Removal of Manganese from Coal Combustion Byproduct Leachate Using Manganese-Oxidizing Bacteria Systems

Kevin L. Hoover and Terry A. Rightnour

Manganese-oxidizing bacteria systems (MOBS), colloquially known as "rock drains," consist of shallow basins filled with rock aggregate to form a growth substrate for manganese-oxidizing bacteria. MOBS have proven highly effective for removing manganese from coal combustion byproduct (CCB) leachate under net alkaline conditions and at low iron concentrations. Manganese is deposited on the aggregate surfaces through bacterial metabolism in the form of a black coating of stable manganese oxides (pyrolusite, etc). To develop better design criteria for use of MOBS in passive wetland treatment systems, two recent MOBS applications at CCB disposal sites were examined for manganese oxide accumulation trends. After a period of approximately one year of system operation, aggregate substrate samples were collected from different depths and distances from the MOBS cell inlets and examined for color value (Munsell) as a measure of manganese oxide accumulation. Results indicate that the majority of pyrolusite accumulation occurs in the upstream end of a MOBS cell, accumulation diminishes with substrate depth, and that increased accumulation occurs at the inlet point to each MOBS cell in a serial flow path. It is recommended that MOBS systems be divided into serial basins of narrow width and 30 m or less in length, with substrate depths of approximately 0.6 m and passive aeration (spill) points between each basin. A substrate rock diameter of 20 to 50 mm appears to optimize the surface area available for manganese accumulation relative to substrate volume. MOBS are best placed at the end of a passive wetland treatment system where iron concentrations are lowest. Manganese removal using MOBS is directly applicable to CCB leachate, mine drainage, and similar wastewaters where influent alkalinity and iron concentration requirements are met, or can be met upstream of the MOBS using constructed wetlands or other passive treatment technologies.

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INTRODUCTION

Aqueous manganese is a common constituent of coal combustion byproduct (CCB) leachate and other waters related to coal mining and storage activities. Manganese is often regulated as a contaminant for permitted discharge points, requiring treatment if concentrations exceed effluent limitations. Conventional chemical treatment to remove manganese normally requires addition of neutralizing agents sufficient to raise the pH of the wastewater to 9.5 SU or greater (Humenick, 1977). This entails the expense of a chemical treatment facility and the long-term costs of chemical addition and maintenance. The utility industry has long sought a passive treatment alternative for manganese removal that could be operated at a lower expense and without the need for costly and potentially hazardous neutralizing agents.

Manganese-oxidizing bacteria systems (MOBS), colloquially known as "rock drains," are one emerging passive technology that shows great promise for treating aqueous manganese. MOBS cells are typically constructed as shallow basins filled with rock aggregate to form a growth substrate for manganese-oxidizing bacteria, which occur naturally in streams and lakes. Under the proper conditions, these bacteria will remove aqueous manganese from water as part of their life processes and deposit it onto the rock aggregate substrate in the form of stable manganese oxides, such as the mineral pyrolusite. MOBS have proven very effective in treating manganese from CCB leachate when used in conjunction with passive wetland treatment, and have also been applied to the treatment of coal mine drainage waters.

Although the influent water quality limitations for application of MOBS are reasonably well known, to date there are no firm criteria available for their design and sizing. To develop better design guidelines, studies were conducted at two CCB disposal sites where MOBS have been applied. Color variations were used to evaluate the extent of manganese oxide accumulation in individual MOBS cells, and additional observations were made regarding manganese oxide accumulation patterns. This study summarizes the findings of this survey and provides recommendations for MOBS design and construction practices based on these results.

Background

Manganese removal is recognized to occur in constructed wetland treatment systems under net alkaline conditions; however, the rate of removal is very low in most constructed wetlands. Hedin and Nairn (1992) established the compliance design removal rate for manganese at 0.5 grams per day per meter squared based on constructed wetland surface area. For CCB discharges with substantial manganese loadings, this removal rate can equate to a requirement for large constructed wetlands, potentially making them impractical due to cost or construction area limitations. Hedin and Nairn (1993) also established that high iron concentrations have a negative impact on manganese removal in constructed wetlands, and an iron influent limitation of 1 mg/L has been suggested as the threshold below which optimum manganese removal will occur. When iron is present at greater concentrations, additional constructed wetland area or other upstream treatment mechanisms are needed to remove the excess iron before significant manganese removal can be expected to occur.

