Characterization of manganese oxide precipitates from Appalachian coal mine drainage treatment systems

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A B S T R A C T

The removal of Mn(II) from coal mine drainage (CMD) by chemical addition/active treatment can significantly increase treatment costs. Passive treatment for Mn removal involves promotion of biological oxidative precipitation of manganese oxides (MnO x). Manganese(II) removal was studied in three passive treatment systems in western Pennsylvania that differed based on their influent Mn(II) concentrations (20–150 mg/L), system construction (zinoculation with patented Mn(II)-oxidizing bacteria), and bed materials (limestone vs. sandstone). Manganese(II) removal occurred at pH values as low as 5.0 and temperatures as low as 2 °C, but was enhanced at circumneutral pH and warmer temperatures. Trace metals such as Zn, Ni and Co were removed effectively, in most cases preferentially, into the MnO x precipitates. Based on synchrotron radiation X-ray diffraction and Mn K-edge extended X-ray absorption fine structure spectroscopy, the predominant Mn oxides at all sites were poorly crystalline hexagonal birnessite, triclinic birnessite and todorokite. The surface morphology of the MnO x precipitates from all sites was coarse and “sponge-like” composed of nm-sized lathes and thin sheets. Based on scanning electron microscopy (SEM), MnO x precipitates were found in close proximity to both prokaryotic and eukaryotic organisms. The greatest removal efficiency of Mn(II) occurred at the one site with a higher pH in the bed and a higher influent total organic C (TOC) concentration (provided by an upstream wetland). Biological oxidation of Mn(II) driven by heterotrophic activity was most likely the predominant Mn removal mechanism in these systems. Influent water chemistry and Mn(II) oxidation kinetics affected the relative distribution of MnO x mineral assemblages in CMD treatment systems.

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1. Introduction

The removal of Mn(II) from coal mine drainage (CMD) is a significant problem for both operating and abandoned coal mines in Pennsylvania and across the USA. Manganese(II)-elevated mine drainage exists in all eastern USA coal producing states. According to the US Office of Surface Mining (OSM) mine drainage inventory, Mn(II) is being treated at more than 700 mine sites in Appalachia (60% of sites) and most coal operators use NaOH to remove Mn(II) from mine drainage. Sodium hydroxide is added to raise the pH to ~9–10 to promote the abiotic oxidation of soluble Mn(II) to insoluble Mn(III/IV) (oxyhydr)oxides (referring to hereafter as “MnO x”). Active Mn(II) removal (i.e. NaOH addition) can double or triple treatment costs due to the chemical consumption needed to achieve high pH conditions (Means and Hilton, 2004). Passive removal of Mn(II) is desirable as it eliminates the need for chemical reagent and the annual treatment costs can be a small fraction compared to active treatment. The success of passive Mn(II) removal systems has been variable due to a lack of design criteria and a poor understanding of the mechanisms that govern Mn(II) oxidation at circumneutral pH.

Passive limestone beds neutralize acidic water and promote biologically-mediated Mn(II) oxidation (Thornton, 1995; Sikora et al., 2000; Vail and Riley, 2000; Johnson and Younger, 2005; Means and Rose, 2005). Widespread and diverse bacteria, fungi, and algae are capable of coupling the enzymatic oxidation of Mn(II) (and subsequent precipitation of MnO x) to O2 reduction at circumneutral pH (Ghiorse, 1984; Tebo et al., 2004; Thompson et al., 2005; Templeton et al., 2005; Hansel and Francis, 2006). Biological Mn(II) oxidation has been exploited to remove Mn(II) from drinking water in sand filtration systems inoculated with Mn(II)-oxidizing bacteria (Mouchet, 1992; Katsoyiannis et al., 2004). In CMD limestone beds, Mn(II) is removed and accumulates in these systems as MnO x coatings that can in turn catalyze additional Mn(II) removal. Wetlands are often placed upstream of limestone beds...
to provide organic C and nutrients for indigenous or inoculated Mn(II)-oxidizing bacteria (Mn(II)OB) (Thornton, 1995; Vail and Riley, 2000; Johnson and Younger, 2005).

