# CASE STUDIES OF LIMESTONE-BED PASSIVE SYSTEMS FOR MANGANESE REMOVAL FROM ACID MINE DRAINAGE[1]

Arthur W. Rose, P.J. Shah and Brent Means[2]

**Abstract**. The main method for passive removal of manganese is the "Pyrolusite" system, in which a bed of limestone is inoculated with Mn-oxidizing bacteria. Nine sites of this type, plus four limestone-lined channels, have been studied. Other information is incorporated from published work. Effective Mn removal requires oxidizing well-aerated water, as well as prior removal of essentially all dissolved Fe and Al, and pH above about 6.5. Most of the Pyrolusite systems removed Mn from influent values of 6 to 30 mg/L to effluent levels between 0.5 to 1.5 mg/L for a period of 2 years or more. Based on the depth distribution of dissolved $O_2$ and Mn oxide precipitate, most Mn removal occurs in the top 0.3 m of the bed, just below the water surface. The deeper parts of beds do not appear to contribute significantly. Most Mn removal rates range from 1.5 to 5 g/m$^2$/day, with the lower values from beds with influents containing appreciable Fe and Al. Several of the systems have failed because of plugging of the inlet area with silt, leaves, Fe and/or Al precipitate, grass and other materials. Several field tests and experiments suggest that special bacterial inoculation may not be necessary. Three successful limestone-lined channels have been observed, one with an Mn removal rate of about 10 g/m$^2$/day. A shallow bed or channel, lined with limestone, and containing algae to enhance $O_2$, appears to be an improved design.

Additional key words: Pyrolusite Systems, coal mine drainage, bacteria

## Introduction

Many passive methods are being utilized for removal of Fe, Al and acidity from acid mine drainage, including wetlands, ponds, anoxic limestone drains, vertical flow systems (SAPS or VFS's), and open limestone channels. These technologies have been extensively described in the literature and their success and limitations discussed (Hedin et al., 1994; Watzlaf et al., 2000; Rose, 2002). Water quality standards also require the removal of Mn from coal mine discharges

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to a 30-day average of 2 mg/L. The common passive systems generally remove only a small proportion of the influent Mn. Although Mn removal to the above standard is difficult, relatively little attention has been directed to passive Mn removal systems.

Currently, the main passive method for removal of Mn is the patented "Pyrolusite System" of Vail and Riley (1995, 1997, 2000; Allegheny Mineral Abatement, no date). In this method, the water to be treated is directed into a bed of limestone fragments. The bed is inoculated with Mn-oxidizing bacteria, and Mn precipitates as coatings of Mn oxides ("pyrolusite"). Vail and Riley (2000) indicated that 11 Pyrolusite systems were in operation and 6 more were in construction. A number of other authors have described Mn removal, but little information exists on their success.

The intent of this paper is to provide information on Pyrolusite and related systems, and to evaluate this method and others for passive removal of Mn.

## Geochemistry of Manganese

In natural environments, Mn occurs in the +2, +3 and +4 oxidation states, though many other states are known chemically. The behavior is somewhat similar to iron, but $Mn^{2+}$ (Mn II) is much more stable in solution than $Fe^{2+}$.

The behavior in terms of pH and Eh (redox state) is illustrated for the system $Mn\text{-}O\text{-}H\text{-}S\text{-}CO_2$ on Figure 1. Simply put, Mn(II) is relatively soluble, but Mn(III) and Mn(IV) are much less so and tend to precipitate as a wide variety of solids. Although pyrolusite ($\beta\text{-}MnO_2$) is the most stable phase in the simple Mn-O-H system, it does not seem to form at low temperatures in solutions of high ionic strength such as sea water and AMD. Therefore, pyrolusite has been suppressed for Figure 1. Birnessite ($\delta\text{-}MnO_2$) and todorokite (approximately $(Ca,Na_2)Mn^{II}(Mn^{IV})_5O_{12}$) are the common low-temperature precipitates in sea water and many other environments, and are the "stable" phases under oxidizing conditions with pyrolusite suppressed. For activities of $10^{-5}$ Mn (~5.5 mg/L Mn), $10^{-2}$ S (~1000 mg/L $SO_4$) and 3 x $10^{-4}$ $CO_2(g)$ (approximately atmospheric concentration), the diagram shows an extensive field of soluble Mn as the $MnSO_4^o$ complex ion. Under aerated conditions along the upper boundary, Mn can oxidize and precipitate at pH as low as about 4. However, oxidation of Mn(II), the normal dissolved state, to Mn(III) or Mn(IV), is negligible until higher pH is reached. By pH 6-

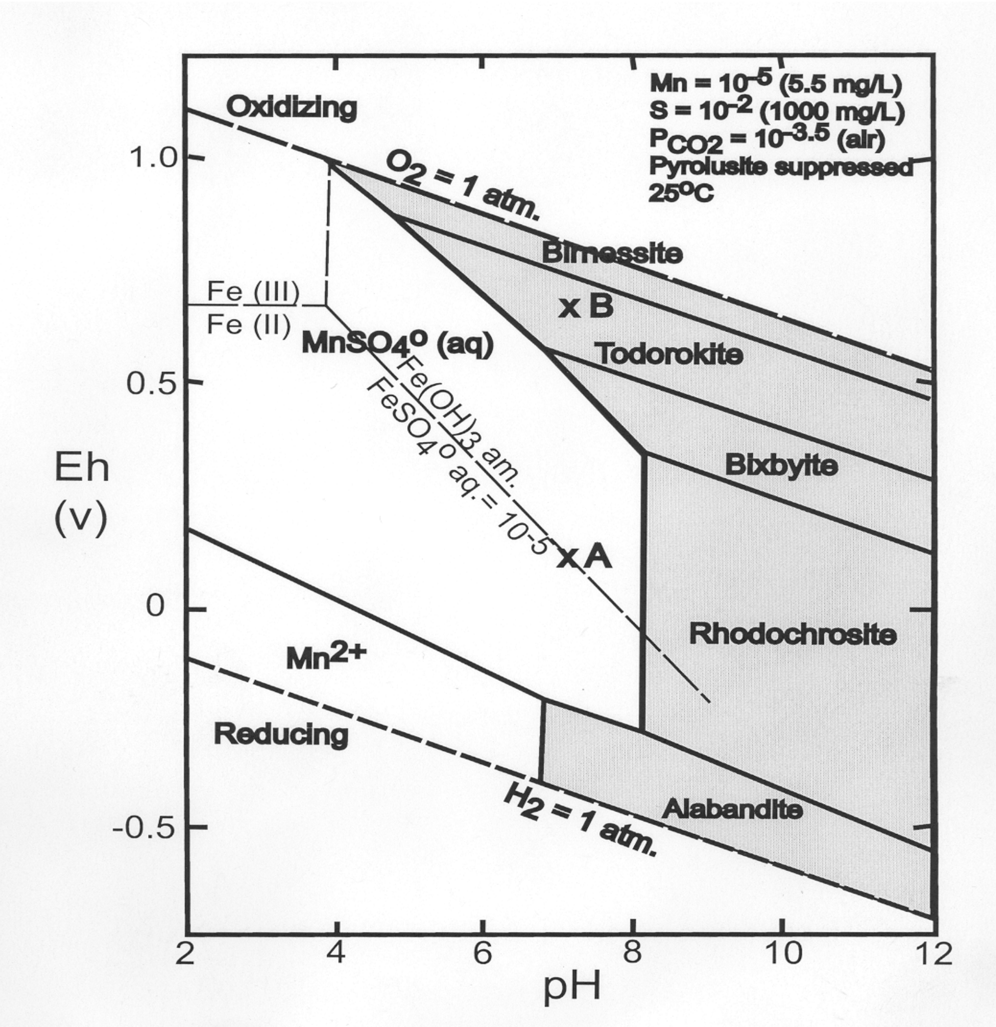

Figure 1. Eh-pH diagram for Mn, calculated from data in Geochemist's Workbench. Shaded area shows insoluble phases under the indicated conditions. Clear area shows soluble Mn. Birnessite = $MnO_2$; todorokite approximated as $Mn^{II}Mn^{IV}{}_3O_7$; bixbyite = $Mn_2O_3$; rhodochrosite = $MnCO_3$; alabandite = MnS. Diagram also shows limit of $Fe(OH)_3$ (am) solubility. $Fe(OH)_3$ precipitates at A. Mn oxide can precipitate at B.

