Sorption of Cr(VI) on Mineral Assemblages of Goethite with Clays and Oxides

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Introduction
Anthropogenic activities have caused Cr(VI) contamination of many natural systems (Grossi et al., 1997). In aqueous solution Cr(VI) is highly mobile; however, adsorption of Cr(VI) to minerals surfaces impedes movement (Mesuree and Fish, 1992). Sorption behavior is dependent upon pH and the presence of competing ions (Richard and Bourg, 1991). Many studies have been conducted to observe the sorption behavior of Cr(VI) on single minerals and surface complexation models (SCMs) have been developed to describe these interactions but there is little information regarding the effects of mineral-mineral interactions on sorption.

Hypotheses
SCMs for single sorbent/sorbate systems need to account for mineral-mineral interactions to accurately predict sorbate behavior with multiple minerals.

Goals
• Measure Cr(VI) sorption on mineral assemblages of goethite, kaolinite, montmorillonite, γ-alumina, hydrous manganese oxide (HMO), & hydrous ferric oxide (HFO) (Table 1) as a function of pH, ionic strength & pCO2.
• Compare predictions from existing SCMs with measured edges of mineral assemblages to assess mineral-mineral interactions.
• Use knowledge gained to create more accurate SCMs for mineral mixtures.

Table 1: Materials

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Purchased/Synthesized</th>
<th>Recipe/Manufacturer</th>
<th>Surface Area m2/g</th>
<th>XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>Synthesized</td>
<td>Schwertmann &amp; Cornell, 2000</td>
<td>30</td>
<td>Figure 1</td>
</tr>
<tr>
<td>HMO</td>
<td>Synthesized</td>
<td>Stress-Gascony et al., 1987</td>
<td>400</td>
<td>Figure 2</td>
</tr>
<tr>
<td>HFO</td>
<td>Synthesized</td>
<td>Lund et al., 2008</td>
<td>300</td>
<td>Figure 3</td>
</tr>
<tr>
<td>Montmorillonite (Wy-2)</td>
<td>Natural purchased</td>
<td>Clay Minerals Society</td>
<td>Not shown</td>
<td></td>
</tr>
<tr>
<td>Kaolinite (KGa403050)</td>
<td>Natural purchased</td>
<td>Clay Minerals Society</td>
<td>Not shown</td>
<td></td>
</tr>
<tr>
<td>γ-Alumina</td>
<td>Synthesized purchased</td>
<td>Inframat Advanced</td>
<td>233</td>
<td>Not shown</td>
</tr>
</tbody>
</table>

References
Dzombak and Morel, 1990; Surface Complexation Modeling: Hydrous Ferric Oxide
Grossi et al., 1997; ES&T 31: 337
Mathur & Dzombak, 2002; Surface Complexation Modeling: Goethite
Lund et al., 2008; Geochim. Cosmochim. Acta 75: 7006
Shelley et al., 2009; J. Colloid Interface Sci. 338: 2
Schwertmann & Cornell, 1991; Iron Oxides in the Laboratory
Steege-Gascony et al., 1987; Appl Geochem. 2: 217

Acknowledgements
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Figure 1: XRD pattern of goethite 28 Cu-Kα
Figure 2: XRD pattern of HMO 28 Cu-Kα
Figure 3: XRD pattern of HFO 28 Cu-Kα

Experimental Method
• Ultrapure water, 10-6 M Cr(VI) & background electrolyte mixed in a 1 L flask; 60 mL control removed; Solids are then added to the solution in prescribed amount and batch slurry is allowed to equilibrate for 1 hr.
• pH is then lowered to ~3.5 and 60 mL of slurry removed; batch slurry is then titrated upward and at each ~0.5 pH increment, a 60 mL aliquot is removed and placed on a rotating shaker.
• After 24 hr, 48 hr, 1 wk & 2 wk of each mixture ~15 mL of slurry is removed from each aliquot, slurry pH rechecked, centrifuged and filtered, then tested for Cr(VI) using UV/VIS spectrophotometry and total Cr analyzed by ICP-OES.

