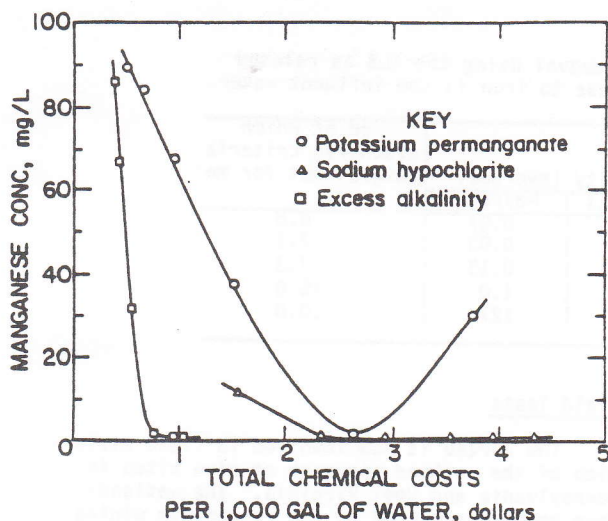


Figure 2. Cost comparison of chemical treatments at site in Greene County, PA.

Mn below 2 mg/L. Removal of Fe^{2+} did not reduce the chemical requirements for NaOCl or KMnO_4 .

To insure that these results were not related to the specific site selected, the test procedure was duplicated at an inactive surface mine in Venango County, where the 170-gal/min flow was being treated with hydrated lime, raising the pH to 8.2. This treated water contained 70 mg/L Mn and less than 2 mg/L Fe.

Total chemical costs per 1,000 gal to reduce Mn to 2 mg/L were \$0.53, \$0.95, and \$1.70 for NaOH , NaOCl , and KMnO_4 , respectively. This assumes the same chemical prices presented earlier, although these prices would normally vary, based on location of the mine site.

In these tests, excess alkalinity was the least expensive method to reduce manganese below effluent limitations, though pH may have to be raised to a point where the final discharge exceeds the effluent limitation for pH (9.0). However, the resultant sludge is thermodynamically less stable than that produced by chemical oxidants.⁹ Our ongoing laboratory tests indicate that 1/4 of the NaOH -precipitated Mn is resolubilized at neutral pH and that nearly half is resolubilized at pH 5.3. In contrast, Mn precipitated by NaOCl or KMnO_4 is stable (at least temporarily) at pH 3.2 and above.

The Bureau has been investigating two alternative approaches to manganese removal. These are admittedly experimental practices, but are options to consider at sites where the cost of manganese removal is a significant problem.

Physicochemical Treatment

The Bureau has developed an in-line aeration and neutralization system (ILS) that functions in a pipeline using energy provided by existing mine water discharge pumps. The system is inexpensive, has no moving parts, and costs less to operate and

maintain than a conventional water treatment system.

The ILS combines two off-the-shelf components: a jet pump (also known as an eductor), which contains a nozzle and a suction chamber, to entrain air and/or an alkaline fluid by Venturi action; and a static mixer, which is an 8-ft pipe with an internal helix, constructed so as to reverse the rotational direction of flow every foot. More detail on the unit and its high efficiency with respect to iron oxidation (at Fe^{2+} concentrations of 350 mg/L or less) can be found in previous publications^{10, 11}.

During field trials of the ILS, it was discovered that manganese was being removed from the mine water for hours and even days (depending on initial concentration) after being treated to neutral or near-neutral pH with the ILS. This was initially disconcerting, since the rate of Mn oxidation below pH 8 is normally extremely slow and because no apparent decrease in Mn occurred in the ILS itself. For example, at a site in Braxton County, WV, Mn decreased from 68 mg/L to 13.5 mg/L during 6 hours of retention in a pond after ILS treatment despite a pH below 7; analysis 11 days later showed that essentially all of the Mn was removed.¹⁰

The mechanism of removal was partially explained at the next field test in Westmoreland County, PA, where influent Mn averaged 14 mg/L. The Mn content of the ILS-treated water was immediately reduced to less than 2 mg/L at neutral pH in filtered samples, while unfiltered samples showed virtually no reduction. A subsequent test at a site in Armstrong County, PA, with influent Mn levels of about 10 mg/L, showed a similar pattern.¹¹ Apparently, the Mn is being removed as, or as part of, very small particles during neutralization and aeration in the ILS. Filtration removed most of these particles; settling removed virtually all of them, given sufficient retention time.