7, an aerated solution is highly supersaturated, and precipitation is more feasible. Under reducing conditions, rhodochrosite ($MnCO_3$) can precipitate at pH above about 8. At lower $CO_2$, $Mn(OH)_2$ precipitates at about pH 10, and probably is responsible for Mn removal in some active treatment.

Another key requirement for Mn oxidation is a low concentration of ferrous iron (Fe(II)). As indicated on Figure 1, if Fe(II) is present in a solution (point A), the oxidation potential of such a solution is considerably below the level required for Mn oxidation to Mn(III) or Mn(IV), and Mn will not oxidize and precipitate. In addition, laboratory experiments show that $Fe^{2+}$ solutions can dissolve previously precipitated Mn oxides (Villinski et al., 2001). The presence of other reducing agents, such as reactive organic matter, can also inhibit Mn oxidation and precipitation.

The above discussion refers to equilibrium conditions, but for Mn, kinetic factors are very important in determining oxidation and precipitation. The oxidation of Mn(II) to Mn(III) or Mn(IV) by dissolved $O_2$ is generally slow. The rate is affected by a wide variety of factors, including pH, oxygen content, catalysis by solid Mn and Fe oxides/hydroxides, bacteria, other cations and anions in solution, temperature, and other factors. For abiotic oxidation at constant pH and oxygen content, Stumm and Morgan (1981) and Hem (1981) suggest a rate equation in the presence of solid Mn oxide of:

$$d[Mn^{II}]/dt = k_o[Mn^{II}] + k_1[Mn^{II}][MnO_2] \qquad (1)$$

where $[Mn^{II}]$ is the concentration of dissolved $Mn^{II}$, $[MnO_2]$ is the effective concentration (abundance of surface sites) of solid Mn oxides and/or hydroxides and $k_0$ and $k_1$ are rate constants. In other words, the oxidation rate increases at higher dissolved Mn concentration, and with increased amounts of solid Mn oxides/hydroxides. Adsorption of Mn(II) on the surface of a solid containing Mn (III) or Mn(IV) enhances the rate of electron transfer from $O_2$ to Mn, as compared to free Mn(II) in solution. The increased rate in the presence of solid Mn oxides/hydroxides makes the reaction autocatalytic, and rates in an initially pristine system tend to increase as more Mn is precipitated.

Oxidation of Mn(II) is relatively rapid under abiotic conditions at high pH, with half-times of tens of minutes to hours at pH 9 to 9.5 (Hem, 1964, p A57). The rate of oxidation slows with decreasing pH. At pH 8.4, Diem and Stumm (1984) found negligible precipitation in aerated $Mn(NO_3)_2$ solutions stored for 4 to 7 years. Rates were only slightly increased by addition of Mn oxides as surface catalysts, but were somewhat increased by addition of Mn oxide plus minor Co or Ni. Much more rapid oxidation and precipitation occurred when bacteria were present.

Photocatalytic effects of light on Mn oxidation and reduction can both enhance oxidation or dissolve Mn oxides. Net enhancement of the Mn oxidation rate in a fast-flowing stream receiving AMD is demonstrated by Scott et al. (2002), but they also show effects suggested to be from photocatalyzed reduction of Mn oxides, both directly and by photolytic $H_2O_2$. Increased $O_2$ and pH from algae may be responsible for some enhancement in sunlight. Sunda and Huntsman

(1990) and others have demonstrated photocatalyzed dissolution of suspended Mn oxides in marine environments.

The identity of the solid phase formed by oxidation of Mn(II) solutions varies with solution chemistry, temperature and other factors, but generally the initial solid contains at least some Mn(III). In experiments in the simple Mn-O-H system, the initial precipitates are generally hausmannite ($Mn_3O_4$) containing both Mn(III) and Mn(II) (Hem and Lind, 1983). This initial phase converts to MnOOH (MnIII) and finally to $MnO_2$ (MnIV). At lower temperature or in the presence of sulfate, the initial precipitate is MnOOH. As indicated above, in more complex solutions such as seawater and AMD, formation of todorokite and birnessite seems to be favored.

Mn-oxidizing bacteria are active in many natural environments. These bacteria, of which many species exist, catalyze the reaction of dissolved $O_2$ with Mn(II) (Ghiorse, 1984). Genera include Leptothrix, Cytophagia, Hyphomicrobium, Pseudomonas, Arthrobacter and many others. The biochemistry of these species is not well understood. Most of these species are aerobic heterotrophs (i.e., they use organic matter and $O_2$ for their major energy source), but some may also obtain energy from oxidation of Mn(II). Fungi, algae and protozoa also are observed to precipitate Mn. Most of these species also precipitate Fe or mixtures of Fe and Mn. The Mn is typically oxidized and precipitated in the sheath outside the cell wall by enzymes released from the bacteria. It is possible that the Mn oxidation is a by product of processes for protecting the cell from oxygen toxicity. Whatever the case, many experiments show that Mn oxidation and precipitation is greatly enhanced by bacteria.

## Published Field Trials on Mn Removal from Acid Mine Drainage

A number of trials have compared treatment variables for removal of Mn from AMD. Sikora et al. (2000) compared beds of limestone with beds of river gravel for a period of 734 days. Water level was maintained just below the surface of the beds. They found that the limestone beds removed Mn from influent containing 8 and 20 mg/L dissolved Mn at a rate 10 to 60 times that of the river gravel, and maintained effluent Mn concentrations less than 1 mg/L. One reason for the difference is that the influent pH of 5.4 increased to about 7 in the limestone, but remained low in the river gravel. Iron was less than 1 mg/L in the influent, and dissolved $O_2$ was at least half of saturation in the zone of major Mn removal, providing good conditions for Mn removal. No difference in removal rate was detected between 5 and 30C. For the limestone beds, most Mn was removed in the first 2 m of the 10-m long beds. Removal rates on an areal loading basis ranged from 3 to 17 $g/m^2/d$ for the limestone beds, and from 1 to 2 $g/m^2/d$ for the river gravel. The value of 17 $g/m^2/d$ is for the initial 2 m of the bed where most of the reaction occurred.

Thornton (1995) experimented with two limestone-filled tanks followed by a vegetation cell for removal of Mn from AMD generated in a coal ash disposal pond. Influent Mn averaged 3.5 mg/L over a period of 495 days, and effluent averaged 0.5 mg/L. A black film coated the limestone and was concluded to be the site of microbial Mn oxidation and precipitation. Iron was very low in the influent (<0.01 mg/L). The areal removal rate is estimated to be 8.5 $g/m^2/d$.

