# RATE OF MANGANESE REMOVAL IN LIMESTONE BED SYSTEMS [1]

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**Abstract:** Manganese removal by limestone beds, as pioneered by Vail and colleagues ("Pyrolusite Systems") can be effective for passively removing Mn from acid mine drainage. This paper reports rates of removal and sizing concepts based on data from eight Mn removal beds.

A representative chemical reaction for Mn removal is
$$Mn^{2+} + 0.5O_2 + H_2O = MnO_2 + 2H^+ \tag{1}$$
Laboratory studies indicate that Mn removal is catalyzed by bacteria and by Mn oxide surfaces, and that at constant pH and oxygen saturation, the rate of Mn removal from solution can be expressed as
$$d[Mn]/dt = k\,[Mn][MnO_2] \tag{2}$$
where $[Mn]$ is the concentration of Mn, $[MnO_2]$ is the surface area of Mn oxide (including the effect of bacteria), $k$ is a rate constant and $t$ is time. Integration of the resulting simplified equation gives the relation
$$Log\,([Mn]/[Mn_0]) = -k_1 St/2.3 \tag{3}$$
where $Mn_0$ is the influent Mn concentration (time 0), $S$ is the surface area of Mn precipitation and $k_1$ is a rate constant including effects of bacteria and surfaces. Based on equation (1), the rate may also be proportional to $(O_2)^{0.5}$ and $(H^+)^{-2}$.
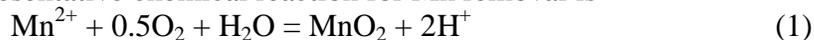
The Mn vs. retention time data for six of the field sites closely fit a rate constant $(k_1)$ of $10^{-3.35}\ hr^{-1}(m_s^2/m_v^3)^{-1}$ where $S\ (m_s^2/m_v^3)$ is the surface area of limestone per cubic meter of bed. Retention time is estimated assuming 50% porosity. Two sites show faster Mn removal. An effect of pH may be present but is not large since the field data show that the limestone buffers pH to between 6.5 and 7.5. A dissolved $O_2$ effect is undoubtedly present but cannot be resolved with the available data. The influent water should be well aerated and open to the atmosphere. Also, Fe and Al must be essentially lacking in the influent or the bed will plug with Fe or Al precipitate.

The following equation can be used to size beds for manganese removal:
$$A(m^2) = -0.276Q\,Log([Mn]/[Mn_o])/(k_1 SD) \tag{4}$$
where $A$ is the bed area, $Q$ is the flow rate (L/min) and $D$ is the depth (thickness, m) of the bed.

Additional Key Words: Acid mine drainage, passive treatment.

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## Introduction

Current laws require removal of manganese from mining discharges to an average concentration less than 2 mg/L. Active treatment to this level commonly requires increase of pH to the 9 to 10 range, which can be expensive and generate effluent that exceeds the pH limit of 9. Similarly, standard passive treatment methods (anoxic limestone drains, vertical flow systems) generally remove little Mn. As a result, removal of Mn from acid mine drainage to meet discharge standards is a difficult and often expensive problem.

Vail and Riley (1995, 1997, 2000) and other workers have shown that Mn can be microbially oxidized and precipitated as Mn oxide in beds of limestone aggregate. The patented Vail and Riley system, termed the Pyrolusite System, has successfully removed Mn at a number of sites, though problems of plugging of such systems with Al and Fe precipitates and with silt have caused problems at many sites (Rose et al., 2003a, 2003b). The latter workers used data from 10 sites to suggest a rate of Mn removal of 2 to 10 $g/m^2/d$, but recognized that the rate might be proportional to Mn concentration.

The purpose of this paper is to report additional data on several field sites, and to show that the removal rate is approximately proportional to Mn concentration. A rate equation for Mn removal in limestone beds is derived and used to develop sizing relations for Mn removal beds.

## Theory

Manganese in acid mine drainage is normally present as $Mn^{II}$, commonly as $Mn^{2+}$ or as a weak complex of $Mn^{2+}$ with $SO_4^{2-}$. The main product of oxidation and precipitation in limestone-bed systems is shown by Rose et al. (2003a) to be todorokite (approximately $(Ca,Na_2)Mn^{II}Mn^{IV}_5O_{12}$). However, a reasonable approximation is to consider that the product is $MnO_2$, so that the oxidation-precipitation reaction is

$$Mn^{2+} + 0.5\ O_2 + H_2O = MnO_2 + 2H^+ \tag{5}$$

Laboratory studies indicate that Mn removal is catalyzed by bacteria and by Mn oxide surfaces (Emerson et al., 1982; Morgan, 2005). A literature review by Morgan (2005) led him to estimate that the approximate half lives for different mechanisms are bacterial oxidation 10 hr, oxide-catalyzed surface reaction 30 days, and homogeneous oxidation 400 days. After the reaction has proceeded to produce a good coating of $MnO_2$ on the substrate, it is assumed in the following discussion that the effects of catalysis by bacteria (attached to the surface) and Mn oxide surface are proportional to the surface area of the Mn oxide. Based on equation (5) and the approach described by LaSaga (1981), the rate of Mn oxidation and precipitation can then be approximated as

