TRACE-METAL MOBILITY DURING IN SITU CHEMICAL OXIDATION (ISCO) OF TCE BY MnO₄⁻: COLUMN EXPERIMENTS

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ABSTRACT

Two series of column experiments were designed to investigate the mobility of trace metals during ISCO of TCE by MnO₄⁻ in the presence of MnO₄ and Fe oxyhydroxides. Results indicated that despite variable pH, concentrations of Mo, Pb, Cu, Cd and Ni are rapidly attenuated from the aqueous phase. In contrast, Zn concentrations were not significantly attenuated, except in the presence of Fe oxyhydroxides, and Cr behaved conservatively under all conditions. The results of extractions and Analytical Electron Microscopy (AEM) analyses indicated that the trace metals are associated with the precipitates formed during ISCO.

RÉSUMÉ

Deux séries d'expérimentations ont été créées pour investiguer la mobilité des métaux en traces pendant la oxidation chimique in situ de trichloréthylène (TCE) par le permanganate de potassium (MnO₄⁻) en présence d'oxyhydroxydes de MnO₂ et Fe oxyhydroxydes. Les résultats ont indiqué que malgré une variation de pH, les concentrations de Mo, Pb, Cu, Cd et Ni se sont atténuées rapidement de la phase aqueuse. Contrairement, les concentrations de Zn ne sont pas atténuées significativement, sauf en présence d'oxyhydroxydes de Fe. Le Cr a agit de façon conservateur sous toutes les conditions. Les résultats de les extractions et de l'exoscopie analytique ont indiqué que les métaux en traces sont associés avec les précipités qui ont été formés pendant l'oxidaion chimique in situ.

1. INTRODUCTION

The common occurrence of recalcitrant groundwater contamination with chlorinated solvents such as trichloroethylene (TCE; C₂Cl₃H) has prompted the need for low impact, efficient, and cost effective remedial techniques. In Situ Chemical Oxidation (ISCO) is one technique that has been employed with success. The effectiveness of MnO₄⁻ for the degradation of TCE during ISCO has been demonstrated in several laboratory and field-based trials (Stewart, 1965; Schnarr and Farquhar, 1992; Nelson et al., 2001).

However, the mobility of trace metals during ISCO treatment is an environmental concern (ITRC, 2001; Crimi and Siegrist, 2003). The dissolution of minerals and the solubility of trace metals usually increase as pH decreases as TCE – MnO₄ react and precipitate Mn oxides according to Equation 1:

\[
\text{C}_2\text{Cl}_3\text{H} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \rightarrow 2\text{HCO}_3^- + 2\text{MnO}_2(s) + 3\text{Cl}^- + 3\text{H}^+ \quad [1]
\]

The valence of Mn in the oxide precipitates could range between II and IV, but it is generally assumed that Mn⁴⁺ is the product and the formula MnO₂ is commonly used to represent these precipitates (Equation 1). Given the uncertainty in the valence of the Mn-oxide product of the reaction, the more general formula MnOₓ will be used hereafter. The increase in oxidation state and decrease in pH indicated by Equation 1 may lead to an increase in trace-metal concentrations through the dissolution of aquifer minerals such as chromite (FeCr₂O₄) and ubiquitous FeOOH coatings [Equations 2 and 3]:

\[
3\text{FeCr}_2\text{O}_4(s) + 7\text{KMnO}_4 + 7\text{H}_2\text{O} \rightarrow 3\text{Fe} (\text{OH})_3 + 7\text{MnO}_2 + 6\text{CrO}_4^{2-} + 7\text{K}^+ + 5\text{H}^+ \quad [2]
\]

\[
(\text{Fe}_{1-x}, \text{Me}_x)\text{OOH} + 3\text{H}^+ \rightarrow 1-x\text{Fe}^{3+} + x\text{Me}^{2+} + 2\text{H}_2\text{O} \quad [3]
\]

where: Me represents trace metals such as Cu, Pb, Zn, Ni, Mo, and Cd. In addition, trace-metal concentrations may be introduced into the groundwater as impurities in the injected MnO₄ solution (Table 1).