Phillips et al. (1994) compared three treatment ponds for removing Mn at influent levels of about 8 mg/L. One treatment pond had a limestone substrate and was seeded with a cyanobacterial-dominated microbial mat that covered the surface after development. Green cyanobacteria also coated the limestone bed. A second pond had a limestone bed coated with cyanobacteria, but no floating microbial mat. A third pond had a pea gravel bed, and developed a very thin cyanobacterial coating. Water in all three ponds had a pH of 7.2 to 7.6, dissolved $O_2$ of 7.3 to 8.3 mg/L and alkalinity of 156-167 mg/L. Temperatures were as low as 4C. Pond 1 with the microbial mat performed much better than the other two, and removed Mn at a rate of 2.6 $g/m^2/d$ at 4C compared to 0.8 $g/m^2/d$ for the limestone pond and 0.37 $g/m^2/d$ for the pea gravel pond. However, the microbial mat was largely lost at one point in the experiment, probably because of snowfall and heavy runoff accentuated by consumption by snails and other herbivores.

At a mine in Australia, up to 5000 $m^3/d$ of processing effluent with elevated Zn, Fe and Mn was passed along a system of ponds and channels to remove the metals (Jones et al., 1995). Most of the Fe and a small part of the Zn and Mn was removed by aeration along a steep channel followed by a settling pond. Manganese at levels of about 2 mg/L was removed to <0.1 mg/L in about 1000 m of algae-filled channel at pH 8. Mn was found to coat the algae as a black precipitate. A distinct diurnal effect was noted, with higher Mn and Zn removal rates during daytime.

Clayton et al. (1999) used algal pond scum in conjunction with limestone beds in aerobic wetland experiments and found that this combination was very effective in removing Mn.

Brant and Ziemkiewicz (1997) and Robbins et al. (1999) found that a system of two limestone beds in Somerset County, PA, decreased Mn concentration from levels of 12 to 40 mg/L in the influent to <2 mg/L in the effluent. The two beds are 20-22 m long, 15 to 20 m wide and 1.2 m thick. The flow rate averaged 19 L/min for a retention time of at least 5 days, and the system operated for at least 5 years. Limestone developed a coating of black slime that contained bacteria, cyanobacteria, diatoms and green algae, all with black coatings on cell surfaces and attachment structures. Lab experiments showed that slime-coated limestone fragments were much more effective in removing Mn than fresh limestone, and aeration slightly improved the removal rate.

Johnson (2002) describes lab experiments showing that active aeration enhances Mn removal. Her reactors, packed with 2 cm dolomite and fine Mn oxide, removed about 99% of influent Mn (20 mg/L) while air was actively bubbled into the bed, but only about 95% when influent was air-saturated. A bacterial population was evidently the main driver of oxidation. Removal of 5 mg/L Fe along with Mn was accomplished in one phase of the experiments, but required strong aeration.

Partial removal of Mn is observed in some vertical flow systems. For example, Schueck (personal communication, 2002) reports removal of Mn from 50 mg/L to 11 mg/L along with Fe and Al in bench tests of a compost-limestone reactor, and 20 mg/L removal in pilot-scale field tests. Similarly, Terry Morrow (personal communication, 2001) reports partial removal of Mn in the McKinley VFS in the Clarion area, PA. The process for removal is uncertain in both cases, but appears to operate at near-neutral pH.

## Observations on Pyrolusite Systems

Pyrolusite systems are a patented procedure developed by Vail and Riley (1995, 1996, 1997, 2000) for removal of Mn. Pyrolusite systems are composed of a bed of limestone fragments about a meter thick through which the Mn-bearing solution flows (Figure 2). The limestone is recommended to be AASHTO #57 (2b, 2.5 cm), though coarser stone has been used recently. The bed is inoculated with Mn-oxidizing bacteria cultured by Vail's company, Allegheny Mineral Abatement, Inc., using water from the site. Several different species of bacteria may be inoculated to different parts of the bed to accommodate differing Mn concentration, oxygen levels, etc. (Robert Riley, personal communication). The dimensions of the bed should provide a retention time of 1.25 to 3 days for the maximum flow rate into the system (Allegheny Mineral Abatement, no date). A plastic liner should surround the bed to keep out soil micro-organisms and a wetland should precede the bed to provide organic matter for metabolism of the Mn-reducing bacteria. Baffles are installed in the bed to divert flow upward and downward and to optimize interaction of microbes with water (Figure 2). The outflow point is designed so that the water level is about 0.3 m (1 ft) beneath the surface of the bed, and to keep the water in the dark to prevent growth of algae. The bed should be built up above the ground surface to avoid standing water and accumulation of leaves. The method is considered by Vail and Riley (2000) to be able to treat water containing Fe and Al as well as Mn.

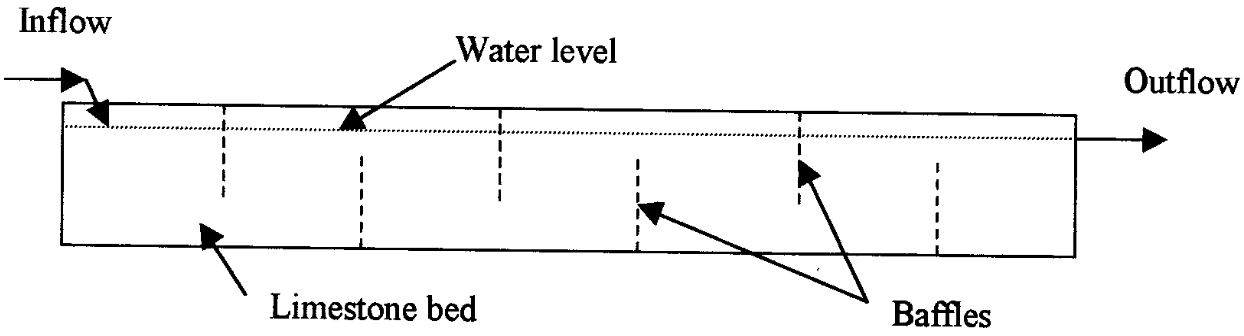

Figure 2. Schematic cross section of a Pyrolusite system.

