

PASSIVE REMOVAL OF MANGANESE FROM ACID MINE DRAINAGE¹

by

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Abstract. Removal of manganese (Mn) from mine drainage is difficult due to the abnormal chemistry of the element. The removal requires the oxidation of Mn(II) (the form found in mine drainage) to the more oxidized forms (Mn(III) or Mn(IV)). The more oxidized forms exist only as solids and will not return to Mn(II) spontaneously. Chemical treatment of Mn often requires a pH near 10 to initiate the oxidation quickly. A stabilized pH of 10 normally causes more harm to aquatic organisms than the Mn and is not desirable, making additional steps in the treatment necessary. Biological removal of Mn can be achieved at near neutral pH levels. The Shade Mining site in Somerset County, PA has been treating Mn to discharge limits since the early 1990's (reducing Mn concentrations from 12 - 25 mg/L in the influent to <2 mg/L in the effluent). The treatment system consists of an anoxic limestone drain discharging into a wetland to remove iron, aluminum, and acidity, while increasing pH and alkalinity. The wetland effluent flows into two limestone beds (Mn removal). The limestone beds developed a black slime coating as the Mn removal increased. This system continues to remove Mn in all weather conditions and has not required chemical treatment since the black coating appeared on the limestone. A laboratory study was conducted using limestone collected from the Shade site to use the same naturally occurring Mn oxidizing microbes. The lab study compared Mn removal rates of microbial oxidation, MnO₂ catalyzed limestone, and fresh uncoated limestone. The microbial removal performed the best (25 mg/L Mn reduced to <2 mg/L in 72 hours).

Additional Key Words: pyrolucite, microbial oxidation

Introduction

Manganese (Mn) is a common

constituent of ground water and surface water receiving acid mine drainage (AMD). Mine drainage which exceeds the current allowable concentration of manganese (Mn) (2 mg/L monthly average or 4 mg/L for grab samples) is required to be treated. Although, high concentrations of manganese may be toxic to aquatic life, the application of the regulatory standards for manganese is based partly on the fact that it can act as a surrogate for other potentially more toxic metals, such as chromium, copper, lead, mercury, nickel, and zinc (Watzlaf, 1988).

Manganese is considered to be a trace

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element, although it is one of the more abundant metallic elements in the Earth's crust. Manganese is not a required constituent of the common silicate or carbonate minerals, but will substitute for iron, magnesium, calcium, and other divalent elements in mineral structures (Hem, 1985). In sedimentary rocks, manganese will substitute for iron (Fe) in siderite and pyrite, and can also substitute for cations in clays. As these minerals weather, manganese is dissolved into solution and may exist in a variety of oxidation states (2+,3+,4+,6+, and 7+), with the 2+ state being the most common in AMD (Watzlaf, 1988; Hem, 1985).

Removal of manganese from mine drainage is difficult due to the abnormal chemistry of the element. The removal requires the oxidation of Mn(II) to the higher oxidized forms (Mn(III) or Mn(IV)). The more oxidized forms exist only as solids and will not return to Mn(II) spontaneously. Manganese oxidation rates are strongly dependent on pH and temperature. Therefore, waters below a pH of 4.0 generally will not precipitate manganese oxides. Manganese oxidation is also slow below a pH of 8.5. Chemical treatment of Mn often requires a pH near 10 to initiate the oxidation quickly. A stabilized pH of 10 normally causes more harm to aquatic organisms than the Mn and is not desirable, thereby making additional steps in the treatment necessary. Manganese can be removed from high iron concentrated waters at lower pH levels than water with little or no iron present. This process (coprecipitation) occurs as iron oxides precipitate and manganese ions are adsorbed to negatively-charged sites on the iron oxide molecule (Watzlaf, 1988).

Removal of manganese can also be accelerated by the presence of microorganisms. Manganese removal was

reported to occur in rock beds containing a black slimy coating (manganese oxide & microbes) on the surface of the rocks and in gravel beds supporting cyanobacteria mats (Gordon and Burr, 1989; Bender et.al., 1994). Manganese removal was reported to be biological in both studies.

