PROCESSES CONTRIBUTING TO THE REMOVAL OF MANGANESE FROM MINE DRAINAGE BY AN ALGAL MIXTURE[1]

by

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Abstract. An aerobic bench-scale experiment utilized algae to raise the pH (from ~ 6 to above 8) and remove manganese from an anaerobic constructed wetland effluent (from >20 mg/L to <0.3 mg/L Mn). Additional laboratory experiments were conducted to further examine the manganese removal mechanisms that occurred in the bench-scale reservoirs. Sequential extractions of the algal mass found that the manganese was predominantly associated with the carbonate and Mn oxide phases, and the algae contained 30 mg Mn per dry gram. The biosorption of manganese by nonliving algae in high pH-high Eh aquatic environments was found to be minimal compared to the manganese removed from solution by precipitation as amorphous manganese oxyhydroxides. Limestone contained in one of the bench-scale reservoirs was found to contain 0.16 mg Mn per g limestone when the limestone surfaces were dissolved. Thus, the removal of manganese by the algal mixture contained in the bench-scale reservoirs was accomplished by the precipitation of manganese carbonates and oxides on the algal mass, the precipitation of amorphous oxyhydroxides, and the binding or precipitation of manganese on the limestone surfaces.

Additional Key Words: algal ponds, limestone, manganese oxides, biosorption

Introduction

Iron and manganese are the two most commonly regulated metals in mine drainage (Kepler, 1988). Iron is relatively easy to chemically remove from mine drainage, but manganese removal is more difficult, more expensive, and produces a large amount of sludge. This difference arises from manganese (II) solubility being six to seven times greater than iron(II) solubility for any Eh in an acidic environment (Crerar et al., 1972). Except for MnO_2, manganese is extremely soluble at pH values below 7. Manganese concentrations in mine drainage can range from less than 2 to greater than 200 mg/L (Wildeman, 1991; Staub, 1992). Federal National Pollutant Discharge Elimination System (NPDES) regulations require that mine drainage discharge waters meet effluent standards of a daily maximum of 4.0 mg/L total manganese, and 2.0 mg/L total manganese on a monthly average (U.S. Code of Federal Regulations, 1985a, 1985b). Also, effluent regulations require the pH of the drainage to be between 6.0 and 9.0 (U.S. Code of Federal Regulations, 1985a, 1985b).

The use of microorganisms for the removal of heavy metals from acid mine drainage has become an important alternative to chemical treatment. Constructed wetlands, emphasizing either aerobic or anaerobic processes, have been proven to substantially increase the pH of the mine drainage and remove many of the heavy metals by forming insoluble metal complexes and precipitates (Brodie etal., 1989, Wildeman and Laudon, 1989). However, in wetlands, manganese is difficult to remove from solution due to the high pH required to form insoluble manganese oxides, carbonates, or sulfides. In previous laboratory, bench-scale, and pilot-scale studies, it has been found that effective removal of manganese is possible through the use of aerobic, algal ponds (Duggan et al., 1992; Wildeman et al., 1993). For these ponds to be effective, the pH of the water entering system had to be above 5.5 (Duggan et al., 1992; Wildeman et al.,

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TABLE 1. Flow rate, effluent pH, and effluent Mn concentration in mg/L for reservoirs LS and NoLS.

	RESERVOIR NoLS			RESERVOIR LS		
DAY #	FLOW	pH	Mn	FLOW	pH	Mn
71	2.1	9.1	3.2	2.5	9.2	1.0
73	3.9	9.3	----	3.9	8.7	0.7
84	2.1	8.5	32.1	2.4	8.5	14.0
86	----	8.5	253	----	8.8	1.4
91	3.0	8.1	13.0	1.5	8.2	0.6
94	4.5	8.2	10.1	4.5	8.5	1.2
97	4.0	8.6	4.8	4.5	8.6	2.2
99	----	8.5	3.2	----	8.4	1.4
100	----	8.3	2.3	----	8.4	0.5
103	3.7	8.5	2.3	3.9	----	1.0
120	3.1	8.1	3.8	1.8	8.1	0.6
125	3.0	8.2	5.0	3.8	8.2	0.3
127	3.0	8.2	7.2	3.7	8.3	0.7

Flow measured in mL/min, Mn in mg/L. Dashed lines (----) represent no data collected. Influent Mn averaged approximately 30 mg/L.

