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 from mineral surfaces impedes movement (Mesures 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.

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 (K2O-2)</td>
<td>Natural purchased</td>
<td>Clay Minerals Society</td>
<td>~52</td>
<td>Not shown</td>
</tr>
<tr>
<td>Kaolinite (K6A-1b)</td>
<td>Natural purchased</td>
<td>Clay Minerals Society</td>
<td>~13.6</td>
<td>Not shown</td>
</tr>
<tr>
<td>γ-Alumina (NaAlO2)</td>
<td>Synthesized purchased</td>
<td>InfraMat Advanced</td>
<td>~233</td>
<td>Not shown</td>
</tr>
</tbody>
</table>

Table 2: Model Parameters

<table>
<thead>
<tr>
<th>HMO DLM (HMO)</th>
<th>7.65 g/Goethite</th>
<th>11.55 g/Montmorillonite</th>
<th>4.35 g/Kaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMO DLM (HMO)</td>
<td>11.55 g/Goethite</td>
<td>4.35 g/Montmorillonite</td>
<td>7.65 g/Kaolinite</td>
</tr>
</tbody>
</table>

References

Dzombak & Morel, 1990. Surface Complexation Modeling: Hydrous Ferric Oxide
Grossi, et al., 1997. ESMF 31:331
Mathur & Dzombak, 2000, Surface Complexation Modeling: Goethite
Mathur, R., & Morel, 2011. GCA 75: 7006
Lund et al., 2008, Geochim Cosmochim Acta 79: 2975
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Acknowledgements

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Experimental Method

• Ultrapure water, 10⁻² 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 hr & 2 wk of 60 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

Hypotheses

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

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 intermediates 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 affecting sorption behavior

Future Work

• Compare SCM predictions for mixtures with HMO, kaolinite and montmorillonite to experimental data & verify model predictions
• Complete edge experiments on mixtures of all minerals based on equal surface area of atmosphere, 0% pCO2 & 5% pCO2 with 0.1 M HFO and 0.01 M NaHCO3, and compare with SCM predictions.

Results and Discussion

• Binary mix experiments conducted with equal mineral surface areas (total surface area 2x title values)
• 0.01 M NaHCO3 10⁻³ 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. -100% when pH ~6; ~90% sorbed at pH ~9; ~75% sorbed at pH ~11

Figure 5: Adsorption of Cr(VI) on mixtures of goethite & clay minerals as function of pH & pCO2. Little variation observed from 0 to 0.1 m pCO2 or with times from 24 hr to 2 wk. UV/VIS & ICP-OES similar indicating no reduction of Cr(VI) in solution: pH ~7.8, pH ~9

Figure 6: Adsorption of Cr(VI) on mixtures of goethite & clay minerals as function of time & pCO2. Little variation observed from 0 to 0.1 m pCO2 or with times from 24 hr to 2 wk. UV/VIS & ICP-OES similar indicating no reduction of Cr(VI) in solution: pH ~7.8, pH ~9

Figure 7: Adsorption of Cr(VI) on goethite edges shown for comparison (Figure 4)

Figure 8: Adsorption of Cr(VI) on goethite edges shown for comparison (Figure 4)

Figure 9: Adsorption of Cr(VI) on goethite edges shown for comparison (Figure 4)

Figure 10: Adsorption of Cr(VI) on goethite edges shown for comparison (Figure 4)

Figure 11: Adsorption of Cr(VI) on goethite edges shown for comparison (Figure 4)

Figure 12: Adsorption of Cr(VI) on goethite edges shown for comparison (Figure 4)

Figure 13: Adsorption of Cr(VI) on goethite edges shown for comparison (Figure 4)

Figure 14: Adsorption of Cr(VI) on goethite edges shown for comparison (Figure 4)

Figure 15: Adsorption of Cr(VI) on goethite edges shown for comparison (Figure 4)

Figure 16: Adsorption of Cr(VI) on goethite edges shown for comparison (Figure 4)

Figure 17: Adsorption of Cr(VI) on goethite edges shown for comparison (Figure 4)

Figure 18: Adsorption of Cr(VI) on goethite edges shown for comparison (Figure 4)

Figure 19: Adsorption of Cr(VI) on goethite edges shown for comparison (Figure 4)

Figure 20: Adsorption of Cr(VI) on goethite edges shown for comparison (Figure 4)