Under the influence of ambient hydraulic gradients, groundwater with low pH and elevated Fe³⁺ concentrations from the ISCO treatment may migrate and encounter aquifer materials with greater acid neutralization capacity (e.g. calcite [CaCO₃]). In this case, Fe released according to Equation 3 will precipitate as Fe oxyhydroxide because of the low solubility at near neutral pH (Stumm and Morgan, 1996). In general MnO₂ and Fe oxyhydroxide minerals have high surface area and are capable of sequestering various trace metals from aqueous solutions through ion exchange, surface complexation and co-precipitation reactions (referred to generally as sorption reactions).

Understanding the degree to which trace metals interact with MnO₂ and Fe oxyhydroxides is essential in order to evaluate trace-metal mobility during the ISCO of TCE by MnO₄. Many researchers have investigated the adsorption and surface complexation characteristics of
Table 1. Metal impurities in permanganate CAIROX™ and LIQUOX™ (From Crimi and Siegrist 2004) and RemOx™ (provided by Carus Chemical Company).

<table>
<thead>
<tr>
<th>Metals</th>
<th>CAIROX™: K(MnO₄)₄</th>
<th>RemOx™: K(MnO₄)₄</th>
<th>LIQUOX™: Na(MnO₂)₄ 40% Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Technical</td>
<td>Free-flowing</td>
<td>USP</td>
</tr>
<tr>
<td>Lead</td>
<td>2.66</td>
<td>2.66</td>
<td>1.33</td>
</tr>
<tr>
<td>Chromium</td>
<td>17.29</td>
<td>13.30</td>
<td>0.67</td>
</tr>
<tr>
<td>Arsenic</td>
<td>5.32</td>
<td>5.32</td>
<td>1.33</td>
</tr>
<tr>
<td>Zinc</td>
<td>7.98</td>
<td>7.98</td>
<td>1.33</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1.33</td>
<td>1.33</td>
<td>1.33</td>
</tr>
<tr>
<td>Copper</td>
<td>19.95</td>
<td>19.95</td>
<td>2.66</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.08</td>
<td>0.13</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND = none detected

Hydrous Manganese Oxides (HMO) and Hydrous Ferric Oxides (HFO) (Crimi and Siegrist, 2003; Crimi and Siegrist, 2004a; Tonkin et al. 2004). While others have investigated trace-metal association in mineral phases (Al et al., 2000; Manceau et al., 2002; Dong et al., 2000; Crimi and Siegrist, 2003; Crimi and Siegrist, 2004b) using various Analytical Electron Microscopy (AEM) techniques and bulk chemical extractions.

The degree of trace-metal association with MnO₄⁻ precipitated during ISCO in field- and lab-based experiments was investigated by Nelson et al. (2001) and Crimi and Siegrist (2003) using Scanning and Transmission Electron Microscopy combined with Energy Dispersive X-ray Spectroscopy (SEM/TEM/EDS) and selective chemical extraction techniques. Crimi and Siegrist (2004a) present aqueous and chemical extraction data to determine the association of Cd with MnO₄⁻ formed during ISCO. In these experiments, the pH was controlled by a Na₂HPO₄ buffer rather than a naturally occurring aqueous or mineral buffer.

Although these studies provide a foundation for understanding trace-metal mobility during ISCO treatment, several important issues remain unresolved:

I. the response of the system during ISCO under naturally buffered conditions (e.g. in the presence of calcite); and

II. investigation of sorption effects using multiple adsorbing mineral substrates.

The purpose of this study was to build on previous research by:

I. monitoring trace-metal mobility during ISCO under conditions with and without natural mineral pH buffering capacity;

II. monitoring trace-metal mobility during ISCO with multiple competing metal ions; and

III. investigate trace-metal sorption with multiple mineral substrates using several complementary analytical techniques.