1993). The results from the bench-scale portion of the study when mine drainage was flowing into the ponds is presented in Table 1. The mine drainage was effluent from one of the treatment cells at the Big Five Tunnel Wetland in Idaho Springs, Colorado. The concentration of Mn in the water averaged 30 mg/L and the pH averaged 5.8. On day 79 of the study, a 100 mg/L solution of Mn that had a pH of 4.9 was pumped into the ponds for about one week.

The pH needs to be above 5.5 because then significant concentrations of bicarbonate will be dissolved in the water, and in a wetland environment, photosynthesis can proceed using this dissolved bicarbonate. A schematic reaction for this photosynthesis is:

$$6\,HCO_3^-\,(aq.) + 6\,H_2O \longrightarrow C_6H_{12}O_6 + 6\,OH^-\,(aq.) + 6\,O_2$$

From this reaction, it is clear that algae can produce the high pH-high Eh environment that encourages the precipitation of manganese oxides (5). However, although photosynthesis provides the environment, it is not clear whether the algae play a more direct role in the removal of the manganese. In particular, it may be the case that Mn could be taken up into living algal cells or biosorbed onto living or dead algal material. In addition, one of the bench-scale studies included limestone in the pond and this enhanced Mn removal. This suggests that Mn was bound or precipitated on the limestone surface.

A better understanding of the manganese removal processes that occurred in the algal reservoirs would be beneficial for designing a large-scale algal pond treatment system. To accomplish this, several laboratory experiments were conducted with the algae and limestone collected from the reservoirs. Because the precipitates were X-ray amorphous, sequential extraction studies were performed to determine the forms of the manganese solids. In addition, manganese uptake by nonliving algae and the concentration of manganese in the reservoir limestone were examined. The purpose of this paper is to present our results on these removal process studies, and use them to show what we consider the dominant removal processes to be.

Materials and Methods

Sequential Extractions

The dry algae from the two reservoirs were collected and mixed together. Small twigs, leaves, and limestone pieces were separated from the algae by hand. The algal mass was broken into smaller pieces and ground into a powder in a coffee grinder. The resulting sample was considered to be homogeneous.

Two extraction sequences were performed: one sequence focusing on determining manganese associated with carbonates, and one sequence examining manganese associated with oxides. Two sequences were performed to separate the carbonate

and manganese oxide phase extractions, because the acetic acid used for the carbonate extraction may also dissolve manganese. To limit this dissolution of manganese oxides, an acetic acid-sodium acetate reagent having a pH of 4.9 was used instead of acetic acid. The extraction sequence is shown in Figure 1.

One gram of algae was used for each extraction, and each extraction sequence was performed in triplicate. Since the first two extraction phases were the same for both sequences, the six algal samples were combined into three, two gram samples, and were later divided back into six, one gram samples. An HCl - HNO_3 total digestion was performed on three additional one gram samples to compare the total metal concentrations to the sum of the metal concentrations from the sequential extraction phases. The extracted phases were analyzed for manganese and iron by flame atomic absorption. Iron was also examined because iron removal at the Big Five wetland fluctuates seasonally, so iron may have also been contained in the wetland effluent used for the bench-scale study.

Nonliving Algae Experiments

Microorganisms possess the ability to immobilize metals by several different methods including extracellular complexation, intracellular accumulation, and oxidation-reduction reactions which produce extracellular precipitates (Brierly, 1990). The cell walls of microorganisms are composed of macromolecules that contain an abundance of anionic functional groups. Thus, except under very acidic conditions, most organisms have an anionic surface charge which enhances their positive metal ion - binding capabilities. This sequestering of metal ions by natural materials, without regard to mechanism or metabolism, is referred to as "biosorption".