At circumneutral pH, Mn(II) may be oxidized by microbiological activity or by surface-catalyzed heterogeneous oxidation on Mn(III/IV) oxide surfaces (Davies and Morgan, 1989; Junta and Hochella, 1994). Currently, the relative importance of biological Mn(II) oxidation versus abiotic surface-catalyzed Mn(II) oxidation in these systems is uncertain (Means and Rose, 2005). However, much of the Mn(II) oxidation observed in natural systems is believed to be biologically-mediated (Hingate et al., 1987; Nealon et al., 1988; Tebo, 1991; Tebo et al., 1997).

The mechanism for biogenic MnO₃₃ formation has been developed from pure bacterial culture studies coupled with X-ray absorption spectroscopy (XAS) and synchrotron radiation X-ray diffraction (SR-XRD) (Bargar et al., 2000, 2005; Villalobos et al., 2003; Webb et al., 2005a). Bacteria use O₂ and a Mn-oxidase enzyme to oxidize Mn²⁺ to Mn³⁺ (likely through Mn⁴⁺) and Mn³⁺ rapidly hydrolyzes to form disordered nanoparticulate (DN) MnO₂. DN MnO₂ then forms small, poorly crystalline Ca-hexagonal birnessite, and finally transitions into Ca-pseudo-orthogonal birnessite (Webb et al., 2005a). While this mechanism has been worked out in fine detail with model biological systems, subsequent mineralogical transformations are critical in controlling the MnO₃₃ mineral(s) found in a particular environment. The stability and predominance of the over 30 MnO₃₃ minerals are strongly dependent on solution chemistry (e.g. freshwater vs. seawater). Calcium in particular is hypothesized to stabilize and promote the growth of biogenic birnessites (Webb et al., 2005b). However, MnO₃₃ minerals are also quite labile and respond to thermodynamic driving forces such that rapid conversion between mineral phases can occur (Bargar et al., 2005; Lopano et al., 2007).

Manganese oxides exert significant control on the distribution of trace metals in soils and aquatic environments because of their high adsorption capacities (Post, 1999). Often occurring as fine grained particles and surface coatings, MnO₃₃ provide large reactive surface areas far more than their proportional concentrations (Jenne, 1968). Several studies have demonstrated that MnO₃₃ can serve as natural sinks for Co, Ni, Zn and other metals in mine tailing sites and streams impacted by mining activities (Fuller and Harvey, 2000; Kay et al., 2001; Tani et al., 2004). MnO₃₃ also participate in a wide range of redox reactions, including oxidation of As(III) to As(V), Cr(III) to Cr(VI), and degradation of organic contaminants (PCBs, phenols and chlorinated solvents) (Manseau and Charlet, 1992; Stone, 1987).

Regardless of the abiotic or microbial oxidation pathway and the subsequent stabilization of the MnO₃₃, the mineralogical and physicochemical properties of the MnO₃₃ formed in CMD treatment systems (or in any other environment) will directly affect their ability to remove additional Mn(II) and other metal co-contaminants. In this study the performance of three passive Mn-removal systems in western Pennsylvania has been monitored and the MnO₃₃ formed in these beds characterized by electron microscopy, XRD and XAS. The objective was to evaluate how aqueous geochemical conditions and MnO₃₃ properties may contribute to the enhanced removal of Mn(II) and associated trace metals.

2. Materials and methods

2.1. Site descriptions

Personnel from the OSM directed the authors to three Mn-removal systems located in western Pennsylvania that differed based on their influent Mn(II) concentrations (20–150 mg/L), system construction (±inoculation with patented Mn(II)OB), and bed materials (limestone vs. sandstone). All of the systems are treating CMD from surface coal mines. Important physical, chemical and operational features of these treatment systems are presented in Table 1.

The treatment system at Site 1 was filled with limestone gravel (4 in.), was not inoculated with Mn(II)OB, and treats an exceptionally high influent Mn(II) concentration of 130–150 mg/L. CMD is conveyed through an underground limestone drain before discharging into a constructed wetland and then enters the limestone Mn-removal bed. Discharge into the wetland comes from a pipe elevated several feet above the ground that provides aeration as the water enters the wetland. The rectangular bed contains five ditches (perpendicular to bed flow, ~½ the depth of the bed) that were added to promote passive aeration and served as the water and sediment sampling locations.

The treatment system at Site 2 was filled with limestone gravel (1 in.) and inoculated with a patented suspension of Mn(II)OB (Pyrolusite Process®, Vail and Riley, 2000), and treats an influent Mn(II) concentration of 20–30 mg/L. CMD flows into a constructed wetland, then into the limestone bed, and is aerated before the limestone bed by discharge through an elevated pipe. The narrow rectangular bed contained three piezometers that were used to collect water samples within the bed.