For this paper, data have been obtained on 10 Pyrolusite and related systems, ranging in age from 1 to 10 years (Table 1). All systems except Middle Branch 2 were inoculated by Allegheny Mineral Abatement, but several were not constructed according to their design and are not considered valid Pyrolusite systems according to them. Other systems, specifically Swisstock 1,

**Table 1. Characteristics of Pyrolusite and Related Systems**

| Site | Location | Length<br>m | Width<br>m | Depth<br>m | Ls.Mass<br>T | Ls. Size<br>cm | Built |
|---|---|---|---|---|---|---|---|
| K & J | Cambria Co., PA | 27 | 2.9 | 0.9 | | 2.5 | 10/91 |
| Swisstock 1 | Cambria Co., PA | 61 | 2.9 | 0.9 | | 2.5 | 4/94 |
| Swisstock 2 | Cambria Co., PA | 29 | 1.5 | | | 2.5-5 | 3/95 |
| PBS | Somerset Co., PA | 64 | 4.6 | 0.9 | | 1.2 | 1/98 |
| Laurel Run | Westmoreland Co., PA | 46 | 12.3 | 1.5 | 1911 | 2.5-6 | 6/97 |
| Stroud | Cambria Co., PA | 61 | 4.6 | | | 5-7.5 | 2/98 |
| Sq.Falls (Glenwhite) | Blair Co., PA | 65 | 25 | 2.13 | 5400 | 1-6 | 5/99 |
| Cambria G | Cambria Co., PA | 80 | 18.5 | | | 6 | 3/00 |
| Middle Br. | Clinton Co., PA | 31 | 17 | 1.52 | 1140 | 6 | 8/01 |
| Middle Br. | Clinton Co., PA | 31 | 17 | 1.52 | 1140 | 6 | 8/01 |

were not monitored and maintained as needed, leading to some of the problems described below. However, all are included as Pyrolusite and related systems for the purposes of this paper. Some data have been obtained from records of the PA DEP mining permit files aad others from monitoring by the PA Bureau of Abandoned Mine Reclamation and the US Office of Surface Mining. Most values for Fe, Mn and Al are total values, and may include suspended material. Flow data for several sites are estimated, as indicated in Table 2.

As shown by Table 2, most of the systems have been effective in removing Mn. The effluent Mn concentrations at most sites are well within effluent limits, with qualifications to be discussed below. Iron is also generally removed, and Al has been removed at most sites. The remaining Al in effluent at Swisstock and Middle Branch is probably in suspension, because at the effluent pH, the Al will be in the form of a precipitate.

A minor to major problem at many of the sites is plugging at the influent end or over much of the surface of the bed, resulting in flow over the surface rather than through the bed. This plugging resulted from various causes. At Swisstock 1, which is in a heavily wooded area on a steep hillside, the surface is plugged by a combination of leaves and organic-rich silt. At Squatter Falls (Glenwhite), the high Fe in the influent has precipitated and blocked flow into the coarse stone. Here, reworking of the influent area was required every 4 weeks in order to avoid overflow of water from the inlet area. The problem was less severe after a vertical flow pond was added before the Pyrolusite system, but reworking remains a continuing task. Similar but much less severe problems have been observed from elevated Fe and/or Al levels at Laurel Run and PBS, requiring occasional reworking of the inflow area to minimize plugging and surface flow. Both systems at Middle Branch developed extensive cover by dirt, grass and algae, as well as a white efflorescence that may be Al hydroxide and/or $CaCO_3$. Much of the flow in the Middle Branch systems was apparently over the surface. This problem was relieved by lowering the outflow point. Only minor plugging problems were noted at Stroud and K & J.

Slight to obvious black Mn oxide coatings are evident beneath the water level in the stone, but plugging by Mn oxide does not appear to be the main problem at any site. The volume of Mn oxide precipitate is small relative to the porosity of the bed. Assuming a porous Mn coating containing 50% water-filled voids in the coating, and that all Mn precipitates in the top 0.3 m (1 ft.) of a bed with 40% void space (see below), the various sites are calculated to have capacity for 40 to 500 years of Mn precipitate before plugging of the total bed. Plugging by Mn in the initial few meters would shorten this time, but Mn plugging does not seem to be an immediate problem.

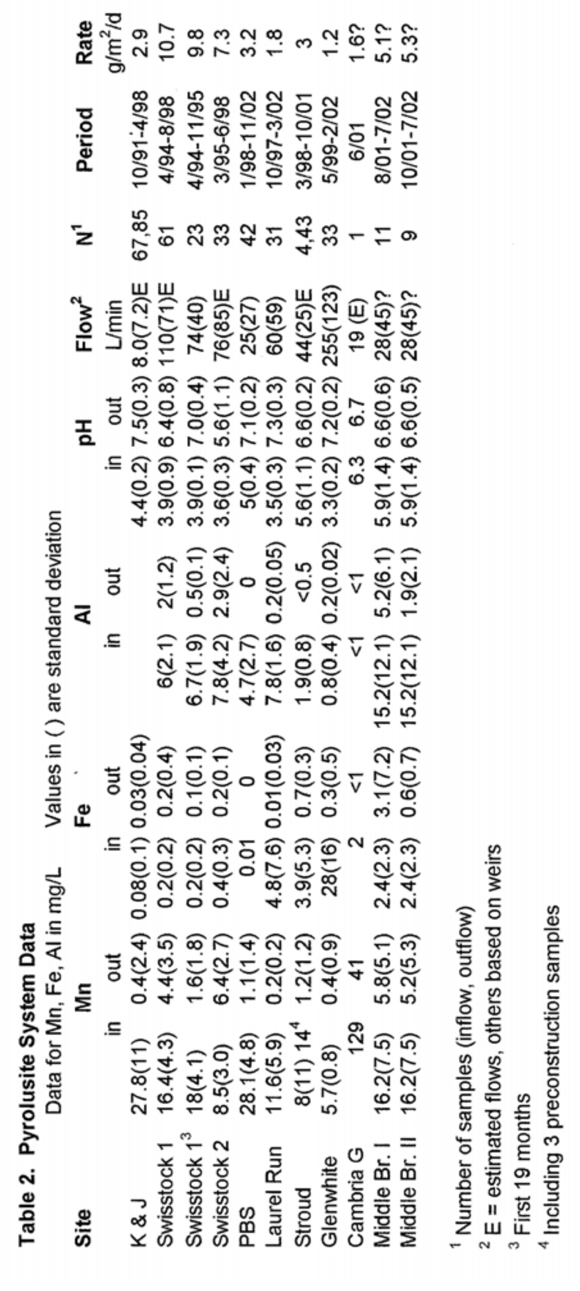

**Table 2. Pyrolusite System Data**

Data for Mn, Fe, Al in mg/L Values in ( ) are standard deviation

| Site | Mn |  | Fe |  | Al |  | pH |  | Flow[2] | N[1] | Period | Rate |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | in | out | in | out | in | out | in | out | L/min |  |  | g/m²/d |
| K & J | 27.8(11) | 0.4(2.4) | 0.08(0.1) | 0.03(0.04) |  |  | 4.4(0.2) | 7.5(0.3) | 8.0(7.2)E | 67,85 | 10/91-4/98 | 2.9 |
| Swisstock 1 | 16.4(4.3) | 4.4(3.5) | 0.2(0.2) | 0.2(0.4) | 6(2.1) | 2(1.2) | 3.9(0.9) | 6.4(0.8) | 110(71)E | 61 | 4/94-8/98 | 10.7 |
| Swisstock 1[3] | 18(4.1) | 1.6(1.8) | 0.2(0.2) | 0.1(0.1) | 6.7(1.9) | 0.5(0.1) | 3.9(0.1) | 7.0(0.4) | 74(40) | 23 | 4/94-11/95 | 9.8 |
| Swisstock 2 | 8.5(3.0) | 6.4(2.7) | 0.4(0.3) | 0.2(0.1) | 7.8(4.2) | 2.9(2.4) | 3.6(0.3) | 5.6(1.1) | 76(85)E | 33 | 3/95-6/98 | 7.3 |
| PBS | 28.1(4.8) | 1.1(1.4) | 0.01 | 0 | 4.7(2.7) | 0 | 5(0.4) | 7.1(0.2) | 25(27) | 42 | 1/98-11/02 | 3.2 |
| Laurel Run | 11.6(5.9) | 0.2(0.2) | 4.8(7.6) | 0.01(0.03) | 7.8(1.6) | 0.2(0.05) | 3.5(0.3) | 7.3(0.3) | 60(59) | 31 | 10/97-3/02 | 1.8 |
| Stroud | 8(11) 14[4] | 1.2(1.2) | 3.9(5.3) | 0.7(0.3) | 1.9(0.8) | <0.5 | 5.6(1.1) | 6.6(0.2) | 44(25)E | 4,43 | 3/98-10/01 | 3 |
| Glenwhite | 5.7(0.8) | 0.4(0.9) | 28(16) | 0.3(0.5) | 0.8(0.4) | 0.2(0.02) | 3.3(0.2) | 7.2(0.2) | 255(123) | 33 | 5/99-2/02 | 1.2 |
| Cambria G | 129 | 41 | 2 | <1 | <1 | <1 | 6.3 | 6.7 | 19 (E) | 1 | 6/01 | 1.6? |
| Middle Br. I | 16.2(7.5) | 5.8(5.1) | 2.4(2.3) | 3.1(7.2) | 15.2(12.1) | 5.2(6.1) | 5.9(1.4) | 6.6(0.6) | 28(45)? | 11 | 8/01-7/02 | 5.1? |
| Middle Br. II | 16.2(7.5) | 5.2(5.3) | 2.4(2.3) | 0.6(0.7) | 15.2(12.1) | 1.9(2.1) | 5.9(1.4) | 6.6(0.5) | 28(45)? | 9 | 10/01-7/02 | 5.3? |