Seeking to improve the performance of passive wetland treatment systems for manganese removal, research has focused on incorporating enhanced growth environments for manganese-oxidizing bacteria. Gordon (1989) demonstrated that bacterially-mediated manganese removal would occur in bench-scale columns filled with small natural river stones of 20 to 45 mm diameter. Thornton (1995) confirmed this finding with a field-scale treatment facility using limestone-filled tanks at a CCB disposal pond site, also using a substrate averaging about 35 mm in diameter. Both studies involved influent waters meeting the same requirements as constructed wetlands for net alkalinity and low iron concentrations. During the 1990s, this concept was applied at numerous passive treatment facilities using shallow basins filled with rock aggregate, these becoming the most common type of MOBS in use today. Although sparsely documented in literature, these MOBS applications are generally recognized as being very effective, sometimes achieving complete manganese removal under ideal conditions.

In terms of MOBS cell sizing, Gordon (1989) also concluded that manganese removal is dominated by hydraulic loading in the manganese concentration range of 2 to 15 mg/L, with 90% or greater removal occurring at hydraulic loadings of 390 to 780 m^3/hr-ha. In an aggregate substrate of 0.6 m thickness, this equates to an average detention time in the substrate of about 3 hours or more. Thornton's (1995) experiment involved substrate detention times of approximately 5.5 hours with an average removal efficiency of 88%. The MOBS cells used on the two sites included in this current study were both sized to have detention times of approximately 16 hours in the substrate. These greater detention times were selected for greater confidence of treatment, as the two sites were regulated for discharge compliance, and this technology was still experimental at the time of their design. Based on the results from the two study sites, Hoover et. al., (1996) proposed a preliminary sizing criteria for compliance systems of 48 hours detention time for the impounded depth of a MOBS cell without substrate, equating to an actual detention time of about 16 hours for most substrate materials. Work is currently underway to quantify MOBS cell sizing as a function of influent flow volume and manganese removal percentage, potentially reducing this sizing requirement for future applications.

Study Site Descriptions

The two MOBS applications selected for study are associated with passive wetland treatment systems receiving leachate from CCB disposal piles. These are referenced herein as Site A and Site B. Both sites have discharge limitations imposed for manganese under NPDES permits, and both sites have achieved discharge compliance through use of passive treatment. The following provides a brief summary of the individual site characteristics.

Site A

Site A, located in southwestern Pennsylvania, is a CCB disposal facility that was closed in 1975. CCB leachate discharging from a pile underdrain is characterized by iron and manganese concentrations averaging 12.46 mg/L and 2.71 mg/L, respectively, at a pH averaging 7.04 SU. In 1994, a passive oxidation and precipitation basin was constructed to remove iron to discharge limitations, but had little effect on manganese. In 1995, a system of eight passive treatment cells was added to remove manganese and additional regulated contaminants. This included four aerobic wetland cells, two MOBS cells, an organic upflow cell, and an algal uptake cell. The MOBS cells were constructed with a 1.2 m substrate depth consisting of 0.4 m layers, from bottom to top, of R-4, R-3, and R-2 grade sandy limestone aggregate (a range of about 25 to 300 mm diameter). The substrate surfaces in each cell measured approximately 7.5 m in width by 39.5 m in length. The upstream oxidation/precipitation basin and wetland cells reduced iron concentrations influent to the MOBS to 0.12 mg/L, and the wetland cells also significantly reduced manganese concentrations. During the study period, manganese concentrations influent to the first MOBS cell averaged 0.28 mg/L, with an average effluent concentration of 0.07 mg/L forming the influent to the second MOBS cell. The second MOBS cell had an average effluent manganese concentration of 0.04 mg/L.