The treatment system at Site 3 includes three ponds in series designed to remove both Fe (in the first two ponds) and Mn (in the final pond) from a circumneutral-pH surface coal mine discharge. In the final pond, a 2-m wide sandstone barrier was constructed across the pond (perpendicular to bed flow and breaching the water surface) to serve as a reactive surface for MnO₂ precipitation. Sandstone was used because of its lower local cost compared to limestone and because the discharge already had a circumneutral pH.

2.2. Sample collection and preparation

Field measurements included influent flow rate (bucket and stopwatch), and electrical conductivity (conductivity cell), dissolved O₂ (galvanic probe), and pH and temperature (combination electrode) using portable meters. Water samples were filtered (0.2-µm) into pre-cleaned centrifuge tubes (pre-washed with 10% HNO₃) and chemically preserved in the field with HNO₃ (for metal analysis) or H₂SO₄ (for total organic C analysis). Water samples were transported to the laboratory on ice and refrigerated at 4°C until analyzed. At Site 1, samples were collected from the influent pipe and the center of each ditch. At Site 2, samples were collected from the influent pipe, several test pits dug into the bed, three piezometers within the bed, and the effluent stream. At Site 3, samples were collected from the pipe into the final pond and from upstream and downstream of the sandstone barrier. Sediment “crust” samples were collected from the top 1-cm of precipitates found in the ditches at Site 1, in the influent surface ditch, test pits and the effluent stream at Site 2, and on the sandstone barrier at Site 3. Sediment samples were collected with sterile spatulas and placed in sterile centrifuge tubes or whirl-paks. All sediment samples were stored on ice for transport to the laboratory. Wet sediments were passed through a 2-mm sieve and the <2-mm sieve fractions were homogenized and used for all solid-phase analyses. Visually these sieve fractions contained mixtures of MnO₂, quartz, and limestone or sandstone fragments.

2.3. Chemical analyses

Water samples were analyzed for dissolved metals, anions, alkalinity, hot-peroxide acidity, total organic C (TOC), and total organic N (TON). Cations (Al, Ba, Ca, Fe, K, Mg, Mn, Na, Si, Sr, Ti, Co, Ni, Zn) were measured using a Leeman Labs PS3000UV inductively coupled plasma atomic emission spectrophotometer (ICP-AES).
Manganese(II) concentrations were determined by the pyridylazo-
naphthol (PAN) method (Goto et al., 1977) and were found to be
identical to the total Mn concentrations measured by ICP-AES. An-
ions (SO$_4^{2-}$, NO$_3^-$, NO$_2^-$, Cl$^-$ and acetate) were measured using a
Dionex DX-100 ion chromatograph. Alkalinity and hot-peroxide
acidity were measured by standard volumetric titrations. TOC and
TON were measured using a Shimadzu 5000A T/OC/T/ON ana-
lyzer. Total P was analyzed by Hach PhosVer 3 with the Acid Per-
sulfate Digestion Test ‘N Tube Method 8190.

Elemental analysis of the sediments was performed by Li meta-
borate fusion followed by ICP-AES. Sediment samples were air-
dried at room temperature for several days until the water content
stabilized. Sediment samples were then heated to 750 °C overnight
to remove organic matter. Each sample was then mixed with Li
metaborate and heated to 900 °C in a graphite crucible for
10 min. The melted liquid was then quickly transferred into a Tef-
lon beaker containing 5% HNO$_3$. The solution was stirred for 15 min
and then analyzed by ICP-AES. Elemental sediment concentrations
were reported in oxide form based on the dry sediment mass.

### 2.4. Electron microscopy

To preserve biological features in the sediments, samples were
fixed in the field with 2.5% glutaraldehyde in 0.05 M Na cacody-
late buffer at pH 7. One drop of the fixed sample was transferred
onto the surface of a glass cover slip that had been washed with
a polylysine solution prior to use. Mineral particles were allowed
to settle onto the cover slip for 20 min. The particle-coated cover
slips were gradually dehydrated in an ethanol series followed by
drying. Critical point drying (31)
slips were gradually dehydrated in an ethanol series followed by
to dry samples
oven-dried at 110 °C overnight. Samples were examined using a
Rigaku Geigerflex microdiffractometer equipped with a graphite
monochromator and a cylindrical image plate area detector. A
Mo tube (50 kV, 40 mA) was used as the X-ray source and a
0.3 mm collimator was used to ensure parallel X-ray beams. Samples
were packed into 0.7 mm diameter quartz capillaries (Charles
Supper Co., Natick, MA) and mounted into a Cu sample holder.
During exposure to the X-ray beam, the sample was oscillated between
2° and 10° omega angle and –30° to +30° phi angle simultaneously
to minimize the effects of sample heterogeneity and preferred
orientation.