[1] Number of samples (inflow, outflow)

[2] E = estimated flows, others based on weirs

[3] First 19 months

[4] Including 3 preconstruction samples

A sample of the black Mn coating on limestone at the PBS site is identified as todorokite, a complex Mn oxyhydroxide of approximate composition $(Ca,Na_2)Mn^{II}(Mn^{IV})_5O_{12}$, accompanied by dolomite and calcite (from the limestone) and possible rhodochrosite (Figure 3). In view of the high amounts of other cations in acid mine drainage, it is not surprising that the precipitate is todorokite rather than simpler Mn oxides or hydroxides.

An example of plugging effects on the effluent chemistry is provided by the Swisstock 1 site, for which Mn data is shown in Figure 4. For the first 18 months of operation, from 4/94 to 11/95, the bed was very successful in removing Mn and Al. However, the site was not maintained after bond release and received flow greatly exceeding the design value of 38 L/min. After 18 months, the surface of the bed had become plugged with leaves and organic matter to the extent that water flowed over the top of the bed along the entire length. After this time, Mn removal was incomplete. Plugging was so complete that in 11/02, a small hole excavated about 1 m (3 ft.) laterally from the surface flow had a water level about 10 cm (4 in.) lower than the surface flow. The Swisstock 2 site showed plugging by sand and silt and non-treatment similar to Swisstock 1 on a more rapid time frame.

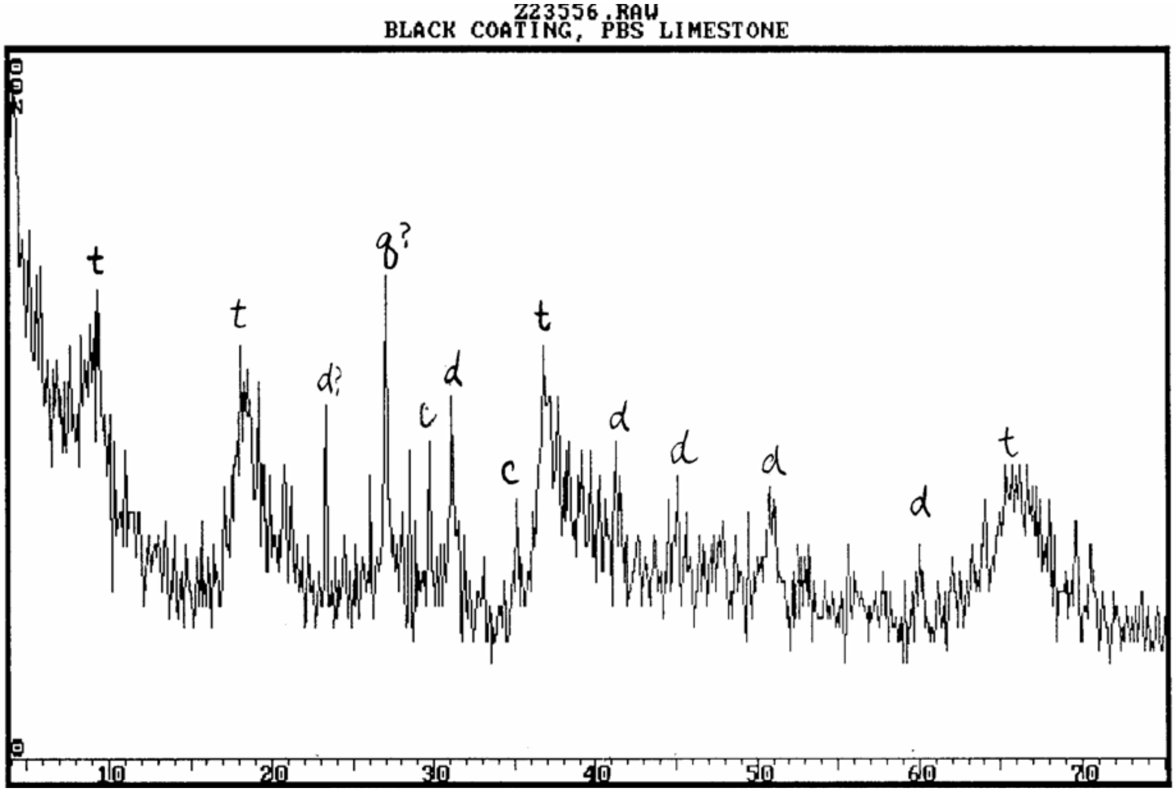

Figure 3. X-ray diffraction pattern of black coating on limestone at PBS site. Peaks are t=todorokite, d=dolomite or possibly rhodochrosite, c=calcite and q= quartz.

Observations at the PBS site suggest that Mn precipitation is much more active near the water surface than at depth in the bed. This pattern was observed in a hole dug in the bed 15 m (50 ft) downflow from the inflow point on 8/28/02. At the water level and just above it at the time of excavation, the surfaces of the limestone fragments were estimated to be 80 to 90% covered with Mn oxide precipitate in thicknesses of 0.2 to 0.5 mm. The cementation above the water level is probably attributable to the fact that water levels were low at this date because of low rainfall, and former water levels were probably higher. The fragments in this zone were cemented together and difficult to dig. About 0.3 m (1 ft.) below the water level, fragments were only about 50% covered with Mn oxide, and the coatings were rarely more than 0.2 mm thick. The fragments were loose and easily dug.