During the flow portion of the bench-scale experiment, the reservoirs froze several times, and some of the algae may have died. However, as seen in Table 1, the effluent manganese concentration continued to meet NPDES standards (2.0 mg/L). Therefore, the biosorption of manganese by the algal mass may have been an integral part of the manganese removal during this period. An experiment was conducted to examine the extent of manganese removal by nonliving algae in high pH environments similar to the conditions produced by photosynthesizing algae.

Live algae, primarily comprised of a branched filamentous green algae, were collected from a local stream. The algae were rinsed several times with deionized water and some of the excess water was removed. One gram of the damp algae was placed into five of six Erlenmeyer flasks. A previous experiment had found that the algae consisted of over 80% water by weight, so each sample contained less than 0.2 g of algae when dry. The amount of excess water varied in the samples, so the actual amount of algae in each sample also varied. To each flask was added 100 ml of effluent from the Big Five wetland, containing 26.5 mg/L Mn. A poison was added to two of the flasks: formaldehyde to one, mercuric chloride to the other. Therefore, three flasks contained live algae, two flasks contained nonliving algae, and one flask contained no algae.

The primary objective of this experiment was to determine the extent of manganese removal by dead algae in conditions similar to those in the bench-scale reservoirs. Therefore, the live algae flasks were monitored for pH and the dead and no algae flasks were adjusted to approximately that same pH with NaOH. To account for the diurnal pH fluctuations with photosynthesis in the live flasks, the pH of the dead and no algae flasks were set slightly lower than the pH of the live algae flasks. A sodium borate buffer was added to the dead and no algae flasks to diminish pH fluctuations. Oxygen was bubbled occasionally into the dead and no algae flasks (which were capped) to provide oxygen which is produced in the live flasks through photosynthesis. The flasks were kept on a windowsill where they received indirect sunlight. Samples were acidified and analyzed for manganese by flame atomic absorption. The experimental set-up is summarized in Table 2.

Limestone Analysis

In Table 1, partial results of the bench-scale experiment show that the presence of limestone in reservoir LS increased manganese removal, especially during the periods when the high manganese solution was being added and at the end of the flow portion of the experiment. Table 1 also shows that the difference in manganese removal between reservoirs was not due to a pH effect. This suggests that manganese was bound or precipitated on the limestone surface. To determine the amount of manganese removed by the limestone, several samples of limestone from reservoir LS were partially dissolved. Several samples of clean unused limestone were also partially dissolved and analyzed for manganese to serve as a comparison.

Three samples of clean unused limestone and three samples of reservoir limestone were collected. Each sample contained between 8 and 11 limestone pieces and weighed between 4.87 and 5.14 g. The samples were placed in 50 ml polyethylene centrifuge tubes with 40 ml of 0.5 M NaOAc-HOAc solution (pH = 4.9), the same solution as used for the carbonate extraction. The solution was allowed to react with the limestone for 30 minutes, so that only the limestone surface would dissolve. The solutions were decanted into separate volumetric flasks. Each sample was then washed with 20 ml of deionized water which was then added to the extraction solutions. The total solution was brought to 100 ml volume with 0.3 N HNO_3, and analyzed for manganese by atomic absorption.

Results

Sequential Extractions

The results of the sequential extractions are expressed in mg metal per one gram original sample.