One possible explanation is that manganese is being physically removed (scrubbed) from solution by small particles of iron hydroxide as they form and swirl in the ILS. It has already been shown in the laboratory that $\text{Fe}(\text{OH})_3$ will adsorb 0.15 mol Mn^{2+} per mol Fe^{3+} at pH 8.0 and that this rises to more than 0.6 mol Mn^{2+} at pH 8.6.¹² Collins and Buol have also reported Mn^{2+} removal at moderate pH during precipitation of iron and attributed the Mn removal to occlusion and sorption of Mn^{2+} by the ferric hydroxide.¹³

We are currently testing this hypothesis by experimenting with the ILS at two mine sites in central Pennsylvania where dissolved manganese equals or exceeds dissolved iron. We have found that virtually no manganese is removed below pH 9 with the ILS. To meet discharge criteria, the pH had to be raised to 10 at both sites. These results, summarized in Table 1, indicate that manganese removal in the ILS is related to iron concentrations. This supports the hypothesis that manganese was being removed by ferric hydroxide at the first three test sites but leaves open the questions of why manganese adsorption was not significant at the Clearfield County site, and if it plays a significant role in conventional mine water treatment facilities.

Table 1. Efficiency of manganese removal using the ILS as related to the ratio of manganese to iron in the influent water.

Site location	Initial water quality (average)			pH at which discharge criteria (2mg/L) met for Mn
	Fe(mg/L)	Mn(mg/L)	Mn/Fe	
Braxton Cty, WV	965	68	0.07	6.8
Westmoreland Cty, PA	527	14	0.03	7.1
Armstrong Cty, PA	75	10	0.13	7.3
Clearfield Cty, PA	50	50	1.0	10.0
Cambria Cty, PA	1	127	127	10.0

Biological Treatment

Background

The Bureau has investigated the use of sphagnum moss bogs or cattail-dominated wetlands as regenerating biological systems, coupled with limestone neutralization, to provide simple, low-cost treatment of acid mine water. Previous studies of sites where acid mine drainage flows into Sphagnum-dominated bogs demonstrated successful natural treatment. For example, a research group from Wright State University studied a site in the Powelson Wildlife Area in Ohio where *Sphagnum recurvum* was found growing in pH 2.5 water. Iron, magnesium, sulfate, calcium, and manganese all decreased while pH increased from 2.5 to 4.6 (due to Na exchange and formation of H_2S) as the water flowed through the bog. A natural outcrop of limestone located at the downstream end provided sufficient neutralization to raise the effluent pH to between 6 and 7.14

A similar study was conducted by a West Virginia University group at Tub Run Bog in northern West Virginia.¹⁵ They found that acid drainage flowing into the wetland area rapidly improved in quality. In 20-50 meters, pH rose from 3.05-3.55 to 5.45-6.05, while only 10-20 meters of flow through the bog was needed to reduce sulfate concentrations from 210-275 mg/L to 5-15 mg/L and iron from 26-73 mg/L to less than 2 mg/L. Manganese levels were not reported, but overall, the water quality of the bog effluent was reported to be equal or superior to that of nearby streams unaffected by mine drainage.

There are at least four potential mechanisms of manganese removal in a wetland. Wetland vegetation, and especially sphagnum moss, has a relatively high cation exchange capacity that is related directly to the equivalent concentration of components present. Cations appear to be adsorbed primarily in the alternating dead cells in the leaves, with an overall effect similar to that of a nonspecific cation exchange resin.¹⁴ In addition, sulfate-reducing bacteria thrive in the anaerobic bottom waters of a bog, utilizing the naturally supplied organic material and causing sulfide mineral precipitation.¹⁵ Manganese can also be removed as a hydroxide precipitate, either associated with iron floc or precipitated due to catalysis by surface area, but this is probably not significant at acid pH.¹⁶ Finally, manganese-oxidizing organisms exist in the wetlands. These include conventional soil bacteria, prosthecate bacteria (including Metallogenium), sheathed bacteria (including *Leptothrix*), and fungi.¹⁷⁻²⁰

Field Tests

The Bureau is now involved in field evaluation of the wetland approach at mine sites in Pennsylvania and West Virginia. The wetlands have been constructed by the respective mining companies for water treatment; the Bureau is facilitating monitoring and evaluation of the sites so that others can learn from these efforts. Four wetland areas that were constructed during 1984, four constructed during 1985, and three "volunteer" wetland areas on mined lands are currently being monitored.