The vertical decrease in coatings correlates with observations of dissolved oxygen measured in the middle inoculation tube in the bed. In 8/02, dissolved $O_2$ was 44% of saturation at 3 cm (1.5 in.) below the water surface, but was only 5.4% of saturation at 1.2 m (4 ft.) depth. Inflow

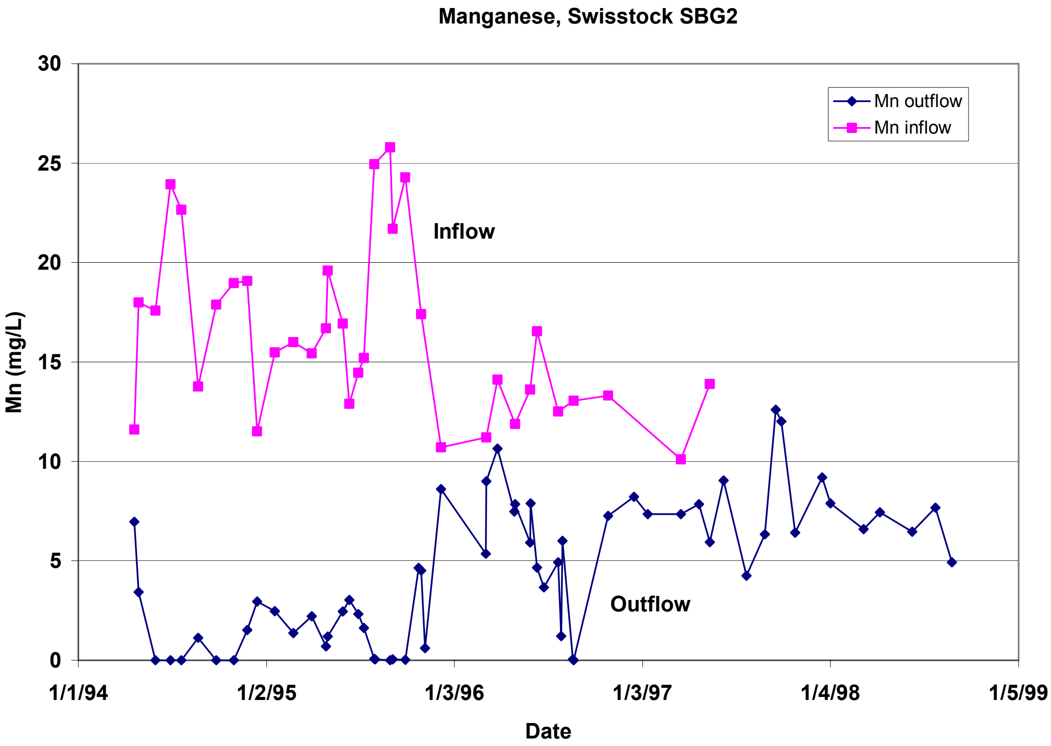

Figure 4. Manganese concentration of influent and effluent of Swisstock 1 Pyrolusite system. Data from files of PA DEP.

water was at 46% of $O_2$ saturation, but outflow water was at only 4.6% saturation. Similar results were obtained in 8/01.

The surface enhancement of Mn oxidation and precipitation is attributed to more rapid oxidation of Mn at the higher dissolved $O_2$ near the water surface vs. slower oxidation at low dissolved $O_2$ at deeper levels. Dissolved $O_2$ in the influent water is consumed by oxidation of Mn, $Fe^{2+}$ and organic matter from the preceding wetland, so that the deeper waters in the bed become depleted in dissolved $O_2$. Mn oxidation rate is highly sensitive to oxidation level, as indicated by Figure 1 and earlier discussion. Oxygen is added from air at the water surface, but downward diffusion and mixing, even with baffles, is so slow that deeper waters are apparently insufficiently oxidizing for rapid Mn oxidation.

Data on dissolved Mn at several points along the length of the bed indicate that oxidation and precipitation of Mn are most rapid in the first part of the PBS bed. In 10/02 when the flow rate was 28 L/min, the Mn concentration decreased from 32 mg/L at the inflow to 7.7 mg/L at 18 m, 0.33 mg/L at 30 m, and 0.33 mg/L at the outflow at 70 m. Thus, the loss of Mn is not linear but is much more rapid in the initial section, probably because Mn oxidation rate is proportional to Mn concentration as indicated in eq. (1). Also, the dissolved $O_2$ is undoubtedly higher in the initial section.

Another factor of interest is the bacterial effect. At all the sites except one bed at Middle Branch and possibly Stroud, the beds were inoculated with Mn-oxidizing bacteria by Allegheny Mineral Abatement. Some sites were reinoculated after a year. However, at Middle Branch, one bed was inoculated, and the other was not. The two beds were identical in construction and the inflow to the beds is split so influent chemistry is identical. As noted above, considerable problems were encountered at this site with silt, grass and precipitate plugging the beds, and causing flow over the surface, so that Mn removal was incomplete in both beds. However, the non-inoculated bed removed as much or more Mn than the inoculated bed (Table 2, Figure 5). Possibly the Mn-oxidizing bacteria were carried the 5 to 10 m from one bed to the other on the

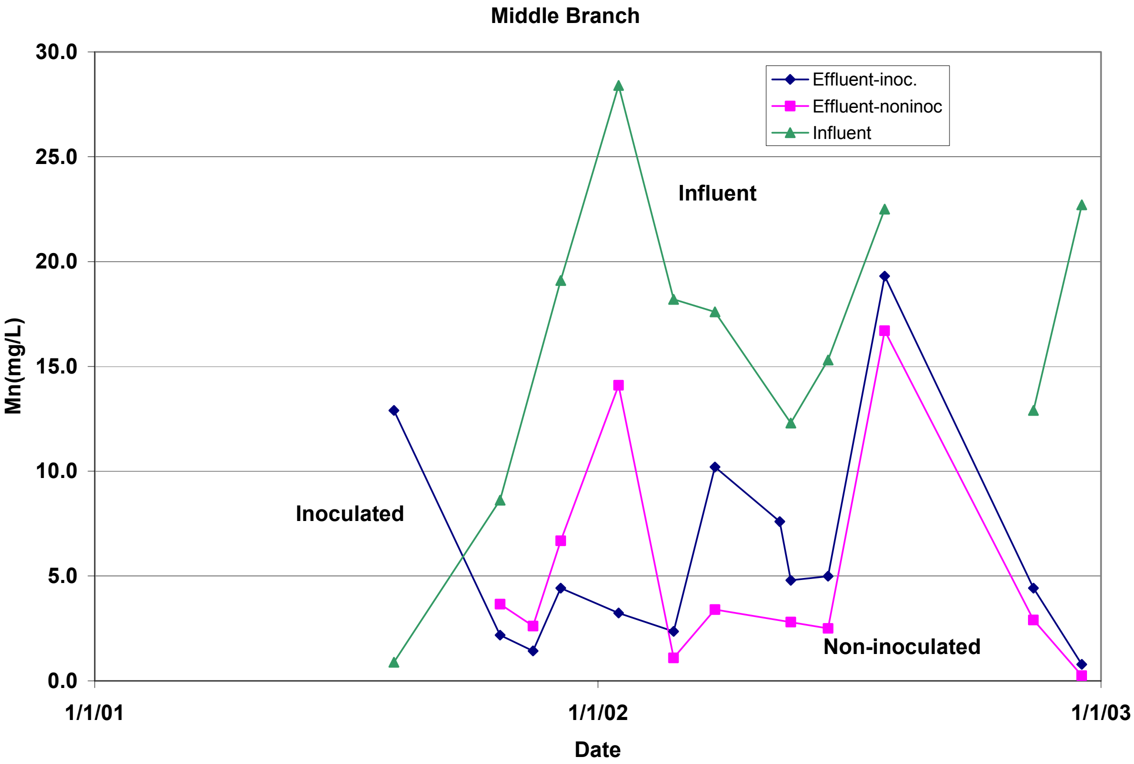

Figure 5. Manganese concentration of the influent and of the effluents from the inoculated and non-inoculated beds at the Middle Branch system. Both beds were affected by flow over the bed surface, but both removed manganese.

feet of birds or animals, or by subsurface flow. If this is true, it indicates that transfer and seeding of the requisite bacteria is relatively easy. Other observations on non-inoculated sites described from the literature above and on the channels described below indicate that appropriate bacteria find the Mn-rich environments naturally, and that special inoculation, though it may speed initiation of the process, may not be necessary.