2. EXPERIMENTAL OVERVIEW –TRACE-METAL MOBILITY EXPERIMENTS

In these experiments, four columns were used and each was constructed from plexiglass (2.9 cm ID, 3.5 cm OD, and 50 cm length). The columns were fitted with nine polypropylene/polyethylene sampling ports/manometers at 5 cm intervals along the length. The influent solutions for the columns were supplied by an eight-channel peristaltic pump from two reservoirs. One reservoir (fluoropolymer bladder) contained 43 mg/L aqueous TCE and 717 mg/L KHCO₃. The second reservoir (opaque polyethylene carboy) contained 226 mg/L dissolved MnO₄⁻ and trace metals at a concentration of 1 mg/L (Mo, Cu, Ni, Pb, Zn and Cr for series one; Mo, Cu, Ni, Pb, Zn, Cr, Fe, and Cd for series two) (Figure 1). The pH of the MnO₄⁻ metal solution was 1.5. The KHCO₃ was added to the TCE solution in order to neutralize the pH at the inlet after mixing with the MnO₄⁻-metal solution. This resulted in a pH of 3.5 at the inlet. The solutions from the reservoirs were pumped to the columns through polyethylene tubing (series one) and Teflon tubing (series two) (0.16 cm ID, 0.32 cm OD), and mixed in a Y shaped fitting at a 1:1 volumetric ratio at the inlet to the columns.

![Figure 1: Schematic of Trace-Metal Mobility Experiments](image-url)
series are referred to as the MnO$_2$-Containing Columns (MCC). The second series of columns was supplied the same influent solutions with the addition of Fe and Cd to the trace metal solution. As ISCO reactions proceeded, both MnO$_2$ and Fe oxyhydroxides accumulated in the columns. Since they contained both MnO$_2$ and Fe oxyhydroxides, the second series of columns are referred to as the MnO$_2$ and Fe oxyhydroxide Containing Columns (MFCC).

The unbuffered columns in both series contained 100% silica sand. The buffered MCC contained 75% silica sand and 25% calcite sand, whereas the buffered MFCC contained 90% silica sand and 10% calcite sand. Polypropylene threads (0.3 mm diameter) were mixed with the sand to facilitate sample preparation for TEM/EDS analysis. The first series was operated for 45 days and the second for 35 days. Details regarding the total volume and influent mass of solutes are provided in Table 2.

Table 2. Solute influent masses supplied to the MCC and MFCC.

<table>
<thead>
<tr>
<th>Pore Volumes</th>
<th>Influent Mass (mg)</th>
<th>TCE</th>
<th>MnO$_2$</th>
<th>Trace Metals</th>
</tr>
</thead>
<tbody>
<tr>
<td>MCC</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Buffered MCC</td>
<td>373</td>
<td>1901</td>
<td>10214</td>
<td>44</td>
</tr>
<tr>
<td>Unbuffered MCC</td>
<td>379</td>
<td>1972</td>
<td>10452</td>
<td>45</td>
</tr>
<tr>
<td>Buffered MFCC</td>
<td>317</td>
<td>1739</td>
<td>9676</td>
<td>41</td>
</tr>
<tr>
<td>Unbuffered MFCC</td>
<td>327</td>
<td>1832</td>
<td>9519</td>
<td>42</td>
</tr>
</tbody>
</table>

2.1 Sampling: Aqueous Phase

Aqueous samples were collected from influent solutions (prior to mixing) and from each of the nine sampling ports along the length of the columns, on a weekly basis. The MCC were sampled beginning at the bottom port, and the MFCC were sampled beginning at the top port. Each sampling port was purged for 0.5 hr prior to sample collection.

