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) arises to mineral surfaces impedes movement (Mesure 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 sorbate/sorbent 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>Model Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>Synthesized</td>
<td>Schwertmann &amp; Cornell, 2000</td>
<td>~30</td>
<td>DLM</td>
</tr>
<tr>
<td>HMO</td>
<td>Synthesized</td>
<td>Stress-Gascony et al., 1997</td>
<td>~40</td>
<td></td>
</tr>
<tr>
<td>HFO</td>
<td>Synthesized</td>
<td>Lund et al., 2008</td>
<td>~30</td>
<td></td>
</tr>
<tr>
<td>Montmorillonite (K5A-1b)</td>
<td>Natural purchased</td>
<td>Clay Minerals Society</td>
<td>~15.6</td>
<td></td>
</tr>
<tr>
<td>γ-Alumina</td>
<td>Sythesized purchased</td>
<td>InfraMax Advanced</td>
<td>~233</td>
<td></td>
</tr>
</tbody>
</table>

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 mix with ~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 2x title values)
• 0.01 M NaHCO3, 10⁻⁴ M Cr(VI) either at 0% pCO2 or in atmospheric conditions
• Pure goethite edges shown for comparison (Figure 4)

Conclusions
• Binary systems containing goethite have sorption near 100% below pH ~8
• Goethite-clay mixtures appear to be dominated by goethite, whereas mixtures of goethite with γ-alumina, HFO, or HMO edges are intermidiate based on prior data
• SCMs for kaolinite and montmorillonite mixtures shift the sorption edge indicating the models require further calibration or that mineral-mineral interactions are effecting sorption behavior

Table 2: Model Parameters

References
Dzombak and Morel, 1990, Surface Complexation Modeling: Hydrous Ferric Oxide
Grossi et al., 1997, Geochimica et Cosmochimica Acta 31: 335
Mathur and Dzombak, 2006, Surface Complexation Modeling: Goethite, Fertilizer Research, 2011, GCA 75, 7006
Lund et al., 2008, Geochim Trans 9:9
Mesure & Fish, 1992, ESA F 9: 2575
Sheller et al., 2009, J Collat Interface Science 338: 2

Acknowledgements
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Figure 1: XRD pattern of goethite 2B Cu-Kα.
Figure 2: XRD pattern of HMO 2B Cu-Kα.
Figure 3: XRD pattern of HMO 2B Cu-Kα.
Figure 4: Adsorption of Cr(VI) on goethite as a function of time (~100% sorbed at pH ~4).- pCO2 ~7.5
Figure 5: Adsorption of Cr(VI) on mixtures of goethite & clay minerals as a function of time & pCO2. Little variation observed from 0 to amine pCO2 or with times from 24 hr to 2 wk. UV/VIS & ICP-OES similar indicating no reduction of Cr(VI) in solution: pH ~6, ~8 pH.
Figure 6: Adsorption of Cr(VI) on mixtures of goethite & clay minerals as a function of time & pCO2. Little variation observed from 0 to amine pCO2 or with times from 24 hr to 2 wk. UV/VIS & ICP-OES similar indicating no reduction of Cr(VI) in solution: pH ~6, ~8 pH.
Figure 7: Adsorption of Cr(VI) on goethite & γ-Alumina mixture. Little variation observed from 0 to amine pCO2 or with times from 24 hr to 2 wk. UV/VIS & ICP-OES similar indicating no reduction of Cr(VI) in solution: pH ~6, ~8 pH.
Figure 8: Adsorption of Cr(VI) on goethite & γ-Alumina mixture. Little variation observed from 0 to amine pCO2 or with times from 24 hr to 2 wk. UV/VIS & ICP-OES similar indicating no reduction of Cr(VI) in solution: pH ~6, ~8 pH.
Figure 9: Adsorption of Cr(VI) on goethite & HMO mixture. Little variation observed from 0 to amine pCO2 or with times from 24 hr to 2 wk. UV/VIS & ICP-OES similar indicating no reduction of Cr(VI) in solution: pH ~6, ~8 pH.
Figure 10: Adsorption of Cr(VI) on goethite & HMO mixture. Little variation observed from 0 to amine pCO2 or with times from 24 hr to 2 wk. UV/VIS & ICP-OES similar indicating no reduction of Cr(VI) in solution: pH ~6, ~8 pH.
Figure 11: Adsorption of Cr(VI) on goethite & montmorillonite mixture. Little variation observed from 0 to amine pCO2 or with times from 24 hr to 2 wk. UV/VIS & ICP-OES similar indicating no reduction of Cr(VI) in solution: pH ~6, ~8 pH.
Figure 12: Adsorption of Cr(VI) on goethite & montmorillonite mixture. Little variation observed from 0 to amine pCO2 or with times from 24 hr to 2 wk. UV/VIS & ICP-OES similar indicating no reduction of Cr(VI) in solution: pH ~6, ~8 pH.
Figure 13: Adsorption of Cr(VI) on goethite & montmorillonite mixture. Little variation observed from 0 to amine pCO2 or with times from 24 hr to 2 wk. UV/VIS & ICP-OES similar indicating no reduction of Cr(VI) in solution: pH ~6, ~8 pH.
Figure 14: Adsorption of Cr(VI) on goethite & montmorillonite mixture. Little variation observed from 0 to amine pCO2 or with times from 24 hr to 2 wk. UV/VIS & ICP-OES similar indicating no reduction of Cr(VI) in solution: pH ~6, ~8 pH.
Figure 15: Sorption data from this study (blue), and Minteq model predictions for Cr(VI) adsorption on kaolinite. Cr(VI) adsorption species are optimized in FITEQL 4.0.
Figure 16: Sorption data from this study (blue), and Minteq model predictions for Cr(VI) adsorption on kaolinite. Cr(VI) adsorption species are optimized in FITEQL 4.0.

Surface Complexation Modeling

Figure 17: Sorption data from this study (blue),and Minteq model predictions for Cr(VI) adsorption on kaolinite. Cr(VI) adsorption species are optimized in FITEQL 4.0.