Study Design / Results

The advantage of biological removal of manganese is that it can be achieved at near- neutral pH levels. The Shade Mining site (Figure 1) in Somerset County, PA has been treating mine drainage to achieve discharge limit levels of manganese since the early 1990s (i.e., reducing manganese concentrations from 12 - 40 mg/L in the influent to <2 mg/L in the effluent). The treatment system consisted of an anoxic limestone drain discharging into a wetland to remove iron, aluminum, and acidity and to increase pH and alkalinity. The wetland effluent flows into two (manganese removal) open limestone beds. The limestone bed dimensions are: Bed 1: 65 feet wide X 65 feet long X 4 feet deep; Bed 2: 47 feet wide X 72 feet long X 4 feet deep, for a combined total volume of 30,436 cubic feet. By estimating the void space between the rocks at 30%, the retention time of the limestone beds would equal 5 days for the highest recorded flow or 6,100 cubic feet/pound of manganese/day. The limestone beds developed a black slime coating as the manganese removal increased. This system continues to remove manganese in all weather conditions and has not required chemical treatment since the limestone developed the black manganese oxide/microbial coating. Fresh limestone was placed in the treatment system in an attempt to determine the length of time it took for the black manganese oxide/microbial layer to develop around the rocks. The coating became noticeable at 8 weeks.

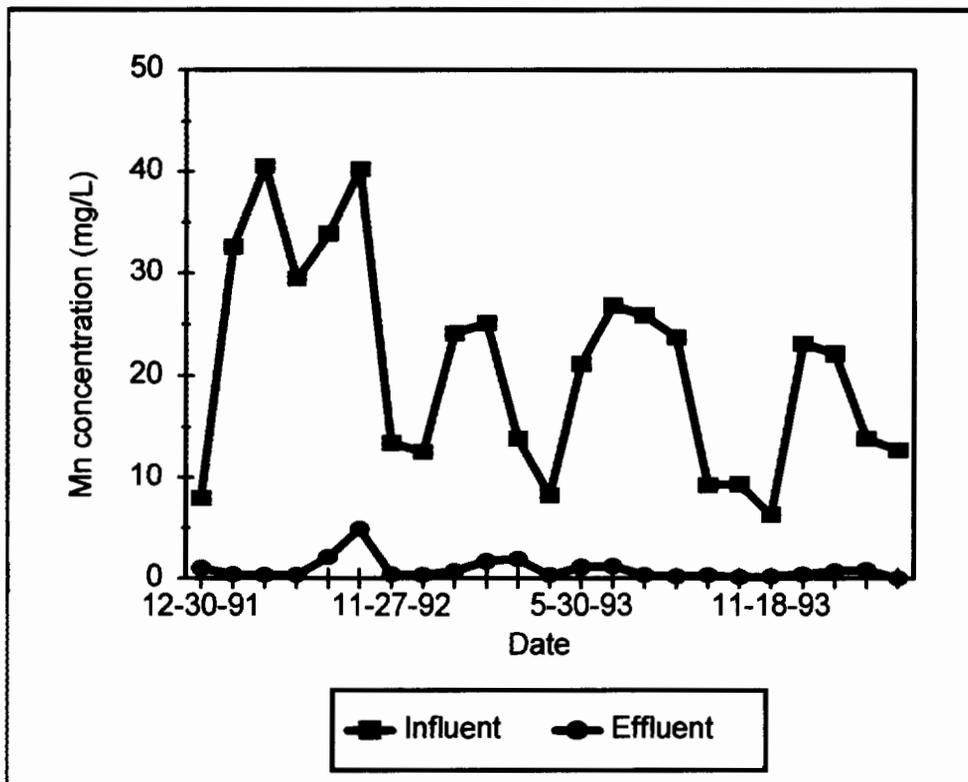


Figure 1, manganese removal at the Shade Mining site.