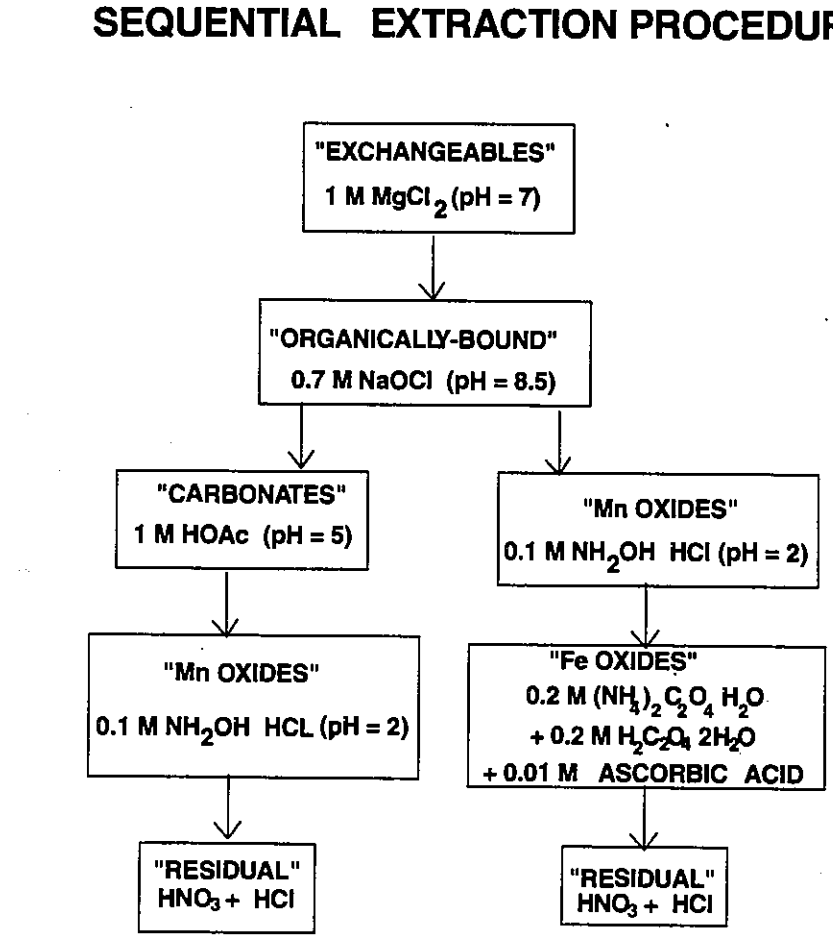

Figure 1. Sequential extraction procedure used on the dried algae. The sequence on the left is the carbonate extraction; the sequence on the right is the oxide extraction.

TABLE 2. Conditions for living vs. nonliving algae manganese removal experiments; pH and Mn in living, nonliving, and no algae flasks for first four days; and pH and manganese concentrations in the flasks after the pH was decreased. Mn concentration is in mg/L; one gram of wet algae was used.

FLASK		A	B	C	D	E	F
INITIAL CONDITIONS							
State of Algae		LIVE	LIVE	LIVE	DEAD	DEAD	NONE
Set pH?		NO	NO	NO	YES	YES	YES
Capped & O_2 Added?		NO	NO	YES	YES	YES	YES
CONDITIONS DURING FIRST FOUR DAYS							
SET UP	pH	8.3	8.2	8.4	8.2	8.2	8.2
	Mn	26.5	26.5	26.5	26.5	26.5	26.5
DAY 1	pH	8.7	8.9	8.7	8.2	8.1	8.1
1430 hr	Mn	14.8	8.3	15.3	20.8	21.4	26.5
DAY 2	pH	8.6	9.0	8.6	8.7	8.6	8.6
1030 hr	Mn	5.9	2.8	5.0	12.3	6.6	15.5
DAY 3	pH	8.9	9.6	9.6	8.9	9.2	9.0
1600 hr	Mn	0.5	<DL	<DL	4.8	1.2	13.0
DAY 4	pH	8.3	8.5	9.2	8.9	9.2	9.0
2130 hr	Mn	<DL	<DL	<DL	2.6	<DL	6.8
CONDITIONS AFTER pH WAS DECREASED ON DAY 6							
DAY 6	pH	7.2	7.2	7.7	7.6	7.4	7.2
DAY 7	pH	7.7	7.7	8.1	7.6	7.4	7.1
	Mn	0.52	0.72	<DL	10.05	9.5	12.4

Notes: Flask D contained formaldehyde, flask E contained mercuric chloride. <DL means less than the detection limit of 0.3 mg/L Mn.