Select samples were examined at the X7B beam line of the Na-
tional Synchrotron Light Source (NSLS) at Brookhaven National
Laboratory. Samples were packed into 1.0 mm diameter quartz
capillaries and SR-XRD patterns were collected with a MAR 345 full
imaging plate detector. During exposure to the X-ray beam, the
samples were fully rotated through 360° during sample collection.
The contribution of instrumental broadening to peak width was
measured using a LaB$_6$ standard. Select samples were examined at the Stanford Synchrotron Radiation Laboratory (SSRL) on beam
line 11–3 using a MAR 345 image plate detector. Analysis of all
XRD patterns was performed using the JADE 6.5 software package.

### 2.5. X-ray diffraction

XRD patterns were collected on both wet and dry samples
(oven-dried at 110 °C overnight). Samples were examined using a
Rigaku Geigerflex microdiffractometer equipped with a graphite
monochromator and a cylindrical image plate area detector. A
Mo tube (50 kV, 40 mA) was used as the X-ray source and a
0.3 mm collimator was used to ensure parallel X-ray beams. Samples
were packed into 0.7 mm diameter quartz capillaries (Charles
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XRD patterns was performed using the JADE 6.5 software package.
IFEFFIT. Phase and amplitude files for the EXAFS fitting were created with FEFF6 (Rehr et al., 1992). Manganese-EXAFS were fit using a model based on a phyllomanganate structure developed by Webb et al. (2005b). A linear combination fitting (LCF) of hexagonal birnessite, triclinic birnessite and todorokite was used to fit the sample Mn-EXAFS spectra.

3. Results and discussion

3.1. Water chemistry

In Appalachian coal mine drainage, Fe, Al and Mn are typically the most important metal contaminants with respect to elevated concentrations and treatment priorities. Manganese in CMD may originate from metal sulfide oxidation (e.g. when Mn is a component of pyrite), and/or from reactions with adjacent minerals (e.g., clays and carbonates) as the CMD is transported from its source to its surface discharge. In a survey of 140 abandoned coal mine discharges in Pennsylvania, the median Mn concentration was 2.35 mg/L with a range from 0.019 to 74.0 mg/L (Cravotta, 2008).

For the surface coal mine at Site 1, the exceptionally high Mn

| Table 2 |
|---|---|---|
| Chemistry of influent water of the three treatment systems (in mg/L). Values presented as ranges reflect spatial variance within the systems and temporal variance over several seasons. | Site 1 | Site 2 | Site 3 |
| Alkalinity (mg CaCO₃/L) | 28 | 5 | 92 |
| Hot-peroxide acidity (mg CaCO₃/L) | 373 | 110 | 19 |
| pH | 5.23 | 4.74 | 7.43 |
| Total organic carbon (mg C/L) 1.0–13 | 8.9–28 | 2.5 | |
| Total nitrogen (mg N/L) 0.07–0.46 | 0.13 | n/a | |
| Total phosphorus (mg P/L) <0.01 | <0.01 | n/a | |
| Mn | 150 | 30 | 27 |
| Fe | <0.05 | 0.62 | 0.11 |
| Al | 8.62 | 7.95 | 0.36 |
| Ca | 225–365 | 230–370 | 175 |
| Mg | 255 | 220 | 95 |
| Si | 6.5 | 5.8 | 3.3 |
| Zn | 0.085 | 0.919 | 0.011 |
| Ni | 0.591 | 0.641 | 0.091 |
| Co | 0.341 | 0.186 | 0.048 |
| Cr | 0.024 | 0.006 | 0.008 |
| Pb | 0.010 | 0.005 | 0.005 |
| Cu | 0.005 | 0.010 | 0.003 |
| SO₄²⁻ | 2010 | 992 | 498 |
| Cl⁻ | 2.4 | 14 | 0.64 |
| NO₃⁻ | 0.44 | 0.12 | 0.81 |