At the volunteer wetland areas, the mining companies are attempting to utilize and enhance already established cattail (*Typha*) growth, and to divert additional mine water to the wetland areas for treatment.²¹ The velocity of the water in these wetlands ranges from 0.1 to 1.0 ft/s (as measured in less vegetated areas). All three sites are removing iron satisfactorily; average values for Mn removal are listed in Table 2.

With an understanding of wetlands gained from pilot-scale tests and observation of the volunteer wetland areas, two new wetland treatment systems dominated by sphagnum moss, and six wetlands dominated by *Typha* have been constructed. The vegetation was transplanted from nearby wetlands by personnel of Brehm Laboratory of Wright State University and by Ben Pesavento of Environment Analytic Co., who are also responsible (under contract by the Bureau) for monthly monitoring and sample collection. These initial wetland areas range in size from 750 to 8,500 ft² (of which 40 to 60 pct is actual wetted area) and treat flows that range from 2-8 gal/min for the smaller wetlands to over 20 gal/min for the larger wetlands.

Preliminary results from the wetlands that contain only sphagnum moss indicate that very little removal of manganese is occurring at these two field sites. This is in accordance with the results of our earlier pilot-scale tests and the findings of Wieder et al; the cation exchange properties of sphagnum moss favor the removal of iron rather than manganese.^{22,23}

However, manganese is being removed in the *Typha*-dominated wetlands, possibly by manganese-oxidizing bacteria. Figure 3 compares influent and effluent manganese concentrations at one of the constructed wetland sites with the population of manganese-oxidizing bacteria (as determined by R. W. Stone of Pennsylvania State University).²⁴ The site contains 3,500 ft² of wetted area, treats an average flow of 20 gal/min (range: 15-30

Table 2. Manganese removal in wetlands dominated by cattails.
(All of these Pennsylvania sites are successfully reducing iron concentrations to within or near effluent limits)

Site location (county)	Age	Average Mn (mg/L)		Average pH	
		Influent	effluent	Influent	effluent
Clarion	volunteer	55	54	3.3	4.5
Clarion	volunteer	36	2	5.6	6.8
Elk	volunteer	19	5	5.5	7.0
Clarion	1 yr. old	16	3	5.4	7.0
Indian	1 yr. old	16	4	5.2	6.8
Jefferson	3 mo. old	70	18	3.4	7.8
Clearfield	3 mo. old	32	4	6.6	8.3
Butler	3 mo. old	35	10	5.5	6.8
Fayette	2 mo. old	22	6	5.6	6.8

gal/min), and consistently lowers iron from 25 mg/L to less than 3 mg/L. Effective manganese removal was initiated by "inoculating" the site with several pounds of sediment from another site from which manganese was being removed, and adding some agricultural limestone and fertilizer (enough to get algae to bloom). The inoculum may not have been necessary, since the bacteria were already present at low concentrations.

However, bacterial action may not be necessary for manganese removal. An alternative explanation is that the manganese is being removed under reducing conditions as rhodochrosite (MnCO_3). The likelihood of this will be determined by measuring the pH, Eh, and CO_2 concentrations in the limestone-enriched organic substrate where we believe the manganese precipitation is occurring. If the water within the substrate is in equilibrium with atmospheric CO_2 , precipitation of MnCO_3 would be limited to pH 7 and above.⁹ Neutralization reactions could reduce this pH limit somewhat by raising CO_2 concentrations.