## Observations on Manganese Removal Channels

Open channels in which Mn was removed have been observed at four sites. The first two were observed during a field trip in Tennessee as part of the 1996 Annual Meeting of the American Society for Surface Mining and Reclamation in Knoxville, TN. At the Skyline Coal Co. Glady Fork Project, a serpentine channel lined with limestone was removing small amounts of Mn from a flow of treated water. At Sequatchie Valley Coal Area 2 near Dunlap, TN, mine drainage with about 25 mg/L Mn was pumped from wells in a reclaimed surface mine and treated by a series of ponds and wetlands to remove Fe to levels of <1 mg/L. The net alkaline effluent with pH about 7.6 flowed down a channel about 0.5 km (¼ mile) long to a pond before final release to a stream. Along this channel and in the pond, black Mn oxyhydroxides (Terry Schmidt, written communication, 2002) were precipitating naturally on the sides and bottom. The Mn concentration at the confluence with the stream was 6 mg/L. Flow in the channel was relatively rapid so the water was well aerated. This site was not inoculated.

The third channel site was at a surface coal mine in north-central PA. A caved portal from a small, long-abandoned underground mine drained an area surface mined a few years earlier. Appreciable limestone was added to spoil during surface mining to inhibit acid generation and release. When sampled in 2002, the flow from the caved adit was net alkaline with a pH of 6.55, alkalinity 347 mg/L as $CaCO_3$, Mn 2.16 mg/L and Fe <0.1 mg/L at a flow rate of 95 L/min and $9^oC$. This water had been flowing for several years down a channel about 0.6 m (2 ft.) wide, with numerous small riffles and zones of turbulence. At a distance of 23 m (75 ft.) down the channel, the Mn concentration had decreased to 0.76 mg/L. Other parameters were essentially unchanged. The channel contained abundant stringy algal growths, and was in open sun a few hours a day. Attached to the algal growths and on the bottom of the channel were black nodules up to about 5 mm in diameter. In addition, some of the normally green algae were colored black with possible Mn precipitate. One of the nodules was analyzed and contained about 50% Mn and negligible Fe, indicating it was an Mn oxide or hydroxide. The aeration of the water combined with $O_2$ generated by the algae, in combination with the alkalinity and lack of Fe is inferred to have promoted Mn oxidation and precipitation. A Mn removal rate exceeding 10 $g/m^2/d$ is estimated.

At the Long Valley site in Tioga Co., a flow averaging 270 L/min flows down a steep channel 0.6 m wide and 23 m long. The Mn concentration is 10 mg/L at the inflow of the channel, 0.5 mg/L at the outflow in winter, and non-detected in summer (Jon Dietz, personal communication, 2002).

## Discussion

The observations from Pyrolusite systems, from other field trials and from theory clearly indicate that Mn can successfully be oxidized and precipitated from acid mine drainage solutions at near-neutral pH, but that some Pyrolusite and related systems have suffered from various kinds of plugging. To avoid plugging, essentially all Fe and Al should be removed prior to inflow into the limestone bed. All the sites with more than a few mg/L of dissolved Al or Fe have experienced problems with plugging by precipitate. Also, a wetland or small pond before the limestone bed is desirable to avoid plugging by silt. At the PBS site, siltation is avoided by inflow through a pipe that drains from the surface of a small wetland (but minor problems with Al precipitate are observed). Leaves are a problem at the Swisstock 1 site, so open areas and an elevated bed surface are preferred for these beds.

The marked decrease in Mn coatings at deeper levels of the bed at PBS, in conjunction with the low dissolved $O_2$ at depth and in outflow at the PBS site, indicates that deep beds are not optimum for Mn removal. Apparently the dissolved $O_2$ is consumed by oxidation of Mn, Fe and organic matter, so that dissolved oxygen is low in water below the surface, and Mn oxidation is appreciably slowed. For this reason, open channels or shallow beds (<0.3 m, 1 ft.) seem preferable for rapid Mn removal. The channels may have to be relatively long in order to provide sufficient area and time for removal. The channels should have sufficient gradient to provide aeration of the water by turbulence. In addition, algae and other oxygen-generating plants seem to enhance oxidation and removal rates, probably by providing $O_2$ and an elevated pH, and perhaps by providing surface area for precipitation. However, some seasonal decreases may occur in the algal effects.

At a number of sites, such as the four channels described above and the field trials in tanks, beds and channels, the systems were not seeded with specialized bacteria, and Mn removal was accomplished. At the Middle Branch site, one bed was not inoculated, but showed Mn removal as good as the inoculated site. From this information, it appears that successful Mn removal does not necessarily require special bacteria, but that the appropriate bacteria are widely distributed in nature. However, it is possible that inoculation speeds up the initial stages of bacterial colonization and may provide more effective bacterial catalysis at low Mn concentration. In general, it is probably more important to have an optimum chemical environment in terms of pH >7, dissolved $O_2$ >5 mg/L and Fe<2 mg/L. Note also that development of Mn oxide coatings may increase reaction rates and enhance rapid removal. It is not clear how the Mn oxide coatings interact with bacteria, but both are probably important.

In this paper, areal rates ($g/m^2/d$) have been used to compare Mn removal rates. This parameter is used because a crucial factor is access of $O_2$. The $O_2$ enters the water only at the air-water surface, or from algae or other plants. Therefore, surface area is a key variable in these systems. In shallow beds and channels, the surface area is also a reasonable parameter.

However, the experimental data on reaction rates indicates that the true relations are complex. In abiotic experiments, the rate is proportional to Mn concentration and is affected by pH, area of Mn oxide coatings and many other factors. The non-linear decrease in Mn vs. distance at PBS is consistent with a rate proportion to Mn concentration. A first-order rate proportional to Mn is discussed in Rose et al. (2003). This produces a negative exponential decrease in Mn concentration. Higher pH is evidently beneficial. At equilibrium with $CaCO_3$, pH will be higher if $CO_2$ can escape from the system to leave a low $P_{CO2}$, so contact with air may be preferable to deep beds that retain $CO_2$. However, the relations are undoubtedly complex, and need to be evaluated with well designed experiments. At the moment, design based on areal loading, plus a minimum retention time, seems the best approach, but collection of good field data to test removal rates proportional to Mn concentration and with terms for Mn oxide and bacterial catalysis are needed.

## Conclusions

1. Manganese can be successfully removed from acid mine drainage by passive methods. The influent water should have pH above about 6 and Al and Fe concentrations less than about 2

mg/L. Experience has shown that where Fe and Al are present, plugging of the bed is likely to occur and Mn oxidation will not be effective until the Fe is removed. The system should contain limestone and be well aerated.

2. Pyrolusite systems successfully remove Mn, but are susceptible to plugging by silt, organic matter, leaves, and Fe and Al precipitates. They should be constructed according to the specifications discussed earlier. Monitoring and maintenance of beds is essential.