Fig. 1. Seasonal water chemistry of Sites 1 and 2. Open symbols represent warm season (April 2006 for Site 1, July 2006 for Site 2) and filled symbols represent cold season (December 2005 for Site 1, February 2006 for Site 2). At Site 1, the six sampling points correspond to the influent pipe and five aeration ditches. At Site 2, the five sampling points correspond to the influent pipe, a test pit, and three piezometers.
concentration (130–150 mg/L) is believed to originate from reactions with the overburden. In a relevant study on Mn content in overburden from a coal strip mine in Tennessee, it was reported that Mn in siderite concretions was the most significant source while exchangeable Mn on clay minerals was a minor secondary source (Larsen and Mann, 2005). For comparison, the EPA secondary maximum contaminant limit for Mn in drinking water is 0.05 mg/L and the NPDES discharge limit for active coal mines is 4.0 mg/L.

The performance of these limestone Mn-removal beds were measured on several occasions between December 2005 and May 2007 to capture seasonal effects and other variability (Table 2). Representative data for Sites 1 and 2 for “warm” and “cold” months are presented in Fig. 1. The influent water temperature at Site 1 was relatively constant because the water emerged from an underground limestone drain. The influent water temperature at Site 2, like water temperature in both limestone beds, was strongly dependent on seasonal surface temperatures. Dissolved O2 (DO) was strongly dependent on water temperature with higher DO in winter and lower DO in summer. Lower DO in summer could also have been caused by increased microbial activity in the beds, likely stimulated by increased productivity of upstream wetlands. The pH in the bed increased more slowly at Site 1 as compared to Site 2, probably because of the higher influent acidity. Dissolved Mn(II) was never completely removed at Site 1, although greater removal occurred during warm months, suggesting biological activity may control Mn removal. Dissolved Mn(II) was removed to <0.05 mg/L before discharge from the bed at Site 2 for all sampling events. Enhanced Mn(II) removal (on a% basis) at Site 2 may have been caused by a combination of the lower influent Mn(II) load, the activity of microorganisms previously inoculated into the bed, and the higher pH in the bed. It has been demonstrated that Mn(II) oxidation occurs by both biological processes and by abiotic heterogeneous reactions with MnO2 surfaces in these beds (Tan, in preparation). The rate of abiotic Mn(II) oxidation has been shown to increase with increasing pH (Brewer, 1975; Davies and Morgan, 1989) such that this process could have been enhanced at Site 2. The rate of biological Mn(II) oxidation by Lepthrix discophora SS1 has been shown to increase significantly between pH 6.0 to 7.5 (Zhang et al., 2002) such that this process could also have been enhanced at Site 2. The performance of the sandstone bed at Site 3 was monitored on only one occasion (May 2007) when the Mn(II) concentration decreased from 27 to 12 mg/L across the sandstone barrier. The speciation of aqueous Mn(II) and the saturation indices (SI) for several Mn minerals were modeled for Site 1 using PHREEQC (Parkhurst and Appelo, 1999). These calculations were performed based on water chemistry measurements from the influent and all of the ditches across the treatment bed for a representative sampling event. Manganese2+ and MnSO4 were the dominant aqueous species of Mn(II) based on these speciation calculations. At the influent end of the bed where the Mn(II) concentration was highest (1.58 mM), Mn2+ and MnSO4 accounted for 37% and 37% of Mn(II)T, respectively. At the effluent end of the bed where the Mn(II) concentration had decreased to 0.41 mM but the SO42- concentration had remained constant (21 mM), Mn2+ and MnSO4 accounted for 60% and 40% of Mn(II)T, respectively. Equilibrium calculations also indicated that the ion activity products for species involved in the precipitation of birnessite, todorokite, hausmanite, bixbyite, pyrolusite, γ-MnO2, manganese and Mn(OH)2 exceed the solubility products of these minerals, suggesting that precipitation of Mn oxides was thermodynamically favorable. Manganese also exceeded the solubility of rhodochrosite (MnCO3) although this mineral was not detected by XRD or Mn-EXAFS spectroscopy.