A laboratory study was conducted using limestone collected from the Shade Mining site. This limestone was used to guarantee the use of the same naturally-occurring manganese oxidizing microbes found at the Shade site. The lab study compared manganese removal rates of microbial oxidation, MnO_2 catalyzed limestone, and fresh, uncoated limestone. The study was completed using the following procedure: Fifteen pounds of limestone were placed in 12 two gallon buckets (four buckets each, for three types of limestone, two aerated and two without aeration). The buckets were filled with one gallon of AMD containing 25 mg/L manganese. Samples were collected at 24, 48, 72, and 240 hours. Results indicate that the microbial encapsulated limestone from the Shade Mining site performed the best (both sets, aerated and nonerated, reduced the

manganese from 25 mg/L to < 4 mg/L in 72 hours) (Figure 2).

Conclusions

This study indicates that passive systems can be designed to remove manganese from AMD. The field site is removing manganese to compliance levels independent of seasonal conditions. The source of the removal is microbial and was naturally inoculated by local organisms. These organisms were also transferred to fresh limestone in eight days and were able to remove manganese in laboratory cells to compliance levels within 3 days. The process is more efficient under aerobic conditions, although the microbes that were not supplied with supplemental air also removed manganese at faster rates than the other test cells.

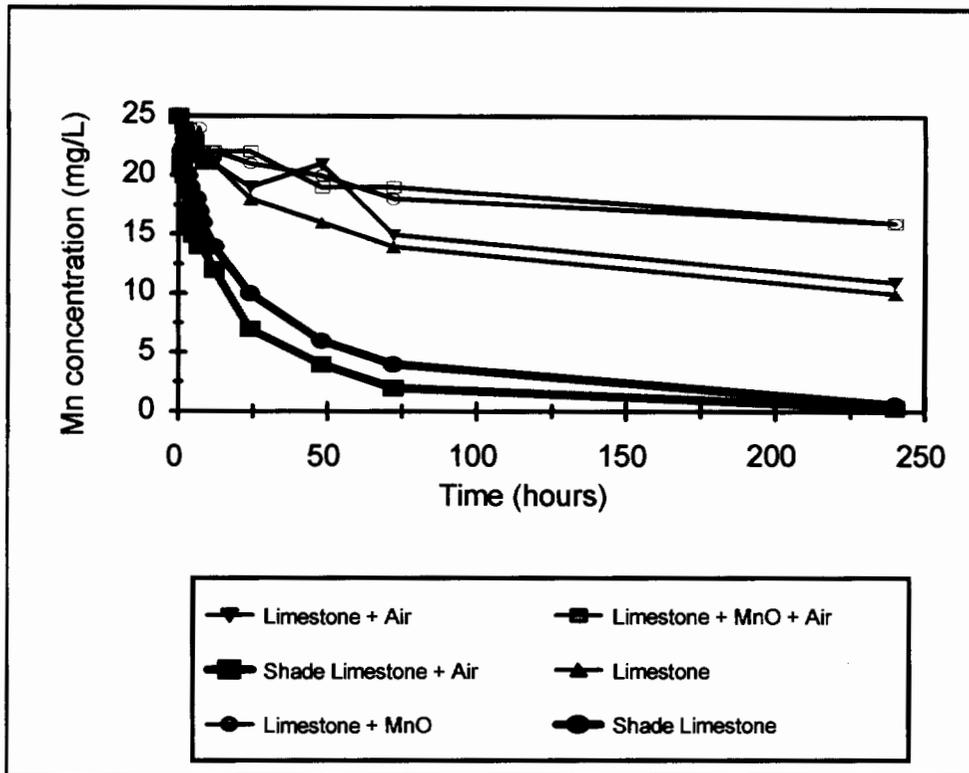


Figure 2, laboratory study of manganese removal (aerated vs. unaerated limestone cells).

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