$$dC/dt = -\ k\ C^n[O_2]^m\ [MnO_2]^p[H^+]^q \tag{6}$$

where C is the concentration of dissolved Mn, [ ] indicates concentrations of other species, n, m, p and q are real numbers and k is a rate constant. The relevance of this relation is indicated by the fact that Stumm and Morgan (1981) and Hem (1981) found that the rate of oxidation and precipitation at constant pH and constant dissolved $O_2$ can be expressed as

$$dC/dt = -k_0C - k_1C[MnO_2] \qquad (7)$$

where $[MnO_2]$ is the surface area of $MnO_2$, and $k_0$ and $k_1$ are rate constants. The first term on the right in equation 7 represents homogeneous oxidation-precipitation of Mn within the solution and is usually very small compared to the second term involving surface catalysis, as indicated by the fact that Diem and Stumm (1984) found negligible Mn precipitation from $Mn(NO_3)_2$ solutions stored for 4 to 7 years at pH 8.4.

Data discussed in the following section suggest that in the limestone bed environment, pH and $P_{O2}$ do not have major effects on the rate. A probable reason for the lack of effect is that the pH is buffered by the limestone, and the solution is aerated during inflow to the bed and by transport across the water surface. As a first approximation, the terms for these constituents are incorporated into the modified rate constant, $k_1$. Assuming that the bacterial and $MnO_2$ catalysis effects are proportional to the surface area of the limestone fragments, denoted by S, the catalytic rate effects can also be incorporated into this constant. If the exponents for C and $[MnO_2]$ in equation 6 are assumed to be unity, as indicated by equation 7, then equation 6 can be simplified to be first order in Mn concentration:

$$dC/dt = -k_1CS \qquad (8)$$

where S is the specific surface area of the limestone fragments.

Equation (8) can be rearranged and integrated to

$$\ln C + K = -k_1St \qquad (9)$$

where K is a constant of integration. At time 0, C is $C_o$, so $K = -\ln C_o$, or

$$\ln C/C_o = -k_1St. \qquad (10)$$

Since $\ln C = 2.3 \log C$, then

$$2.3 \log C/C_o = -k_1St \qquad (11)$$

$$\log C/C_o = -k_1St/2.3 \qquad (12)$$

As indicated by the discussion above, pH and $P_{O2}$ can have an effect on the reaction rate. Inclusion of these variables would add terms for these variables to the equation, possibly as

$(H^+)^{-2}$ and $P_{O2}^{0.5}$. The effects of these variables will be discussed further below.


### Field Observations and Data on Manganese Removal

Data for 10 limestone removal beds were presented in Rose et al. (2003a,b). Data for 3 additional sites have been collected since those papers were written. In particular, data at several points along the length of the latter sites have been collected to establish the nature of the Mn vs. retention time relationship.

At most sites, water samples were collected from holes dug in the limestone bed to expose the water to a depth of 10 to 15 cm. Samples were also collected from the influent and effluent streams. The samples were filtered through a 0.45 μm filter, and acidified for metal

determination.   Filtered samples were also collected for alkalinity and acidity.   Values for pH, temperature and specific conductance were measured in the field with calibrated meters. Dissolved $O_2$ was measured with a YSI dissolved oxygen meter. At some sites, Eh data were collected with a Pt electrode calibrated with Zobell solution (Langmuir, 1971).   Analyses were by certified commercial labs, and by ACTLABS of Ancaster, Ontario.    At one site, acidity and alkalinity were measured in the field, as noted below, but at most sites the acidities were measured by hot peroxide methods in the lab.

At the Cumberland site in Tennessee, water with 38.6 mg/L Mn flows at a rate of 300 L/min into a serpentine limestone bed (Figure 1).  The stone in the bed is 7.6 x 3.8 cm in size.    Water samples were collected on 8/6/04 from Inoculation Ports (IP) and from holes (RH) excavated in the limestone bed as shown on Figure 1.   Unfortunately, the inflow zone of the bed was partially plugged and the flow was short circuited across the surface to RH-3, so this point is taken as the first useful measurement point, with a Mn concentration of 35.6 mg/L.  Mn concentrations in the IP points are much lower than the RH points.    This data, plus observations at other sites, indicates that the deep water tapped by the IP's is probably relatively stagnant and not representative of Mn behavior in the flowing system.   Therefore, only the data from samples at RH-3, -2, -1, and the outlet are used (Table 1).  The outflow Mn concentration is 5.5 mg/L.
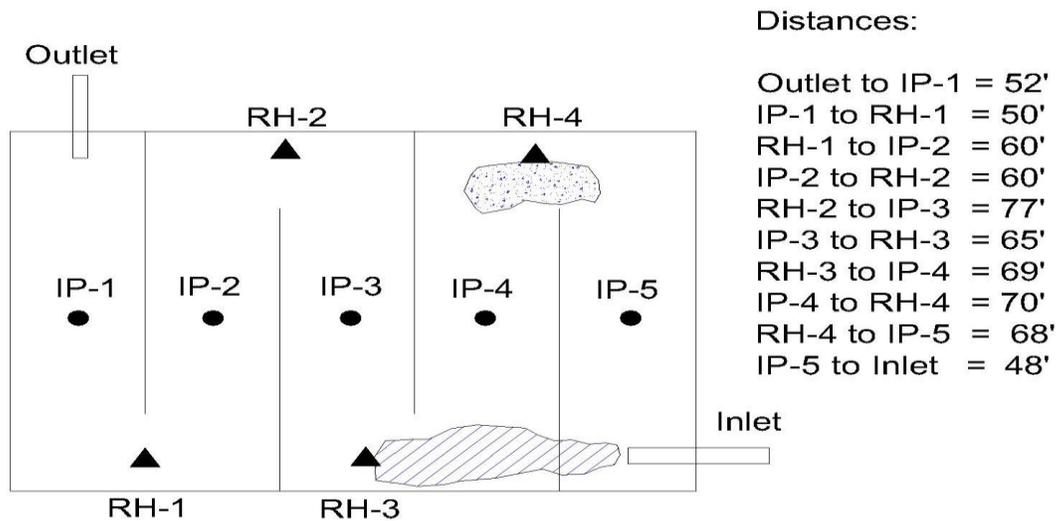