Results and Discussion
• Binary mix experiments conducted with equal mineral surface areas (total surface area x 2 title values)
• 0.01 M NaClO4, 10-4 M Cr(VI) either at 0% pCO2 or in atmospheric conditions
• Pure goethite edges shown for comparison (Figure 4)

Figure 4: Adsorption of Cr(VI) on goethite as a function of pH. Little variation observed from 0 to 400 atm pCO2 or with times from 24 to 4 hr. UV/VIS/IOP-OES similar indicating no reduction of Cr(VI) in solution. pH = 7.8

Figure 5: Adsorption of Cr(VI) on mixtures of goethite & clay minerals as function of time & pCO2. Little variation observed from 0 to 4 atm pCO2 or with times from 24 to 4 hr. UV/VIS/IOP-OES similar indicating no reduction of Cr(VI) in solution. pH = 7.8

Figure 6: Adsorption of Cr(VI) on mixtures of goethite & γ-alumina as function of time & pCO2. Little variation observed from 0 to 4 atm pCO2 or with times from 24 to 4 hr. UV/VIS/IOP-OES similar indicating no reduction of Cr(VI) in solution. pH = 7.8

Figure 7: Adsorption of Cr(VI) on mixtures of goethite & kaolinite as function of time & pCO2. Little variation observed from 0 to 4 atm pCO2 or with times from 24 to 4 hr. UV/VIS/IOP-OES similar indicating no reduction of Cr(VI) in solution. pH = 7.8

Surface Complexation Modeling

Conclusions
• Binary systems containing goethite have sorption near 100% below pH 6
• Goethite-clay mixtures appear to be dominated by goethite, whereas mixtures of goethite with γ-alumina, HFO, or HMO edges are intermediate based on prior data
• SCMs for kaolinite and montmorillonite mixtures shift the sorption edge indicating the models require further calibration that mineral-mineral interactions are affecting sorption behavior.

Figure 8: Sorption data from this study (green), and modeling work from Goethite and HFO (Dzombak and Morel, 1995), and Kaolinite DLM (Schaller, et al., 2009) all parameters in Table 2.

Figure 9: Sorption data from this study (green), and modeling work from Goethite and HFO (Dzombak and Morel, 1995), and HNO3 optimized DLM (Toner, et al., 2004) all parameters in Table 2.

Table 2: Model Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.8</td>
</tr>
<tr>
<td>pCO2</td>
<td>4 atm</td>
</tr>
<tr>
<td>Time</td>
<td>24 hr</td>
</tr>
</tbody>
</table>

Figure 10: Sorption data from this study (green), and modeling work from Goethite and HFO (Dzombak and Morel, 1995), and HNO3 optimized DLM (Toner, et al., 2004) all parameters in Table 2.

Figure 11: Sorption data from this study (green), and modeling work from Goethite and HFO (Dzombak and Morel, 1995), and HNO3 optimized DLM (Toner, et al., 2004) all parameters in Table 2.

Figure 12: Sorption data from this study (green), and modeling work from Goethite and HFO (Dzombak and Morel, 1995), and HNO3 optimized DLM (Toner, et al., 2004) all parameters in Table 2.

Figure 13: Sorption data from this study (green), and modeling work from Goethite and HFO (Dzombak and Morel, 1995), and HNO3 optimized DLM (Toner, et al., 2004) all parameters in Table 2.

Figure 14: Sorption data from this study (green), and modeling work from Goethite and HFO (Dzombak and Morel, 1995), and HNO3 optimized DLM (Toner, et al., 2004) all parameters in Table 2.

Figure 15: Sorption data from this study (green), and modeling work from Goethite and HFO (Dzombak and Morel, 1995), and HNO3 optimized DLM (Toner, et al., 2004) all parameters in Table 2.

Figure 16: Sorption data from this study (green), and modeling work from Goethite and HFO (Dzombak and Morel, 1995), and HNO3 optimized DLM (Toner, et al., 2004) all parameters in Table 2.

Figure 17: Sorption data from this study (green), and modeling work from Goethite and HFO (Dzombak and Morel, 1995), and HNO3 optimized DLM (Toner, et al., 2004) all parameters in Table 2.

Figure 18: Sorption data from this study (green), and modeling work from Goethite and HFO (Dzombak and Morel, 1995), and HNO3 optimized DLM (Toner, et al., 2004) all parameters in Table 2.