Site B

Site B, located in north-central West Virginia, is an active CCB disposal facility where net alkaline leachate emanates from several seeps below the toe of the fill pile. The site has been used as a test bed for passive treatment technologies since 1988, when four small wetland cells were constructed and proved effective at treating iron, but not manganese. Two additional wetland cells were added in 1992 to improve manganese removal, but removal rates remained similar to those reported by Hedin and Nairn (1992), and insufficient construction area was available to sufficiently enlarge the wetlands to fully treat manganese. In 1996, the system was further modified to add three MOBS cells and, following a brief colonization period for the bacteria, almost total removal of manganese was achieved. The Site B MOBS cells contain 0.6 m of 25 to 50 mm diameter limestone aggregate with substrate surface dimensions of approximately 4.5 m in width by 27.5 m in length each. During the study period, influent manganese concentrations to the first MOBS cell averaged 6.01 mg/L, and effluent concentrations from the third MOBS cell averaged 0.02 mg/L. Iron concentrations averaged 1.21 mg/L at the influent and 0.33 mg/L at the effluent. The internal discharge points of the first and second MOBS cells were not sampled as part of the monitoring program for the system.

METHODOLOGY

Because bacterial removal of manganese generates a distinctive black coating on the affected MOBS substrate, it is reasoned that the degree of change in substrate coloration from initial clean conditions can be used as a measure of the degree and extent of manganese oxide accumulation within a MOBS cell. The limestone aggregate substrates used at the two study sites are generally light-colored and homogeneous in coloration on their unweathered surfaces, allowing for ready visual identification of manganese oxide coatings. After one year of operation at both systems, it was observed that the extent of visual manganese oxide coating was not consistent throughout the MOBS cells, and that the coating appeared to diminish from the upstream end of each cell to its downstream end. To determine whether this was truly the case, a sampling program was developed to measure color variations along the length of the substrates on both sites and through their depths on one site.

Aggregate substrate samples were collected by random grab method at 6 m intervals starting at the influent point on Site A and 6 m from the influent point on Site B. At Site A, substrate samples were collected from just beneath the surface and 0.3 m below the surface for each sample point, and from 0.6 m below the surface at the 6 m, 18 m, and 30 m sample points in the first MOBS cell. At Site B, samples were collected from just beneath the surface only. Samples were maintained in individual sealed plastic bags in a wetted condition until examination.

For each collected sample, a random selection of three substrate rocks was laid out in a tray, and small paper fragments were allowed to randomly drop onto their wetted surfaces from a height of approximately 0.6 m until ten fragments had adhered to the samples. The color of the rock surface below each paper fragment was recorded by hue, value, and chroma using a Munsell color chart. The substrate rocks were then overturned and the process repeated, yielding twenty color measurements from each sample. The chroma and value measurements were averaged to summarize the data for each sample.

RESULTS

After review of the averaged hue, value, and chroma data, it was determined that hue and chroma would be of little use to this study. Hue is a property measurement that does not lend itself to numeric averaging within the Munsell system. Although being light in overall color, the unweathered rock surfaces possessed an initially low chroma, and the black manganese oxide coatings also developed a low chroma, resulting in little differentiation by that measure. The results for value were distinctive and were thus selected for use in this evaluation.

As shown by Figures 1 and 2, substrate surface color values tend to increase from upstream to downstream within the MOBS cells. Value is inversely related to degree of manganese oxide accumulation, as higher values are associated with lighter rock surfaces. This indicates a diminishing trend in manganese oxide accumulation with distance from the MOBS cell inlets. This trend appears to be linear in nature within individual cells, but the trend breaks between cells.

In Figure 1, both Site A MOBS cells show consistently higher values with depth within each sample column. The average of sample values within each depth range is significantly higher than the average sample values in the overlying depth range. This indicates a diminishing trend in manganese oxide accumulation with depth similar to that observed for distance from the inlet.