Figure 1. Plan view of the Cumberland, TN site (not to scale).  IP = Injection Port, RH = hole excavated
        in bed.   Patterns indicate flow over the surface.

Acidities for these samples are cold acidity measured in the field, and alkalinities are field measurements.    .

The Mn vs distance data for the Cumberland samples are plotted on Figure 2a.   Because the width and depth of the channels are approximately constant, the distance along the flow path is

proportional to time.  The points are clearly non-linear, and suggest a first order relation of Mn vs. time.  The same data are plotted in Figure 2b as log C vs. distance, and show a reasonable fit to a linear relation.

At the DeSale #2 site in northeastern Butler Co., PA, a limestone bed receives the outflow from vertical flow ponds at a rate of 260 L/min with 37.6 mg/L Mn (Table 1).   Stone in the bed is R4, which is about 10 cm in size.   Samples were collected on 7/8/04 from 6 holes excavated in the bed, plus the influent and effluent.  Data for this site are also plotted on Figures 2a and 2b.  The data indicate a non-linear relation, and reasonably fit a linear log C vs. distance plot.

At the Fairview site in Elk County, PA, aerated water with 128 mg/L Mn flows into a wide limestone bed at a rate of 60 L/min and is depleted to 56 mg/L after 17 m in the bed.  A concentration of 82 mg/L at a greater distance results from short circuiting of part of the flow over the surface along one side of the wide bed.   The stone is AASHTO #3, about 6.3 cm maximum size.  Water samples were collected from 6 holes dug in the bed, plus the influent and effluent.  Acidities are hot lab acidities, and alkalinities are lab values.   Data for this site are also plotted on Figures 2a and 2b, and show a non-linear relation for C vs. distance, but approximating a linear fit to log C vs. distance.

Several sets of samples were previously reported from the PBS site in Somerset Co., PA (Rose et al., 2003a, 2003b).  One set of data from this site includes filtered samples from the inflow, from a hole in the bed at 18 m and from the outflow at 64 m.  This data also is non-linear but fits a linear log C vs. distance plot indicating a first order relation with Mn concentration (Fig. 2a,b).

Based on this data, it is concluded that a first order removal rate for Mn in limestone beds is a good approximation.

### Derivation of rate equation

To convert the flow rates and distances to retention time in the bed at various points, it is assumed that the porosity of the sized aggregate in these beds is 50%.  This porosity is in the range of measurements at similar beds (Watzlaf et al., 2000).   The retention time (T) in hours can then be calculated as

$$T = 8.33 \ LWD/Q \qquad (13)$$

where L, W and D are the length, width and depth of the bed in meters, and Q is the flow rate in L/min.

The specific surface area of the fragments is estimated by assuming that the fragments are cubes of the maximum fragment size.   This is not highly accurate, but is considered to be proportional to the true surface area for beds with a limited range of fragment sizes.   If the individual fragment has a side d cm, then its volume is $d^3$ cm$^3$.   Given 50% porosity, then the volume of fragments per cubic meter is 0.5 x $10^6$ cm$^3$, and the number of fragments is 0.5 x $10^6/d^3$, or 0.5 x $(100/d)^3$.  Based on these relations, the specific surface area, in square meters of surface per cubic meter of bed, is