Additional water chemistry parameters were measured, on a less frequent basis, to examine nutrient status. At Site 1, concentrations of total organic C (TOC) downstream of the wetland were 4.3 mg C/L in December 2005 and increased to 8.4 mg C/L in April 2006. For one sampling event (September 2006), TOC ranged from 1.0 to 13 mg C/L across the bed, total N ranged from 0.07 to 0.46 mg N/L, and total P was less than 0.04 mg PO43−/L. At Site 2, influent TOC concentrations downstream of the wetland were 8.9 mg C/L in February 2006 and increased to 28 mg C/L in July 2006. For one sampling event (May 2007), total N at Site 2 ranged from 0.07 to 0.24 mg N/L.
3.2. Trace metal chemistry

Trace metals are also of concern in CMD. In a survey of 140 abandoned coal mine discharges in Pennsylvania, the most abundant trace metals, in order of median concentrations (in µg/L), were Zn (140), Ni (85), Co (58), Ti (5.8), Cu (2.0), Cr (1.2), Pb (0.20) and Cd (0.12) (Cravotta, 2008). Elevated trace metals were found in both water and sediment samples at Sites 1 and 2 (Fig. 2, Table 2). The relative concentration trends of Zn > Ni > Co were found in both of these discharges, however, the influent concentrations of all metals were significantly higher than the median values reported by Cravotta (2008). Dissolved metal concentrations versus distance through the limestone beds were normalized to their respective influent concentrations in order to demonstrate preferential removal of trace metals versus Mn (Fig. 2). At Site 1, all trace metals were removed preferentially compared to Mn(II) and the order of preferential removal was Co > Zn > Ni > Mn(II). At Site 2, all dissolved trace metals were essentially removed within the first 5 m of the bed, and all to lower normalized concentrations compared to Mn(II). This selective uptake of trace metals into Mn oxides is consistent with several other studies on trace metal interactions with MnO$_x$ (Fuller and Harvey, 2000; Kay et al., 2001; Tani et al., 2004).

Kay et al. (2001) and Tani et al. (2004) used sequential extraction techniques to investigate the mechanisms of trace metal removal by MnO$_x$. Their results indicated that Co can be removed by both sorption onto the MnO$_x$ surface and by co-precipitation into the MnO$_x$ structure. X-ray spectroscopy studies have shown that Co(II) can be oxidized after adsorption onto the MnO$_x$ surface by either oxide-bound Mn(IV), oxide-bound Mn(III) or O$_2$, and further incorporated into the MnO$_x$ structure (Manceau and Charlet, 2000).
3.3. Mineralogy of Mn precipitates

The basic building block of MnO₂ minerals is octahedrally coordinated Mn, which can assemble into three major structural groups: chains (e.g., pyrolusite), tunnels (e.g., todorokite), and layers (e.g., birnessite and “buserite”). Chain structures consist of edge-sharing octahedra, tunnel structures are formed when multiple chains share corners to produce square or rectangular cross sections, and layer structures consist of stacked sheets of edge-sharing octahedra (Post, 1999). Birnessite and buserite (not an official mineral name) have similar layer structures and have been identified as important forms of biogenic MnO₂ (Webb et al., 2005a). Birnessites are fine-grained and relatively poorly crystalline with an interlayer spacing of 7 Å that incorporates cations and water molecules. Buserite has a 10 Å interlayer spacing and contains an extra water layer that is lost upon drying causing the structure to collapse to a 7 Å interlayer spacing. This dehydration process is irreversible and often used to distinguish between buserite and todorokite, which also has a 10 Å interlayer spacing but is stable upon drying (Post, 1999). However, some cations such as Ca, Mg, Ni and Cu can stabilize the 10 Å spacing in the buserite structure from collapse upon drying (Tebo et al., 1997).

At Site 1, thick, black-grey MnO₂ coatings were observed in every ditch in the limestone bed. In test pits dug into the bed at Site 1, MnO₂ coatings did not extend very deeply beyond the air-water interface. Similarly, in test pits dug into the bed at Site 2, black MnO₂ precipitates were found to accumulate at the air-water interface and decrease with depth. At Site 3, exceptionally thick, black MnO₂ precipitates covered the exposed sandstone surfaces. Compared to the MnO₂ precipitates found in the limestone beds, precipitates on the sandstone bed appeared darker with less clay content and debris.