Samples collected for cation and anion analyses were drip collected into 50 mL beakers. The solution was filtered through 0.2 µm nylon filter membranes. All samples for cation analyses were acidified to a pH below 1 with trace-metal grade HNO$_3$. Any MnO$_2$ present in the samples was reduced to soluble Mn (II) with glucose prior to analysis. Trace-element analyses were conducted by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) for samples from the MCC and by Inductively-Coupled Plasma Optical-Emission Spectroscopy (ICP-OES) for samples from the MFCC. Lower limits of detection (LLD) were determined as the mean plus three times the standard deviation of the blanks (MCC: Ni – 0.047; Cu – 0.00073; Zn – 0.012; Pb – 0.00013; Mo – 0.00053; Cr – 0.076 mg/L, ICP-MS) and (MFCC: Ni – 0.0078; Cu – 0.066; Zn – 0.042; Pb – 0.028; Mo – 0.069; Cr – 0.0076; Cd – 0.0028; Fe – 0.015 mg/L, ICP-OES). Samples collected for anion analyses were treated with glucose to reduce excess MnO$_2$ to MnO$_2$ floc, centrifuged, and the supernatant was filtered using 0.2 µm nylon filter membranes. Chloride concentrations were determined by Ion Chromatography (IC) with a detection limit of 0.1 mg/L.

Samples for TCE analysis were collected in flow-through cells with zero head space. Residual MnO$_2$ was immediately reduced with sodium metabisulfite (Na$_2$S$_2$O$_3$) and samples were stored in 20 mL glass vials capped with Teflon-lined rubber septa caps. TCE analyses were conducted by Gas Chromatography (GC) (detection limit = 0.001 mg/L).

Measurements of pH (Orion model 815600 combination pH electrodes) were made in a sealed flow-through cell. Total MnO$_2$ concentrations were determined using a Hach DR/2010 spectrophotometer. Samples for these analyses were collected from the exit port of the flow-through cells and filtered using 0.2 µm nylon filters. As a result of the low flow rate (approximately 0.7 mL/min), three days were required to collect a complete set of samples.

2.2 Sampling: Solid Phase

The solid phase in each column was sampled after the completion of the experiments. The following samples were collected at each sampling port:

I. 2.0 g for chemical extractions;
II. 0.5 g for SEM/EDS analyses; and
III. 2 polypropylene threads for TEM/EDS analyses.

The chemical extractions targeted hydrous Mn and Fe oxides using a 0.25 M hydroxylamine hydrochloride/0.15 M hydrochloric acid digestion (Hall, 1996). The solutions from these extractions were analyzed for trace metals (Ni, Cu, Zn, Pb, Mo, Fe, Cd, and Cr) and (Mn) using ICP-OES. The LLD for each element was determined as the mean plus three times the standard deviation of the 0.25 M hydroxylamine hydrochloride/0.15 M hydrochloric acid blanks (Ni – 0.042; Cu – 0.021; Zn – 0.084; Pb – 0.16; Mo – 0.013; Cr – 0.021; Cd – 0.050; Fe – 0.033; and Mn – 0.046 ppm).

In preparation for TEM/EDS analysis, the polypropylene thread samples were removed from the column sand at each port location and then embedded in (NANOPLAST FB101) immediately after removal from the columns. The embedded threads were sectioned by diamond-knife ultramicrotomy and the sections were collected on Formvar-coated 200-mesh Ni grids and 600-mesh Cu grids (no Formvar coating). An alternative technique was also used to prepare secondary coatings for TEM/EDS analyses that formed within the columns. Samples of sand were sonicated in ethyl alcohol to remove the coatings from the sand materials, and the resulting suspensions were then transferred directly onto 200-mesh Ni and Cu grids using a pipette. TEM/EDS analyses were collected at 200 kV in a JEOL-JSM-2011 TEM/STEM equipped with an EDAX Phoenix EDS system and a Gatan GIF 2001 image filter.
3. RESULTS AND DISCUSSION

3.1 Aqueous Geochemistry

The average inlet TCE and Cl concentrations for the MCC were 43 (± 13 mg/L) and 0 mg/L, respectively. The average inlet MnO$_4$ concentration was 229 (± 11 mg/L) and 234 (± 15 mg/L) for the MCC and MFCC, respectively (Table 3 and 4). TCE concentrations in the MCC decreased from 43 mg/L to below detection at a distance of 5 cm from the inlet. On average the reaction consumes 71 mg/L of MnO$_4$, while producing 33 mg/L of Cl (Table 3 and 4).