The values at the discharge from the first to second MOBS cells at both sites show the downstream cell inlet value to be lower than the upstream cell outlet value. This indicates a greater manganese accumulation rate at the influent point to the second cell as compared to the outlet point of the first. This effect may also be occurring between the second and third MOBS cells on Site B, but the difference may be obscured by the greater sampling distance from the inlet point as compared to those on Site A.

Additional observations made during the examination process indicate that manganese accumulation does not occur where algae are present on the surface of the substrate rocks, or at least has no chromatic expression on the rock surface beneath the algae. Sharply defined areas of no manganese oxide accumulation were also observed on the contact points between individual rocks and extended beyond the actual point of physical contact between the rocks. Although not measured in situ as part of this study, the zones of non-deposition appeared to occur where rock surfaces were within approximately 1 - 3 mm of each other. There was no discernable photo-dependence to the accumulation surfaces, such as greater accumulations occurring on surfaces that were exposed to light as opposed to those that were shaded within the water column.

Figure 1 – Site A Substrate Color Values

Sample Depth	Distance from MOBS Cell No. 1 Inlet						
	0 m	6 m	12 m	18 m	24 m	30 m	36 m
0.0 m	2.45	2.00	2.10	2.73	2.78	3.23	3.50
0.3 m	2.65	2.30	2.95	3.23	3.78	4.08	4.50
0.6 m		4.40		3.30		4.35	

Sample Depth	Distance from MOBS Cell No. 2 Inlet						
	0 m	6 m	12 m	18 m	24 m	30 m	36 m
0.0 m	2.58	2.95	3.50	4.00	3.63	4.24	4.25
0.3 m	3.20	3.48	4.00	4.55	4.60	4.65	4.88

Figure 2 – Site B Substrate Color Values

Sample Depth	Distance from MOBS Cell No. 1 Inlet				
	0 m	6 m	12 m	18 m	24 m
0.0 m		2.03	3.05	2.63	2.75

Sample Depth	Distance from MOBS Cell No. 2 Inlet				
	0 m	6 m	12 m	18 m	24 m
0.0 m		2.45	3.00	3.00	3.18

Sample Depth	Distance from MOBS Cell No. 3 Inlet				
	0 m	6 m	12 m	18 m	
0.0 m		3.45	3.75	3.84	

DISCUSSION

The primary outcome of this study is to confirm that manganese oxide accumulation is not uniform within MOBS cells under the observed conditions. This suggests that spacially-dependent mechanisms are in operation to enhance or retard manganese-oxidizing bacterial activities within MOBS cells, and that design practices may be able to improve MOBS performance by focusing on the enhancement mechanisms.

The diminishing trend of manganese oxide accumulation with distance from the cell inlet may be explained simply by reduction in manganese concentrations by upstream bacterial consumption, with downstream bacteria having less manganese available to form oxides. However, this is not consistent with the observation that manganese accumulations increase at the next downstream cell inlet point. Sufficient manganese must remain in solution to allow this rejuvenated accumulation to occur by another mechanism. Although oxygen can be expected to diffuse into shallow flowing water by atmospheric contact, it may still represent a rate-limiting factor to manganese-oxidizing bacteria if sufficient oxygen cannot diffuse to meet consumption demands during passage of water across the substrate. In this case, rejuvenated accumulation would be expected at points of accelerated aeration, such as piped outfalls from one cell to another. Multiple outfall/aeration points would thus be expected to improve manganese removal efficiency.

The diminishing trend in manganese accumulation with substrate depth may be the result of surface consumption, oxygen depletion, and/or preferential flow paths. Water levels in MOBS cells are typically maintained at approximately the substrate surface elevation to maximize the degree of substrate contact with the water, with inlet and outlet points being surface pipes. In a such a situation with no downward driving head, the bulk of water flow can be expected to occur in the near-surface substrate horizons, where the shortest flow path and least overall resistance from substrate friction are present. This problem could be partially overcome by using submerged-entry pipes at the outlet points of the MOBS cells, redirecting some flow deeper into the substrate to reach the pipe mouth, but would still not guarantee complete substrate contact. If entering another downstream MOBS cell, the pipe discharge would still have to be exposed to the atmosphere to achieve the interpreted advantage of re-oxygenation. The results from the first MOBS cell on Site A indicate that little manganese accumulation occurs at a depth of about 0.60 m, and deeper substrates are probably not worth the investment in their added installation costs.