The averages and standard deviations of the metal concentrations are given in Table 5 for manganese and Table 6 for iron. The individual sample measurements can be found in Duggan, (1993).

The total amount of manganese contained in the algae is approximately 30 mg/g. Manganese appears to be primarily concentrated in the carbonate and Mn oxide phases, but a moderate amount is also contained in the Fe oxide phase. For the carbonate sequence, 83% of the total manganese was removed by the carbonate and Mn oxide extractions, and 85% by the Mn oxide and Fe oxide extractions in the oxide sequence.

Nonliving Algae Experiments

The pH and manganese concentration in each flask for the first four days of the experiment is given in Table 2. In order to examine the manganese removal processes occurring in the flasks and to evaluate the solubility of the manganese precipitates that had formed, the pH of the solutions were decreased to between 7.2 and 7.7 with HCl on Day 6. At this pH, manganese oxyhydroxides may dissolve, adsorbed manganese may desorb, but $MnCO_3$ and MnO_2 should remain insoluble. Again, pH measurements were taken on Day 7 when samples were taken. The results are given in Table 2.

After the samples were taken on Day 7, 50 ml of additional Big Five wetland effluent were added to flasks D-DEAD, E-DEAD, and F-NONE, and oxygen was bubbled into them. For the next few days, the pH of the flasks were slowly increased to more closely monitor manganese removal versus pH. The results are given in, Table 3.

Limestone Analysis

The manganese concentration, expressed in mg Mn per g limestone, for the six limestone samples is given in Table 4.

TABLE 3. Mn (mg/L) and pH in dead and no algae flasks.

FLASK	DAY 8		DAY 9		DAY 10 AM		DAY 10 PM		DAY 11	
	pH	Mn	pH	Mn	pH	Mn	pH	Mn	pH	Mn
D-DEAD	7.6	11.5	7.9	9.1	8.1	10.0	8.5	7.2	8.9	4.7
E-DEAD	7.4	13.5	7.85	10.6	8.1	9.1	8.5	6.2	8.8	2.1
F-NONE	7.3	13.8	8.0	12.4	8.2	13.2	8.6	8.2	9.0	4.1

TABLE 4 Results of limestone dissolution analysis. Manganese concentration is mg Mn per g limestone.

SAMPLE #	LIMESTONE	# PIECES	WEIGHT (g)	Mn (mg/g)
1	reservoir	10	4.948	0.16
2	reservoir	8	4.932	0.18
3	reservoir	11	5.131	0.15
4	clean	9	5.139	<DL
5	clean	10	4.874	0.0072
6	clean	9	4.910	<DL

<DL = Manganese concentration less than detection limit (0.3 mg/L). Therefore, assuming a 5 g limestone sample, Mn (mg/g) = <0.006.

Discussion

Sequential Extractions

Due to selectivity difficulties, the sequential extraction results may not reflect the exact manganese concentrations contained in each phase. Some of the manganese contained in the Mn oxide phase was removed by the carbonate extraction, as seen by the lower manganese concentration in the Mn oxide phase for the carbonate sequence. Because MnO_2 readily adsorbs manganese(II), the manganese released by the carbonate extraction may have been adsorbed manganese rather than dissolved manganese oxides. The HOAc-NaOAc reagent used for the carbonate extraction had a pH of 4.9, which could have been low enough to have caused the desorption of adsorbed manganese that was not removed by the $MgCl_2$ extraction, but was high enough to prevent the dissolution of MnO_2.

The main objective of the sequential extractions was to determine the forms of the manganese removed by the algae. The formation of manganese oxides, especially MnO_2, would be desirable due to their insolubility and high sorption capacity (Stumm and Morgan, 1981). Exchangeable and organically-bound metals could be easily released into solution, and are therefore considered undesirable metal removal mechanisms. Since the precipitates formed on the algal biomass appear to be primarily insoluble manganese oxides and carbonates, the release of manganese from these precipitates would be unlikely.