Table 3. Influent and effluent concentration of Chloride and MnO$_4$ in the MCC.

<table>
<thead>
<tr>
<th></th>
<th>Unbuffered</th>
<th>Buffered</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inlet</td>
<td>Outlet</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Week 1</td>
<td>33.5</td>
<td>29.2</td>
</tr>
<tr>
<td>Week 3</td>
<td>24.5</td>
<td>22.6</td>
</tr>
<tr>
<td>Week 5</td>
<td>30.4</td>
<td>28.3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MnO$_4$ (mg/L)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Week 1</td>
<td>240</td>
<td>149</td>
<td>233</td>
<td>185</td>
</tr>
<tr>
<td>Week 3</td>
<td>218</td>
<td>154</td>
<td>218</td>
<td>171</td>
</tr>
<tr>
<td>Week 5</td>
<td>234</td>
<td>162</td>
<td>232</td>
<td>171</td>
</tr>
</tbody>
</table>

Using the reaction rate from Yan and Schwartz (1999) (6.5 × 10$^{-4}$ s$^{-1}$), the average inlet TCE concentration of 43 mg/L from the MCC, the residence time ($t_r$) to the 5 cm position from the MCC (16 minutes), and the sample collection time (30 minutes), the expected concentration of TCE in the sample was calculated (7 mg/L). The observed rate of TCE degradation in the MCC is approximately 2.45 × 10$^{-3}$ s$^{-1}$ three to four times greater than that observed by Yan and Schwartz (1999) (assuming a TCE concentration of ½ the detection limit 5 cm from the inlet).

Table 4. Influent and effluent concentration of Chloride and MnO$_4$ in the MFCC.

<table>
<thead>
<tr>
<th></th>
<th>Unbuffered</th>
<th>Buffered</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Inlet</td>
<td>Outlet</td>
</tr>
<tr>
<td>Chloride (mg/L)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Week 1</td>
<td>48.6</td>
<td>43.9</td>
</tr>
<tr>
<td>Week 3</td>
<td>37.7</td>
<td>37.9</td>
</tr>
<tr>
<td>Week 5</td>
<td>28.5</td>
<td>28.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MnO$_4$ (mg/L)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Week 1</td>
<td>226</td>
<td>112</td>
<td>222</td>
<td>122</td>
</tr>
<tr>
<td>Week 3</td>
<td>227</td>
<td>149</td>
<td>223</td>
<td>149</td>
</tr>
<tr>
<td>Week 5</td>
<td>220</td>
<td>150</td>
<td>222</td>
<td>163</td>
</tr>
</tbody>
</table>

A mass balance calculation was conducted for the MCC using Equation 1 and the average input TCE concentration of 43 mg/L. The results suggest that 35 mg/L of Cl should have been produced and approximately 78 mg/L of MnO$_4$ should have been consumed. These calculated values agree with the observed results from the MCC within the error for respective analyses (Table 3).

The HCO$_3$ alkalinity in the influent solution (TCE reservoir) was sufficient to raise the pH to 3.5 after mixing with the low-pH, metal-containing influent solution. The additional proton acidity added to the system as a result of the TCE-MnO$_4$ reaction (Equation 1) causes the pH to drop below the initial value of 3.5 in each of the unbuffered columns (Figure 2). In these columns the pH is near constant, ranging between 2.2 and 3.4, along the entire flow path for the duration of the experiments. In contrast, there is an increase in pH observed near the inlet to the buffered columns and the pH reaches a stable range between 6.2 and 6.5 a short distance along the flow path (Figure 2). With increasing time, the flux of acidity into the columns causes the depletion of calcite and the pH near the inlet to the buffered columns declines to a range similar to that observed in the unbuffered columns (Figure 2B and 2C). The pH neutralization reaction front migrates along the flow path versus time and the rate of migration is dependent on the initial calcite content in the column. After five weeks, the reaction front migrated approximately 7.5 cm in the MCC (25% calcite) and approximately 27.5 cm in the MFCC (10% calcite) (Figure 2C).