$$S \ (m^3/m^2) = 0.0003d^2 \ [100/d]^3 \qquad (14)$$

706

| Point | Distance | pH | DO | Eh | T | Acidity | Alkalinity | Mn | Fe | Al | Ca | Mg | SO4 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | m |  | mg/L | mv | C | mg/L CaCO3 | mg/L CaCO3 | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| **A. TN site** | Bed depth = 1.5 m |  |  |  | Flow = 300 L/min |  | Stone size 3.8 x 7.6 cm |  |  |  |  |  |  |
| Inlet |  | 4.81 | 8.18 |  | 20.7 | 208 | 0 | 38.8 |  | 5.7 | 127 | 122 |  |
| RH-3 | 0 | 5.18 | 7.5 |  | 17.9 | 178 | 5 | 35.6 |  | 4.4 | 130 | 125 |  |
| IP-3 | 19.8 | 6.16 | 2.92 |  | 12.5 | 110 | 48 | 8.9 |  | 0.6 | 136 | 133 |  |
| RH-2 | 43.3 | 6.5 | 3.4 |  | 11.7 | 122 | 22 | 16.2 |  | 0.75 | 134 | 130 |  |
| IP-2 | 61.6 | 6.3 | 2.4 |  | 12.8 | 96 | 52 | 10 |  | 0.56 | 139 | 136 |  |
| RH-1 | 79.9 | 6.47 | 3.04 |  | 12.2 | 88 | 53 | 7.6 |  | 0.36 | 149 | 146 |  |
| IP-1 | 94.5 | 6.86 | 0.31 |  | 13.3 | 86 | 86 | 2.1 |  | 0.12 | 153 | 150 |  |
| Outlet | 110.4 | 6.72 | 1.66 |  | 12.7 | 78 | 65 | 5.5 |  | 0.14 | 146 | 140 |  |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **B. Desale #2** | Bed depth =1.5 m |  |  |  | Flow = 260 L/min |  | Stone Size = 10 cm |  |  |  | 7/8/2004 |  |  |
| 1 | 0 | 4.11 | 4 | 348 | 22.3 |  | 0 | 37.6 |  |  | 207 |  |  |
| 2 | 4.6 | 6.02 | 5 | 228 | 24.4 |  | 10 | 36.3 |  |  | 217 |  |  |
| 3 | 10.4 | 6.41 | 4 | 196 | 24.4 |  | 28 | 28.9 |  |  | 219 |  |  |
| 4 | 16.2 | 6.7 | 3 | 156 | 23.4 |  | 43 | 25.8 |  |  | 225 |  |  |
| 5 | 22.9 | 6.97 | 2.6 | 117 | 25.5 |  | 75 | 28.3 |  |  | 236 |  |  |
| 6 | 29 | 7.19 | 1.4 | 120 | 23 |  | 97 | 20.7 |  |  | 244 |  |  |
| 7 | 35.7 | 7.01 | 3.2 | 124 | 25 |  | 63 | 20.2 |  |  | 235 |  |  |
| Effluent | 54.9 | 7 | 3.5 | 111 | 22.7 |  | 68 | 21.4 |  |  | 236 |  |  |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| **C. Fairview** | Bed depth = 1.2 m |  |  |  | Flow = 60 L/min |  | Stone size = 10 cm |  |  |  | 8/6/2004 |  |  |
| Influent | 0 | 4.56 | 3.8 | 375 | 12.8 | 287 | 16.4 | 128 | <0.2 | 0.87 | 189 | 223 | 1537 |
| 1 | 2.1 | 6.12 | 3.77 | 313 | 19.8 | 242 | 31.8 | 124 |  | 1.8 | 203 | 218 | 1493 |
| 2 | 5.3 | 6.43 | 2.07 | 311 | 15.9 | 108 | 121.8 | 107 | <0.2 | <0.2 | 227 | 205 | 1500 |
| 3 | 9 | 6.46 | 1.34 | 294 | 15.3 | 71 | 136.2 | 88 | <0.2 | <0.2 | 254 | 211 | 1492 |
| 4 | 12.8 | 6.52 | 0.65 | 272 | 16.5 | 30 | 138.6 | 84 | <0.2 | <0.2 | 258 | 209 | 1497 |
| 5 | 17.1 | 6.65 | 0.51 | 153 | 18.3 | -16 | 146.4 | 56 | <0.2 | <0.2 | 241 | 175 | 1245 |
| 6 | 19.2 | 6.57 | 0.97 | 137 | 19.9 | 42 | 139.4 | 82.4 |  | <0.2 | 242 | 196 | 1390 |
| Effluent | 23.2 | 6.65 | 2.28 | 279 | 20.5 |  |  | 83.1 |  | <0.2 | 237 | 189 |  |

| Point | Distance | pH | DO | Eh | T | Acidity | Alkalinity | Mn | Fe | Al | Ca | Mg | SO4 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | m | | mg/L | mv | C | mg/L CaCO3 | mg/L CaCO3 | mg/L | mg/L | mg/L | mg/L | mg/L | mg/L |
| **PBS** | | Bed depth = 0.9 m | | | Flow = 24 L/min | | | Stone size = 2 cm | | | Data for 10/22/02 | | |
| Influent | 0 | 4.72 | | | | 109 | 1.6 | 32 | 0.99 | 9.97 | 296 | 289 | 1761 |
| 1 | 18 | 6.83 | | | | | | 7.7 | 0.02 | <0.2 | 299 | 211 | |
| 2 | 64 | 7.82 | | | | 0 | 82 | 0.33 | 1.09 | 0.11 | 368 | 293 | 1820 |
| **K & J** | | Bed depth = 0.9 m | | | Av. Flow 6.5 L/min | | | Stone size = 2.5 cm | | | Averages 10/91-4/98 | | |
| | 0 | 4.4 | | | | | | 27.8 | 0.08 | | | | |
| | 27 | 7.5 | | | | | | 0.4 | 0.03 | | | | |
| **Swisstock 1** | | Bed depth = 0.9 m | | | Av. Flow = 74 L/min | | | Stone size = 2.5 cm | | | Average 4/94-11/95 | | |
| | 0 | 3.9 | | | | | | 16.4 | 0.2 | 6 | | | |
| | 61 | 6.4 | | | | | | 4.4 | 0.2 | 2 | | | 700 |
| **Laurel Run** | | Bed depth = 1.5 m | | | Av. Flow = 60 L/min | | | Stone size = 2.5-6 cm | | | Average 10/97-3/02 | | |
| | 0 | 3.5 | | | | | | 11.6 | 4.8 | 7.8 | | | |
| | 46 | 7.3 | | | | | | 0.2 | 0.01 | 0.2 | | | |
| **Stroud** | | Bed depth = 0.9? | | | Av. Flow 44 l/min | | | Stone size 5-7.5 cm | | | Average 3/98-10/01 | | |
| | 0 | 5.6 | | | | | | 8 | 3.9 | 1.9 | | | |
| | 61 | 6.6 | | | | | | 1.2 | 0.7 | <0.5 | | | |