Total iron averaged 8.6 mg per g dry algae, and as expected, was associated primarily with the Fe oxide phase. The minimal amount of iron removed in the carbonate and Mn oxide steps suggests that the sequential extraction procedure was reasonably effective in separating amorphous Mn and Fe oxides. Iron removal was assumed to be complete by the bench-scale reservoirs due to the precipitation of ferric hydroxides at above neutral pH's.

Nonliving Algae Experiments

Previous laboratory experiments found that manganese removal from neutral solutions by an algal sample was minimal or nonexistent (Duggan, 1993). However, the biosorption of most metals by nonliving biomass is extremely pH dependent due to the occupation of adsorption sites by protons or other metals, metal solubility, metal hydration, and metal competition (Hawke et al., 1991; Harris and Ramelow, 1990). Therefore, it was important to examine manganese biosorption in high pH

Table 5. Average manganese concentrations and standard deviations in the sequential extraction study. Units are mg Mn / gram of dry algae.

EXTRACTION PHASE	CARBONATE SEQUENCE Mn (mg/g)	OXIDE SEQUENCE Mn (mg/g)
EXCHANGEABLES	Avg. = 2.4 s = .029 rsd = 1.2%	
ORGANICALLY-BOUND	Avg. = 1.0 s = 0.046 rsd = 4.6%	
CARBONATES	Avg. = 10.0 s = 0.19 rsd = 1.9%	
Mn OXIDES	Avg. = 14.8 s = 0.69 rsd = 4.7%	Avg. = 20.4 s = 0.36 rsd = 1.8%
Fe OXIDES		Avg. = 6.7 s = 0.25 rsd = 3.7%
RESIDUAL	Avg. = 1.6 s = 0.065 rsd = 4.1%	Avg. = 1.2 s = 0.034 rsd = 2.8%
SUM OF EXTRACTION PHASE AVERAGES	29.8	31.7
TOTAL DIGESTION	Avg. = 29.3 s = 3.65 rsd = 12.5%	

Avg. = average Mn concentration of the three samples, s = standard deviation, rsd = relative standard deviation.

Table 6. Average iron concentrations and standard deviations in the sequential extraction study. Units are mg Fe/ gram of dry algae.

EXTRACTION PHASE	CARBONATE SEQUENCE Fe (mg/g)	OXIDE SEQUENCE Fe (mg/g)
EXCHANGEABLES	Avg. = 0.4 s = 0.095 rsd = 24%	
ORGANICALLY-BOUND	Avg. = 0.1 s = 0.0080 rsd = 8.0%	
CARBONATES	Avg. = 0.1 s = 0.019 rsd = 19%	
Mn OXIDES	Avg. = 0.4 s = 0.073 rsd = 18%	Avg. = 0.025 s = .000 rsd = 0%
Fe OXIDES		Avg. = 7.7 s = 0.39 rsd = 5.1%
RESIDUAL	Avg. = 6.8 s = 0.17 rsd = 2.5%	Avg. = 0.9 s = 0.16 rsd = 18%
SUM OF EXTRACTION PHASE AVERAGES	7.8	9.1
TOTAL DIGESTION	Avg. = 8.8 s = 0.76 rsd = 8.6%	

Avg. = average Fe concentration of the three samples, s = standard deviation, rsd = relative standard deviation.

environments similar to the conditions in the reservoirs.

The decrease in manganese in flask F-NONE during the first four days of the experiment was accompanied by the formation of light brown amorphous precipitates, probably manganese oxyhydroxides. Flasks D-DEAD and E-DEAD removed more manganese than flask F-NONE, indicating that some biosorption of manganese to the biomass did occur. However, the average manganese concentration in the three live algae flasks was

consistently lower than the average in the dead flasks, suggesting that the live algae were catalyzing manganese removal by other methods than biosorption.