3. Limestone surfaces greatly enhance the precipitation of Mn, because of the increased pH they impose and because of the favorable surface area for deposition. Additional research should be conducted to determine the optimum aggregate size.

4. Open channels may be preferable to deep beds in terms of cost of construction and limestone. The open channel will provide much better oxygenation, which is needed for Mn oxidation. The flow in the channel will tend to inhibit sedimentation. Algae and other plants appear to increase rates of oxidation and precipitation, though there may be significant seasonal effects.

5. Rates of removal in beds are commonly 2 to 3 $g/m^2/d$, and rates of 8 to 17 $g/m^2/d$ are observed in some Mn removal systems. Additional research is needed to determine the removal rates in limestone channels.

6. Inoculation with specialized bacteria does not appear to be required, though it may shorten startup time and rates at low concentration.

7. Additional research is needed to determine:

   a. Whether first order rates proportional to Mn concentration are more appropriate than rates in $g/m^2/d$.

   b. A more accurate removal rate based on channels and on “effective” bed areas rather than total constructed bed areas. The true effects of pH and Mn concentration should also be studied.

   c. The role of O2 in enhancing performance, using side by side limestone-lined channels, one with aeration devices and one without.

   d. The role of surface area in Mn removal, using side by side limestone constructed channels with varying aggregate sizes.

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## Literature Cited

Allegheny Mineral Abatement. No date. Design of the treatment bed. Allegheny Mineral Abatement, Inc., Midland, MD, 4 p.

Brant, D.L. and P.F. Ziemkiewicz, 1997. Passive removal of manganese from acid mine drainage. *In:* Proc. Amer. Soc. for Surface Mining and Reclamation, Austin, TX, May 1997, p. 741-744.

Clayton, L.A., J.L.Bolis, T.R. Wildeman, and D.M. Updegraff. 1999. A case study of the aerobic and anaerobic removal of manganese by wetland processes. p. 515-526. *In* L.H. Filipek and G.S. Plumlee (eds.). The environmental geochemistry of mineral deposits, Part B. Reviews in Economic Geology, v. 6B, Society of Economic Geologists.

Diem, D. and W. Stumm, 1984. Is dissolved manganese being oxidized by $O_2$ in the absence of Mn bacteria or surface catalysts? Geochimica et Cosmochimica Acta, v. 48, p. 1571-1573. http://dx.doi.org/10.1016/0016-7037(84)90413-7

Ghiorse, W.C. 1984. Biology of iron- and manganese-depositing bacteria. Annual Review of Microbiology, v. 38, p. 515-550. http://dx.doi.org/10.1146/annurev.mi.38.100184.002503

Hedin, R.S., R.W. Nairn, and R.L.P. Kleinmann. 1994. Passive treatment of coal mine drainage. U.S. Bureau of Mines, Information Circular 9389, 35 p.

Hem, J.D. 1964. Chemical equilibria and rates of manganese oxidation. U.S. Geological Survey, Water Supply Paper 1667A, p A1-A64.

Hem, J.D. 1981. Rates of manganese oxidation in aqueous systems. Geochimica et Cosmochimica Acta, v. 45, p. 1369-1374. http://dx.doi.org/10.1016/0016-7037(81)90229-5

Johnson, K., 2002. The importance of aeration in passive treatment schemes for manganese removal. *In* Mine water treatment: A decade of progress. National Conference, November 11-13, 2002, Newcastle upon Tyne, UK, 13 p.

Jones, D.R., B.M. Chapman and R.F. Jung. 1995. Passive treatment of mine water. p. 755-763. *In* T.P. Hynes and M. C. Blanchette (eds.). Proceedings, Sudbury '95, Mining and the Environment, v. 2.

Phillips, P., J. Bender, R. Simms, S. Rodriguez-Eaton, and C. Britt. 1994. Manganese and iron removal from coalmine drainage by use of a green algae-microbial mat consortium. p. 99-108. *In* Proceedings, International Land Reclamation and Mine Drainage Conference. (Pittsburgh, PA, April 1994). U.S. Bur Mines Special Pub. SP06a-94, v 1.

Robbins, E.I., D.L. Brant, and P.F. Ziemkiewicz, 1999. Microbial, algal and fungal strategies for manganese oxidation at a Shade Township coal mine, Somerset Co., Penna. *In:* Proc. Amer. Soc. for Surface Mining and Reclamation, Scottsdale, AZ, August 1999, p. 634-640.

Rose, A.W. and J.M. Dietz. 2002. Case studies of passive treatment systems: Vertical flow systems. p. 776-797. *In* Proceedings, 2002 National Meeting, American Society of Mining and Reclamation. (Lexington, KY, June 9-13, 2002). American Society of Mining and Reclamation. http://dx.doi.org/10.21000/jasmr02010776

Rose, A.W., B. Means and P.J. Shah, 2003. Methods for passive removal of manganese from acid mine drainage. *In:* Proc. West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV, April 2003, 11 p.

Sikora, F.J., L.L. Behrends, G.A. Brodie, and H.N. Taylor. 2000. Design criteria and required chemistry for removing manganese in acid mine drainage using subsurface flow wetland. Water Environment Research, v. 72, p. 536-544. http://dx.doi.org/10.2175/106143000X138111

Scott, D.T., D.M. McKnight, B.M. Voelker, and D.C. Hrncir. 2002. Redox processes controlling manganese fate and transport in a mountain stream. Environmental Science and Technology, v. 36, p. 453-459. http://dx.doi.org/10.1021/es010951s

Stumm, W. and J.J. Morgan. 1981. Aquatic chemistry. Wiley-Interscience, 779 p.

Sunda, W.G. and S.A. Huntsman. 1990. Diel cycles in microbial Mn oxidation and Mn redox speciation in coastal waters of the Bahamas. Limnology and Oceanography, v. 35, p. 325-338. http://dx.doi.org/10.4319/lo.1990.35.2.0325

Thornton, F.C. 1995. Manganese removal from water using limestone-filled tanks. Ecological Engineering, v. 4, p. 11-18. http://dx.doi.org/10.1016/0925-8574(94)00003-N

Watzlaf, G.R., K.T. Schroeder, and C. Kairies. 2000. Long-term performance of alkalinity-producing passive systems for the treatment of mine drainage. p. 262-274. *In* Proc. 17th Annual Meeting, American Soc. for Surface Mining and Reclamation, Tampa, FL, June 2000.

Vail, W.J., and R.K. Riley. 1995, 1996. Process for removing manganese from solutions including aqueous industrial waste. U.S. Patent 5,441,641. See also U.S. Patents 5637210, 5510032.

Vail, W.J., and R.K. Riley. 1997. The abatement of acid mine drainage pollution using the Pyrolusite Process. *In* Proceedings, 19th Annual Conference, National Association of Abandoned Mine Lands Programs. (Aug. 17-20, 1997, Davis, W.V.).

Vail, W.J. and R.K. Riley. 2000. The Pyrolusite Process®: A bioremediation process for the abatement of acid mine drainage. Green Lands, v. 30 (4), p. 40-46.

Villinski, J.E., P.A. O'Day, T.L. Corley, and M. Conklin. 2001. In situ spectroscopic and solution analyses of the reductive dissolution of $MnO_2$ by Fe(II). Environmental Science and Technology, v. 35, p. 1157-1163. http://dx.doi.org/10.1021/es001356d