Based on SEM images, samples from all three sites showed similar surface morphologies regardless of influent Mn(II) concentrations, zinoculation with patented Mn(II)/OB, or bed materials (limestone vs. sandstone). An extremely coarse, “sponge-like” texture of the MnO₂ precipitates were commonly observed in samples from all three sites (Fig. 3). Biological features that resembled bacterial cells, freshwater diatoms and fungal mycelia were also observed in samples from all three sites. It was possible to isolate and examine just the MnO₂ precipitates using whole mount high resolution TEM (Fig. 4). The coarse morphology observed in SEM images was consistent with TEM images of the MnO₂ precipitates which revealed fibrous nm-sized lathes and thin sheets. Elemental analysis by EDS confirmed that this material was a Mn oxide with trace amounts of Ca and Al. SAED rings demonstrated that this material was relatively amorphous and non-crystalline.

XRD and SR-XRD patterns also established that the MnO₂ precipitates collected from these systems were relatively amorphous and non-crystalline (Fig. 5). Identification of the specific MnO₂ minerals was operationally defined based on the presence/absence of a specific diffraction peak from wet and oven-dried samples.

![Fig. 4. Transmission electron micrograph of MnO₂ particles collected from Site 1. Elemental analysis in lower panel obtained from energy dispersive spectroscopy from most electron-dense portion of upper panel (Cu signal comes from TEM Cu grid).](image-url)
XRD patterns from all samples from all sites showed strong peaks at 10 Å d-spacing. Several synthetic and natural Mn oxides have 10 Å d-spacings, including todorokite and buserite (Post, 1999; Bilinski et al., 2002). For Site 1, XRD patterns showed the sample contained calcite, quartz and a 10 Å Mn oxide. The wet sample had a strong peak at 10 Å and a very weak peak at 7.0 Å. After drying, the 10 Å peak diminished and the 7.0 Å peak became more significant which suggests that this sample contained mostly buserite. For Site 2, XRD patterns showed the sample contained quartz, dolomite, and a 10 Å Mn oxide. The wet sample had a strong peak at 10 Å and a very weak peak at 7.0 Å. After drying, the 10 Å peak did not disappear nor did the 7.0 Å peak increase which suggests the MnO\textsubscript{x} in this sample could be todorokite or buserite with cations incorporated into the interlayer (helps resist collapse upon drying) (Fig. 5). The MnO\textsubscript{x} from Site 3 had an additional, uncharacteristic, very broad peak at ~8.5 Å that could be a result of the partial loss of water from the birnessite interlayer (Fig. 6).

Manganese-EXAFS spectroscopy was used to further characterize these samples (Fig. 7) and quantify the relative distribution of MnO\textsubscript{x} minerals. Using an assemblage of three presumed MnO\textsubscript{x} mineral standards; hexagonal birnessite, triclinic birnessite and todorokite, linear combination fitting (LCF) of the EXAFS spectra was used to calculate the relative distribution of these minerals (Table 4). The predominant MnO\textsubscript{x} minerals at all sites were hexagonal birnessite and triclinic birnessite. Todorokite was found to account for 14–29% of the MnO\textsubscript{x} minerals at Site 1, 0–5% of the MnO\textsubscript{x} minerals at Site 2, and 2% of the MnO\textsubscript{x} minerals at Site 3. At Site 3, the MnO\textsubscript{x} was essentially pure hexagonal birnessite. Manganese EXAFS spectroscopy compliments XRD results and further clarifies the phases presents in these samples. At Site 1, the presence of todorokite and birnessite is consistent with similar findings from cemented MnO\textsubscript{x} crusts collected at Pinal Creek, Arizona (Bilinski et al., 2002). The transformation of buserite to todorokite can occur under atmospheric conditions in laboratory experiments, and this process is affected by temperature, pH and the addition of pyrophosphate (a Mn(III) complexant) (Cui et al., 2006, 2008). Bilinski et al. (2002) postulated that todorokite and birnessite at Pinal Creek were transformed from buserite under different conditions. This could explain differences in MnO\textsubscript{x} mineral assemblages at Site 1 (i.e. ditch 1 vs. ditch 4) promoted by changes in water chemistry through the limestone bed.