Figure 2: pH versus distance in the MCC and MFCC. A) first week, B) third week, C) fifth week.

3.2 Trace-Metal Mobility MCC

The concentrations of Mo, Cu, Pb, and Ni decrease to values near their respective detection limits within the first few cm of the flow path in the MCC, irrespective of the pH conditions (Figure 3). In contrast, the Zn concentrations are variable in space, but in general they remain high in comparison with Mo, Cu, Pb, and Ni. The concentrations of Cr are similar to the input concentrations throughout the course of the experiment. These trends in aqueous concentrations indicate that Cr behaves conservatively in
the aqueous phase in the presence of MnO\(_x\) and although concentrations are more variable, Zn can also be considered to behave conservatively. Geochemical speciation calculations for MnO\(_x\)-containing solutions suggest that Cr is present in the hexavalent (Cr VI) form. In contrast with Cr and Zn, the trends in aqueous concentrations of Mo, Cu, Pb, and Ni suggest that these elements are affected by sorption reactions involving MnO\(_x\). Tonkin et al. (2004) reviewed data from previous adsorption studies involving HMO and compiled a database of surface-complexation constants. Based on their data we would expect that these trace metals would undergo surface complexation reactions in the pH range we observe according to the order Pb>Cu>Zn>Ni (Cr and Mo were not included in their study). Our results are consistent with this expectation with the exception of Zn and Ni. The reversal in the order of Ni and Zn sorption that we observe can not be explained with certainty but it is likely related to the effects of competition for available surface sites.

The suggestion that the trace metals are removed from the aqueous phase by sorption on MnO\(_x\) is supported by data from the solid phase extractions (Figure 4). The extractable Mn is greatest near the column inlet, consistent with the observation that the TCE-MnO\(_4\) reaction goes to completion within the first 5 cm of the flow path. Of the trace metals added to the MCC, all were detected in the extractions except Pb (high detection limit). In each case the concentrations of extractable metals are greatest near the column inlet, coincident with the greatest accumulation of MnO\(_x\). The extraction data indicate that sorption of Cr and Zn did occur, although the extractable concentrations are approximately one order of magnitude lower than those of Cu and Ni (Figure 4).

In contrast with the aqueous data, the extraction data provides some indication of the effect of Ca on MnO\(_x\) coagulation first observed by Stumm (1970) and the control of pH on the sorption of metals. The extractable concentrations of Cu and Ni are greatest in the buffered MCC as is expected on the basis of the surface complexation constants compiled by Tonkin et al. (2004). Furthermore, the concentrations of Cu and Ni both display an increase in concentrations beyond the pH reaction front. This is attributed to the specific adsorption of Ca to the surface of MnO\(_x\) increasing the coagulation of MnO\(_x\), which translates into higher MnO\(_x\) surface area and increased surface complexation reactions yielding higher extractable concentrations of Cu and Ni in the buffered MCC beyond the pH reaction front. In the case of Mo, which forms an oxyanion (MoO\(_4\)) in aqueous solution, the extraction data suggests that sorption was greatest at low pH since Mo was not detected in the neutral pH region of the buffered MCC (Figure 4). This trend is consistent with surface complexation involving oxyanions (Dzombak and Morel, 1990), as mineral surface charge is positive at low pH and negative at neutral pH.