Table 2. Summary of data on sites studies by Rose et al. (2003a).
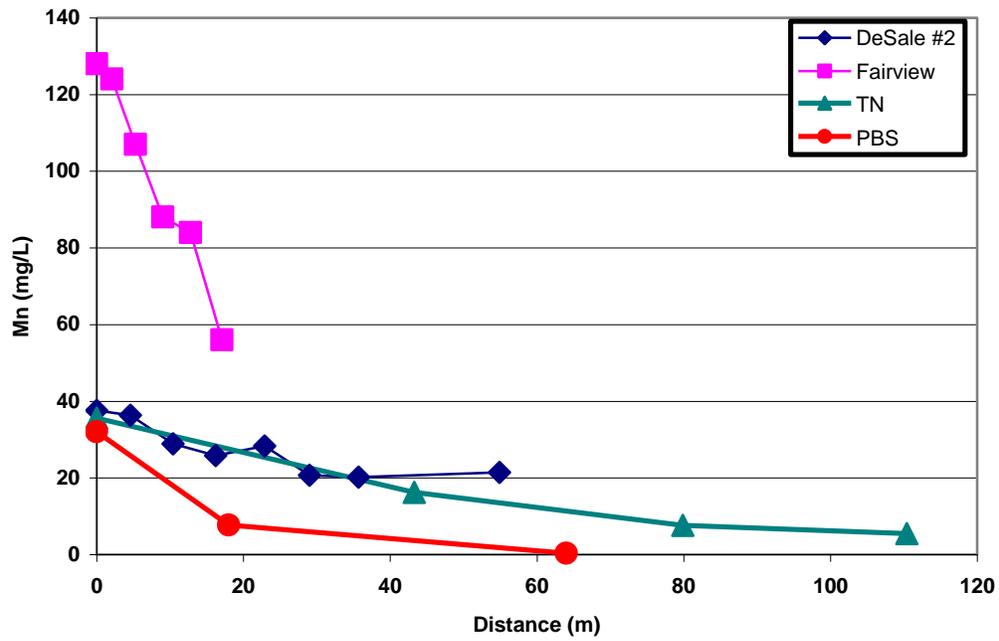
Figure 2a.   Plot of Mn concentration vs. distance along bed, showing non-linear trend.
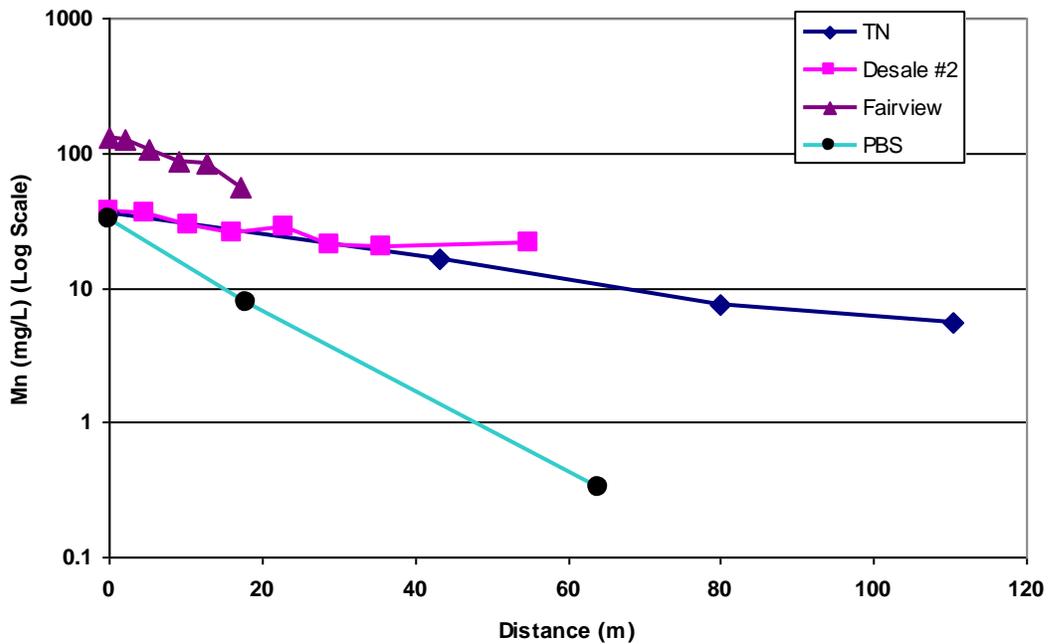


Figure 2b.   Plot of manganese concentration vs. distance on log scale, showing near-linear trend.