For Site 2, XRD showed that the 10 Å MnO\textsubscript{x} mineral could be todorokite or cation-stabilized buserite while EXAFS spectroscopy showed relatively low (0–5%) todorokite content. Discerning todorokite and cation-stabilized buserite by XRD alone can be difficult (Arrhenius and Tsai, 1981; Giovanoli and Arrhenius, 1988). Mandernack et al. (1995) showed that Ca and Mg can stabilize the structure of buserite from collapsing at room temperature, but this effect at higher temperatures is not clear. For Site 3, XRD showed a relatively amorphous MnO\textsubscript{x} mineral while EXAFS spectroscopy identified the mineral assemblage as nearly 100% hexagonal birnessite. The relatively simple MnO\textsubscript{x} mineralogy at Site 3 could be due to differences in influent water chemistry compared to Sites 1 and 2 (Table 2). In particular, the alkaline pH and lower concentrations of Al and other trace metals could favor the formation of a more relatively “pure” MnO\textsubscript{x} precipitate. The relatively simple MnO\textsubscript{x} mineralogy at Site 3 could also be due to faster kinetics of...
Mn(II) oxidation and precipitation. Both high pH and high DO promote more rapid biotic (Zhang et al., 2002) and abiotic Mn(II) oxidation (Davies and Morgan, 1989). Alkaline water breaching the sandstone barrier was well aerated providing both of these conditions and helps explain how the Mn(II) concentration could decrease from 27 to 12 mg/L across the barrier in just a few minutes residence time.

### 3.4. Environmental implications

The “active” removal of Mn(II) from CMD is considerably more expensive than “passive” removal in limestone beds. The Mn oxides formed in these passive treatment systems are themselves extremely important in the further removal of Mn(II) and trace metals from CMD. In this study it was found that MnO₃ formed in CMD treatment systems were primarily poorly crystalline layered buserite of small particle size and coarse texture, which scavenged trace metals such as Co, Ni and Zn. In one of the CMD treatment systems (Site 1), trace metals were preferentially removed likely via co-precipitation with Mn oxides. The crystallite sizes of Mn₃O₄ minerals formed in the ditches in Site 1 were calculated using Scherrer’s equation based on the full-width half-maximum (FWHM) of the 10 Å peak. The crystallite size was shown to be smallest at the influent end of the bed (5.0 nm) where more trace metal incorporation could have occurred.

![Fig. 6. Comparison of synchrotron radiation X-ray diffraction patterns from moist MnO₃-rich sediments collected from all three sites. Wavelength of the synchrotron radiation was 0.97516 Å.](image1)

![Fig. 7. Manganese K-edge EXAFS spectra from natural MnO₃-rich sediments collected from the three Mn(II)-removal systems. The measured spectra (symbols) are shown with model fits (lines). Spectra were fit as a linear combination of hexagonal birnessite, triclinic birnessite, and todorokite. Results of the fits are included in Table 4. The samples shown were collected from (top to bottom): A – Site 1 ditch 1 (circle); B – Site 1 ditch 5 (up triangle); C – Site 2 influent trench (down triangle); D – Site 2 effluent stream (diamond); and, E – Site 3 barrier (square).](image2)

<table>
<thead>
<tr>
<th>Site number, sample name</th>
<th>% Hexagonal birnessite</th>
<th>% Triclinic birnessite</th>
<th>% Todorokite</th>
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<tr>
<td>Site 1, ditch 2</td>
<td>59</td>
<td>12</td>
<td>29</td>
</tr>
<tr>
<td>Site 1, ditch 4</td>
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<td>24</td>
<td>14</td>
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<tr>
<td>Site 2, influent trench</td>
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<td>35</td>
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<tr>
<td>Site 2, effluent stream</td>
<td>45</td>
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<td>5</td>
</tr>
<tr>
<td>Site 3, barrier</td>
<td>98</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

![Table 4 Results from linear combination fitting (LCF) of Mn K-edge EXAFS spectra from MnO₃-rich sediments collected from the three Mn(II)-removal systems. Mn K-edge EXAFS spectra are shown in Fig. 7.](image3)
The assemblage of MnO₄ minerals identified by XRD (Figs. 5 and 6) and quantified by LCF of the Mn-EXAFS spectra (Table 4 and Fig. 7) were relatively similar for the two biologically active Mn-removal beds (Sites 1 and 2). The findings suggest biserotive and todorokite may be common products in CMD treatment systems despite differences in construction, microbial community structures, nutrients sources, and influent water chemistry. However, the MnO₄ identified at Site 3 was essentially pure hexagonal birnessite. At Site 3 it is believed that Mn(II) precipitation was promoted by the alkaline, aerated water chemistry and by the catalytic effects of the MnO₂/sandstone surfaces during the relatively short residence time across the sandstone barrier.

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