The aqueous data and the solid phase extraction data are consistent in that they indicate that the formation of MnO\(_x\) during the reaction of TCE and MnO\(_4\) leads to the sorption of a variety of trace metals and significant decreases in their aqueous concentrations. This is consistent with Cd concentrations observed in the experiments conducted by Crimi and Siegrist, 2004. This process was investigated in greater detail with discrete analyses of MnO\(_x\) using STEM/EDS. Bright field TEM images were acquired from the MnO\(_x\) coatings collected 1 cm and 5 cm from the inlet to the MCC (Figure 5A and 5B respectively). In cross section, the MnO\(_x\) coatings from

**Figure 3:** Normalized trace-metal concentrations during the last week of ISCO in the MCC and MFCC
Figure 4: Extractable trace-metal concentrations in ppm from the MCC and MFCC after completion of ISCO. The dash-dot dash line indicates the position of the pH reaction front.

the MCC occur as fibrous masses surrounded by finer grained, interstitial MnO_x with no discernable habit. The fibrous crystal habit suggests some crystallographic ordering, however selected-area electron diffraction (SAED) suggests that the material is amorphous.

Analyses of the MnO_x from the MCC by STEM/EDS display detectable Si, Mo, Pb, Cl, K, Ca, Ni, and Cu (Figure 5C and 5D). There are artifact peaks from the Ni grid in spectra D4, D5, and D6, and artifact peaks from the Cu grid in spectra C1, C2, D1, D2, D3, and D7. Despite these artifacts, Cu is detected in samples with Ni
grids (spectra D6) and Ni is detected in samples with Cu grids (spectra C1 and D7). The STEM/EDS data demonstrate a strong tendency for metal sorption close to the column inlet (Figure 5). At this scale the terms buffered and unbuffered that are used to describe the columns are not meaningful because calcite is rapidly depleted near the column inlet (Figure 2) and the pH is low in this region throughout the experiment for both columns. Despite the low pH, the data demonstrate that the cationic metals Cu, Ni, and Pb are associated with the MnO₃ with greatest abundances near the inlet. The sorption of Pb and Mo is particularly strong near the MCC inlet, to the extent that these metals have not been detected in association with the MnO₃ beyond the 1 cm distance.

![STEM/EDS images](image1)

**Figure 5**: Images and EDS spectra for samples from the MCC. A) TEM bright field image of sonicated samples collected 1 cm along the flow path in the unbuffered column. B) TEM bright field image of coated polypropylene thread sample (thread is in the upper left hand corner) 5 cm along the flow path in the buffered column. Representative STEM/EDS analyses from C) 1 cm along the flow path and D) 5 cm along the flow path.

### 3.3 Trace-Metal Mobility MFCC

The influent solution compositions for the MFCC are identical to the influent solution composition for the MCC with the exception of the addition of Cd and Fe (1 mg/L) to the group of trace metals. The trends in Cd concentrations are similar to Mo, Cu, Ni and Pb in the MCC, suggesting that sorption on either MnO₃ or Fe oxyhydroxide is the principle control on Cd concentrations. Trivedi and Axe, (2000) stated that the affinity of Cd ions for HMO is greater than for HFO. The concentrations of Fe display trends that are consistent with the solubility control by precipitation of Fe³⁺ oxyhydroxide. The Fe concentrations are slightly elevated at low pH in the unbuffered MFCC and the low pH regions of the buffered MFCC, and near the detection limit in the neutral pH regions of the buffered MFCC.

The behavior of Mo, Cu, Pb, Ni, Cr, and Zn in the MFCC is very similar to that described previously for the MCC, but there are several distinct differences. In contrast with the MCC, the concentration of Zn decreases to very low levels in the neutral pH region of the buffered column. This pH dependency, which was not observed in the MCC system, relates to the solubility control on Fe³⁺. The Fe³⁺ precipitates in the form of Fe oxyhydroxide at neutral pH (Stumm and Morgan, 1996) and Fe oxyhydroxide is an effective substrate for the sorption of aqueous Zn. While Uygur and Rimmer (2000) demonstrate that calcite grains are capable of Zn sorption, they also indicate that the sorption of Zn is increased when Fe oxyhydroxides are present as coatings on the calcite surfaces. The trends in the sorption of aqueous Pb concentrations also differ among the MFCC and the MCC. Concentrations of Pb reach values in the range of 0.03 to 0.06 mg/L in the unbuffered MFCC and in the low pH regions of the buffered MFCC, while dropping below detection in the neutral pH regions of the buffered MFCC. The Pb concentrations are uniformly low in both the buffered and unbuffered MCC (0.001 mg/L). The elevation of Pb concentrations in the low-pH regions of the MFCC system have not been satisfactorily explained but it may relate to competition for surface-complexation sites among Cd and Pb ions.