The available information on chemistry, flow, bed size and other parameters at PBS, K&J, Swisstock #1, Laurel Run and Stroud, which have relatively good treatment and data, is listed in Table 2, after Rose et al. (2003a, b). Of the other sites reported previously, Glenwhite is affected by severe Fe plugging, flow for Cambria G was based on only one estimated value, both sites at Middle Branch were severely affected by flow over the bed surface, and Swisstock #2 showed only very limited and erratic treatment, so data from these sites are not used.

The values for Mn, specific surface, and retention time for the eight sites with good data (TN, DeSale, Fairview, PBS, K&J, Swisstock #1, Laurel Run and Stroud) are summarized in Table 3 and plotted as Log $C/C_o$ vs. St/2.3 in Figure 3, where $C_o$ is the influent Mn concentration. The data for the 8 sites have a reasonably good linear fit to the equation

$$\text{Log } C/C_o = -10^{-3.35}ST \qquad (15)$$

with an $R^2$ value of 0.83.

## Discussion

Points for four of the sites (DeSale, Fairview, PBS and K&J) fall relatively close to the regression line. Two (Stroud and Tennessee) fall distinctly below it. However, these sites indicate a faster rate than the regression line, so the rate indicated by the line is a conservative value.

In terms of bacterial activity, note that Stroud, with a rate more rapid than the regression, was not inoculated with Mn-oxidizing bacteria by the Vail and Riley procedure, but Tennessee, Swisstock, K&J, PBS and Laurel were. DeSale and Fairview were not inoculated. An effect of inoculation on the rate is not evident.

As indicated above, a dependence on pH and $P_{O2}$ is expected, based on their participation in the reaction (equation 5). Also, for systems lacking Mn oxide surfaces and bacteria, Mn does not oxidize and precipitate at significant rates below about pH 9 (Hem, 1981, Diem and Stumm, 1984). The pH in the beds is strongly dependent on reaction with the limestone, which generates an outflow pH near 7. The ouflow pH values are shown on Fig. 3. The data suggest that sites with pH less than 7 tend to have <u>faster</u> rates of Mn removal than sites with pH greater than 7. This is opposite from the direction expected, and deserves further investigation.

Few data exist to evaluate the effect of dissolved $O_2$ (DO). At some decreased DO concentration, the reaction must slow or stop because of lack of oxidant. However, if the oxidation is bacterial, the rate may be insensitive to dissolved $O_2$ over a large range of values, as it is for pyrite oxidation from 21% down to 1% $O_2$ in air (Hammack and Watzlaf, 1990). At the sites studied, the DO values tend to decrease from the influent water down flow in the beds, at least partly because of consumption of $O_2$ by Mn oxidation. However, $O_2$ must also enter the water surface in the beds, replenishing some of the consumption. Note that the Tennessee site, with a higher than average removal rate, has a DO of 3 mg/L in the last sample point in the bed. This relatively high concentration is apparently adequate for good reaction. DO values at depth in the bed at PBS and Tennessee tend to be less than 1 mg/L (Rose et al., 2003a,b). Amounts of precipitated Mn in the deeper zones are smaller than near the water surface, indicating that low DO values are not favorable to reaction, and that deep beds are not an efficient design.

**Table 3. Summary of data on Mn removal**

| Site | Flow L/min | Length m | Width m | Depth m | Stone Size cm | Mn in mg/L | Mn out mg/L | Log C/Co | t hr | S m2/m3 | St/2.3 | k |
|------|-----------|----------|---------|---------|---------------|------------|-------------|----------|------|---------|--------|---|
| TN | 300 | 110 | 9.75 | 1.22 | 6 | 35.6 | 5.5 | -0.811 | 36.33 | 50 | 790 | -1.03E-03 |
| DeSale #2 | 260 | 35.7 | 22.9 | 1.5 | 10 | 37.6 | 20.2 | -0.270 | 39.29 | 30 | 512 | -5.27E-04 |
| Fairview | 60 | 17.1 | 10.4 | 1.22 | 6.3 | 128 | 56 | -0.359 | 30.12 | 48 | 624 | -5.76E-04 |
| PBS | 24 | 18 | 4.6 | 0.9 | 2 | 32 | 7.7 | -0.619 | 25.86 | 150 | 1687 | -3.67E-04 |
| K&J | 6.5 | 27 | 2.9 | 0.9 | 2.5 | 27.8 | 0.4 | -1.842 | 90.31 | 120 | 4712 | -3.91E-04 |
| Swisstock #1 | 74 | 61 | 2.9 | 0.9 | 2.5 | 16.4 | 4.4 | -0.571 | 17.92 | 120 | 935 | -6.11E-04 |
| Laurel | 60 | 46 | 12.3 | 1.5 | 4 | 11.6 | 0.2 | -1.763 | 117.83 | 75 | 3842 | -4.59E-04 |
| Stroud | 44 | 61 | 4.6 | 1 | 6 | 8 | 1.2 | -0.824 | 53.12 | 50 | 1155 | -7.13E-04 |
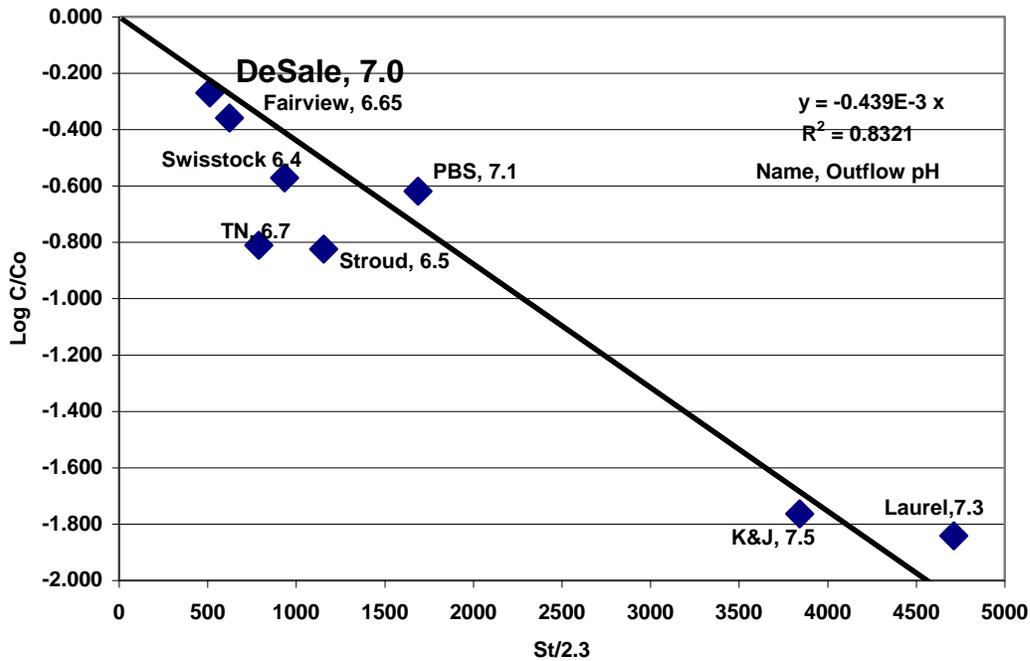
Figure 3. Plot of Log $C/C_o$ vs. St/2.3. The slope of the least squares line is $10^{-3.35}$ (=0.439E-3), which is adopted as the typical rate constant for Mn removal in the limestone beds.