The presence of algae apparently prevents the growth of manganese-oxidizing bacteria on rock surfaces, although this does not appear to be a detriment to the performance of the two study sites. In some instances algal mats could limit oxygen diffusion from the water surface and retard manganese removal processes beyond the aerated cell inlet point. Algae do not appear to grow well where the water surface is several centimeters below the substrate surface, so reduction of water levels in MOBS cells could be a method of combating algae on sites where its growth is interpreted to be a detriment.

The presence of non-depositional aureoles around substrate rock contacts suggests that very narrow spacings between rocks are not conducive to the growth of manganese-oxidizing bacteria. This may be related to slow diffusion of manganese and oxygen into the narrowest parts of the rock voids, essentially creating local starvation zones in the interference spacing between the rocks. If the interference spacing width is constant, the percentage of rock surface area affected by non-depositional aureoles would be expected to increase relative to total surface area as the rock diameter decreases, thereby decreasing the removal efficiency of the substrate. Conversely, as the rock diameter increases, the ratio of its surface area to volume decreases, also potentially decreasing removal efficiency relative to a given substrate volume. Using a two-dimensional, hexagonal close packing model of spherical aggregate contacts, an estimate was made of the ratio of net effective linear surface area relative to total cross-sectional substrate area for scenarios of interference spacings ranging from 1 to 3 mm. It was found that the maximum ratio of surface area to total substrate area occurred at a rock diameter of approximately 20 mm. The ratio dropped rapidly below this diameter, but tapered off much more gradually above it, with the ideal range appearing to be about 20 to 50 mm. This diameter range corresponds to the substrate sizes used for the Gordon (1989) and Thornton (1995) projects, giving additional experimental evidence that it is effective. This is also the substrate size range used on Site B, which appears to have a better overall manganese removal rate than Site A.

CONCLUSIONS

MOBS represent an important emerging tool for passive treatment of CCB leachate and other manganese-bearing wastewaters. Additional work is needed to fully quantify design standards for MOBS cells, particularly with regard to their response under different influent flow and manganese loading conditions. However, several general conclusions can be drawn from this study that may improve the performance of new MOBS applications:

- Influent iron concentrations should not exceed 1.0 mg/L, and influent alkalinity should exceed acidity. (An influent pH of 6 SU or higher appears to give the best performance.) These influent standards can be achieved by upstream passive wetland treatment for most CCB leachate situations.

- Multiple, short MOBS cells are preferable to a single, long cell for reducing manganese accumulation efficiency losses observed for substrate distance from the inlet point. Cell lengths of 30 m or less are recommended.

- Multiple, short MOBS cells are also preferable for introducing aeration points at the connection points between cells. Provision should be made for head loss and passive aerators, such as splash plates, in association with intercell connections.

- Narrow MOBS cells are preferable to wide cells to improve flow path control and spreading through the substrate. A maximum cell width of 7.5 m is recommended.

- Substrate depths of 0.6 m are effective, and deeper substrates do not appear to participate significantly in manganese oxide accumulation in horizontal flow situations. Shallower substrates may also be effective, but data for their performance are not currently available.

- The optimum substrate size range appears to be 20 mm to 50 mm (about 1 to 2 inches) in diameter. Care should be taken to exclude smaller material that could fill aggregate voids and reduce removal efficiency.

- A cumulative detention time of 16 hours in MOBS cell substrates appears to be effective for compliance-level manganese removal with influent concentrations of up to 15 mg/L. Lesser detention times may be considered for non-compliance situations.

- MOBS should be placed at the end of passive wetland treatment systems, where the highest alkalinity and lowest iron concentrations can be expected.

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