When the pH of the flasks was lowered on Days 6 and 7, the manganese was solubilized to a much greater extent in the dead and no algae flasks, though the final pH of these flasks was slightly lower than in the live algae flasks. This also suggests that the live algae are removing manganese from solution by different processes than the dead and no algae flasks. The results of the sequential extractions concluded that the live algae manganese removal process is primarily precipitation of manganese carbonates and oxides, which are stable at above neutral pH's. The nonliving algae appear to have removed Mn(II) by a combination of Mn(II) hydroxide precipitation and cell wall adsorption. Adsorption is easily reversible if the pH decreases, and manganese oxyhydroxides are more soluble than MnO_2.

During the portion of the experiment after the additional Big Five effluent was added to the dead and no algae flasks, the adjusted pH of each flask was usually maintained within 0.1 pH unit of the others. Though the no algae flask contained slightly higher manganese concentrations at the beginning and throughout this experiment, the manganese removal trends are very similar for the dead and no algae flasks.

Using a pK_{sp} for $Mn(OH)_2$ of 12.8 (Stumm and Morgan, 1981) and a pH of 8.2, the concentration of Mn^{2+} in a saturated solution of $Mn(OH)_2$ is 6.2 g/L. Consequently, the precipitate is not likely to be $Mn(OH)_2$. Inspection of a manganese stability diagram (Duggan, 1993) suggests that $MnCO_3$ is the most likely precipitate that could be easily dissolved. Within a three day period, the no algae flask removed 9.65 mg/L Mn, and the dead algae flasks removed an average of 9.5 mg/L Mn. It appears that at high pH's such as those found in the reservoirs, the abiotic precipitation of manganese as $MnCO_3$ appears to be a more predominant mechanism to remove manganese from solution than biosorption.

Limestone Analysis

The clean limestone contained negligible amounts of manganese. The average manganese concentration for the reservoir limestone was 0.16 mg/g. Reservoir LS contained 12 kg of limestone, which would account for 1920 mg Mn removal:

(0.16 mg Mn/g l.s.) X (12000 g l.s.)
= 1920 mg Mn

As seen in Table 1, the manganese removal effect of the limestone is most evident during periods when the system was stressed by either high manganese concentrations or cold weather. The addition of limestone to a treatment system might allow for faster flow rates by increasing the manganese removal capacity of an algal pond.

Two mechanisms can account for the removal of Mn by the limestone. The first possibility is the precipitation of $MnCO_3$ on the surface. Because calcite is more soluble than rhodochrosite, exchange of Mn for Ca on the limestone surface is possible. The other possible mechanism is that the carbonate surface catalyzes the precipitation and oxidation of Mn (II). In this case, the limestone would be acting as any other rock surface in providing metal oxide sites to speed the oxidative precipitation of MnO_2 (Wehrli and Stumm, 1989). The competition between formation of carbonates or oxides in aerated alkaline solutions is dependent upon the carbon dioxide and oxygen pressures (Lind, et al. 1987). However, unless the pressure of oxygen is extremely low, it appears that manganese oxides are usually formed.

Conclusions

Sequential extractions of the algal mass found that the manganese was predominantly associated with the carbonate, Mn oxide, and Fe oxide phases. The total manganese sequestered by the algae was approximately 30 mg/g. The sequestering of manganese by biosorption to nonliving algae does not appear to be an important manganese removal mechanism in this study. However, the precipitation of amorphous manganese oxyhydroxides and binding of manganese to limestone surfaces probably did increase the amount of manganese removed from the mine drainage. The primary removal mechanism in the bench-scale reservoirs appears to be the precipitation of insoluble manganese oxides and carbonates on the algae, which is catalyzed by the high-pH, high-Eh aquatic environment produced by the photosynthesizing algae. Therefore, an algal pond treatment system should be concerned with the health of the algae to insure this environment is maintained. Nonliving algae and limestone alone would not likely remove enough manganese from most mine drainages to meet NPDES standards.

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