Evidence at a site not discussed above suggests that a lack of DO many have stopped Mn precipitation. At this site, an unconventionally deep limestone bed (1.5 m) with a relatively small surface area received water with Mn of 104 mg/L, a pH of 6.3, and a DO of 4.6 mg/L. The outflow contained Mn of 90 mg/L, a pH of 6.7, and a DO of essentially 0. Interestingly, equation 5 shows that a consumption of 4.6 mg/L of DO equates to the oxidation of approximately 14 mg/L of Mn. It appears as though the thickness of the bed hindered the replenishment of oxygen throughout the bed and Mn oxidation ceased after the available oxygen was consumed.

## Sizing of Beds

The rate information developed above can be used to design the size of beds for removal of Mn. If the area of bed is denoted A, which equals LW in equation 13, then

$$T = 8.33AD/Q \tag{16}$$

$$A = TQ/8.33D \tag{17}$$

Combining with equation 12 (Log $C/Co = -k_1ST/2.3$),

$$A(m^2) = -0.276 \, Q \, \text{Log} \, C/C_o/(k_1SD) \tag{18}$$

The next step is to assign values to the parameters $C/C_o$, S, D and Q. For $C_o$, the observed influent Mn concentration should be used. For C the desired effluent Mn should be used. A C value of 1 mg/L would give a safety factor to ensure reaching an effluent standard of 2 mg/L, though it should be recognized that according to equation 15, a decrease from 2 to 1 mg/L Mn

requires as much retention time as from 100 to 50 mg/L. The depth D of the water-saturated bed should be relatively small, probably 0.3 to 0.6 m of water-saturated bed. An additional air-filled thickness (0.15 m) should be added in the design to ensure that flow is through the bed rather than over the surface during periods of increased flow. However, it is the water-saturated thickness that should be used in equation 18. A value of 0.5 m is suggested as reasonable. The value of S depends on the size of limestone aggregate to be used. For roughly equidimensional stone, the value can be calculated from equation 14 or found from Figure 4. In general, relatively coarse stone is probably preferable to minimize problems of plugging, though previous removal of essentially all Al and Fe, and a settling pond to remove silt is the key to long-term treatment. The value of Q (in L/min) should be near the maximum value determined from long-term monitoring of the discharge.

The bed area can then be calculated from equation 18. For example, consider the following input parameters:

$$\text{Influent Mn} = C_o = 30 \text{ mg/L}$$

$$\text{Desired effluent Mn} = C = 1 \text{ mg/L}$$

$$\text{Flow} = Q = 100 \text{ L/min}$$

$$\text{Bed depth} = D = 0.5 \text{ m}$$

$$\text{Stone diameter} = d = 5 \text{ cm (with fines removed)}$$

$$k_1 = 10^{-3.35} \text{ hr}^{-1}(m^2_s/m^3_v)^{-1}$$

From Fig. 4, $S = 60 \text{ m}^2/\text{m}^3$.

$$\text{Log } C/C_o = \text{Log } 1/30 = -1.48$$

The bed area can then be calculated as

$$A = -0.276 \text{ x } 100 \text{ x } (-1.48)/(10^{-3.35} \text{ x } 60 \text{ x } 0.5) = 40.85/0.0134 = 3048 \text{ m}^2 \qquad (19)$$

In principle, any combination of length and width with this area can be used, though large widths are to be avoided in order to avoid problems of channelization. For example, a bed 20 m wide and 150 m long would be satisfactory, or one 10 m wide and 300 m long.