The solid phase extraction data for the MFCC are very similar to the corresponding data from the MCC, displaying a general trend toward decreasing metal concentrations versus distance along the flow path (Figure 4). The STEM/EDS analyses from the MFCC were obtained from MnO₃ and there was little indication of discrete Fe oxyhydroxides in the samples that were investigated. Similar to the STEM/EDS analyses of samples from the MCC, most of the trace metals were detected in association with the MnO₃ near the column inlet (Figure 6). Chromium was not detected in the STEM/EDS investigations providing further evidence that Cr behaves conservatively in the aqueous phase. The previous suggestion that Zn sorption is a consequence of

![STEM/EDS images](image2)

**Figure 6**: Images and spectra of samples from the MFCC. A) TEM bright field image of sonicated sample collected 1 cm along the flow path. B) TEM bright field image of sonicated sample collected 35 cm along the flow path. Representative STEM/EDS analyses from C) 1 cm along the flow path and D) 35 cm along the flow path in the MFCC.
the precipitation of Fe oxyhydroxide is supported by STEM/EDS analyses of mixed MnOx and Fe oxyhydroxide (Figure 6), collected 35 cm along the flow path in the buffered MFCC. Analyses of this sample demonstrate the presence of Zn, but none of the other trace metals are detected. The presence of Al and Ti peaks in spectra D1 and D2 are a result of feldspar (Na, K, Ca) AlSiO₃ and ilmenite (FeTiO₃) dissolution at low pH in the presence of MnOx. The feldspar and ilmenite occur as impurities (<5%) in the silica sand.

4. CONCLUSIONS

The results from the MCC demonstrate the tendency for removal of the trace metals Mo, Pb, Cu, Ni, and to a lesser extent Zn, from solution by sorption on MnOx, which is independent of pH in the range 2.2 to 6.5. The results from the MCC also reveal the inability of the MnOx reaction products to sequester Cr(III) over the same pH range. The mechanism by which trace-metal sorption occurs is most likely surface complexation and/or co-precipitation. The observed order of trace-metal sorption in the MCC was Mo>Pb>Cu>Ni>Zn>Cr.

The results from the MFCC are similar in that most of the trace metals are strongly sorbed by the MnOx and Fe oxyhydroxides in the MFCC, however the data display a pH dependency that is related to the solubility of Fe oxyhydroxide. The aqueous concentrations of Zn decrease to very low levels in the neutral pH region of the MFCC, indicating that the precipitation of Fe(III) oxyhydroxide that results from a pH increase associated with calcite dissolution, causes sorption of Zn on the Fe(III) substrate. Similar to data from the MCC, the Cr concentrations in the MFCC dataset indicate that Cr(VI) behaves conservatively in the presence of both MnOx and Fe oxyhydroxides.

Results of chemical extractions from the MCC and MFCC demonstrate that the observed decreases in aqueous concentrations of trace metals can be explained by corresponding increases in the concentrations of trace metals associated with the MnOx and Fe oxyhydroxides. The results of STEM/EDS analyses from the MCC and the MFCC systems also demonstrate that trace metals are sorbed by MnOx and Fe oxyhydroxide and analyses indicate that Mo, Pb, Cu, Ni, Cd, and Zn are associated with the discrete MnOx and Fe oxyhydroxide phases.

References