In either case, substrate pH is critical in determining whether manganese is removed. Agricultural limestone has been incorporated into almost all of our wetlands. The four wetlands constructed this year include a 6-inch base of agricultural limestone and a 12- to 18-inch layer of lightly fertilized spent mushroom compost as a substrate in areas where vegetation other than sphagnum moss is planted. The decomposing organic material in the mulch provides a low-Eh environment, thereby preventing ferric hydroxide from coating the limestone. This has resulted in an effluent pH of about 7 and removal of 20-30 mg/L Mn (Table 2). Limestone is not incorporated into the substrate for sphagnum moss, since this would result in preferential adsorption of calcium rather than iron. Selection and sequencing of vegetation type are thus important for optimal removal of both iron and manganese.

Summary

Manganese can be removed by methods other than addition of excess alkalinity.²⁵ Chemical oxidizing agents can be used in a conventional treatment facility to provide a neutral-pH legal discharge at most locations; Bureau testing indicates that although this is more expensive than raising the pH to 10, the resultant sludge is more resistant to resolubilization. Either approach requires careful monitoring to maintain a legal discharge, which means that personnel must

be allocated to watch over the water treatment operation.

Alternatively, the ILS can be used to remove manganese at neutral pH. However, it appears that if iron is low or absent, a pH of 10 is still required. More research is needed to determine if the manganese-iron ratio actually controls the pH at which manganese is removed, and if so, what the critical values are.

Wetlands are less expensive than chemical treatment and are cheaper to "operate" than the ILS. However, it is impossible at this time to evaluate the long-term performance of the constructed wetlands. Based on limited observations of up to one year, it appears that manganese removal from acid mine water occurs only in slightly acidic or neutral wetlands. Ongoing tests indicate that moderate manganese concentrations (14-30 mg/L) can be successfully reduced to at or near effluent limits in these wetlands; we believe that additional manganese removal is possible.

There are thus a number of options avail-

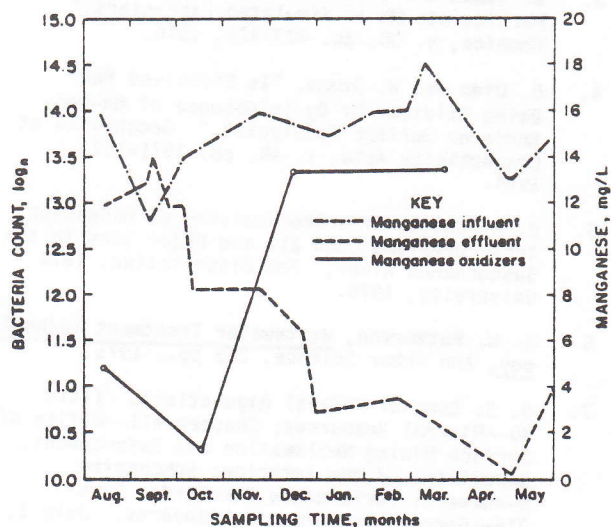


Figure 3. Population of manganese-oxidizing bacteria compared with manganese removal in a wetland with mixed vegetation.

Table 3. - Alternative approaches for control of manganese in acid mine water.

Method	Advantages	Disadvantages
Excess alkalinity	Well understood. Conventional approach. Utilizes existing equipment. Discharge into an AMD-contaminated stream may improve downstream water quality.	Increases treatment costs by 20-100 pct. Discharge of highly alkaline water can be detrimental if receiving stream has little buffering capacity. Mn can be resolubilized.
Oxidizing agents	Water can be treated at near-neutral pH. Use of KMnO_4 enables user to regulate dosage by color. Stable MnO_2 is produced.	Typically more expensive than excess alkalinity. Overtreatment could be dangerous to stream biota. Hypochlorite loses potency with age.
In-line system	Inexpensive. Water can be treated at near-neutral pH. Low-maintenance. Can be portable	Requires at least 20 psi water pressure. May not remove manganese if iron is low.
Wetland	Inexpensive. Low-maintenance. Alternative to chemical treatment.	Requires large area. Most appropriate for small flows. Experimental.

able. Table 3 summarizes the advantages and disadvantages of each approach. Ongoing research will provide additional information on these options, and will perhaps lead to the development of new ones.

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