Several other factors are important in design. As indicated above, the influent should have negligible Fe and Al. Concentrations less than 1 mg/L are desirable, though somewhat higher values may be acceptable with occasional maintenance to open up plugged zones. Inflow of clay, silt, sand and organic particulates should be avoided by a settling pond preceding the bed. The influent water should be well aerated by splashing over riffles or from an elevated pipe. Adequate elevation decrease along the bed should be provided to ensure flow, and at least 0.15 m of unsaturated bed should be available to prevent flow over the surface and to keep leaves and other organic debris from plugging the bed or from entering the bed and generating reducing conditions. Vail and Riley (2000) suggest that the bed should be lined to keep out soil bacteria, but some beds seem to function well without a liner. However, the bed should maintain water in most of its depth, even during dry periods, in order to preserve active bacteria and Mn-oxide surfaces.
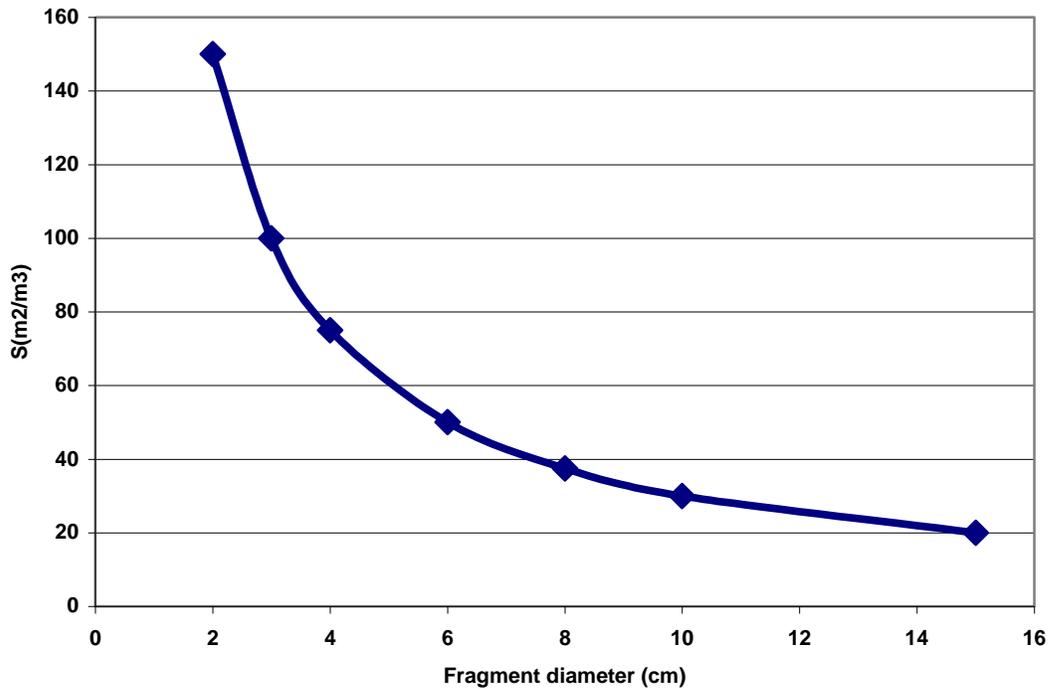
Figure 4. Plot of the theoretical value of S (specific surface area of stone) vs. maximum fragment diameter, as used in equations in the text.

When dealing with very elevated concentrations of Mn (>60 mg/L), a series of smaller beds separated by aeration steps may be more effective than a single large bed.

After many years, the bed may begin to plug with manganese precipitate. At this time, the bed will have to be agitated with an excavator and the permeability restored. Possibly methods can be developed to recover the Mn, perhaps by flushing with an $Fe^{2+}$ solution to dissolve the Mn precipitate and then reprecipitating it.

## Conclusions

1. Mn concentrations along several Mn removal limestone beds indicate that the rate of Mn oxidation and precipitation is first order with respect to Mn, i.e., proportional to Mn concentration at constant pH and dissolved $O_2$.

2. Data from 8 sites for which reasonably good data are available indicate that the rate of removal in limestone beds can be fit by the equation

$$2.3 \, Log \, (C/C_o) = -k_1 ST \qquad (20)$$

where C and $C_o$ are the outflow and inflow Mn concentrations, T is the retention time in the bed in hours, S is the specific surface area of the limestone aggregate in $m^2/m^3$, and $k_1$ is a rate constant with a value of about $10^{-3.35}$ m/hr.

3. The required area A of a limestone bed for manganese removal can be estimated using the relation:

$$A(m^2) = -0.276 \, Q \, Log \, (C/C_o)/(k_1 SD) \tag{21}$$

where Q is flow in L/min, D is the depth of water saturation in the bed in meters and S is the specific surface of the limestone aggregate in $m^2$ of surface per $m^3$ of volume.

4. Satisfactory performance of the removal system also depends on having negligible Fe, Al, organic matter and sediment in the influent water, well aerated influent, and a permeable limestone bed with high porosity.

5. The precise effects of pH and dissolved $O_2$ are not clear, but do not appear to have major effects on beds designed according to the above approach.

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