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

Ann M. Gilchrist* and Carla M. Koretsky
Department of Geoscience, Western Michigan University, MI 49008, USA (*correspondence: ann.m.gilchrist@wmich.edu)

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) ions 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/Source</th>
<th>Surface Area m2/g</th>
<th>Reference</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-Gascoigne 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 (HwY-2)</td>
<td>Natural purchased</td>
<td>Clay Minerals Society</td>
<td>~52</td>
<td>Not shown</td>
</tr>
<tr>
<td>Kaolinite (KGA-1b)</td>
<td>Natural purchased</td>
<td>Clay Minerals Society</td>
<td>~13.6</td>
<td>Not shown</td>
</tr>
<tr>
<td>Alumina (γ-A1-O)</td>
<td>Synthesized purchased</td>
<td>Infamat Advanced</td>
<td>~233</td>
<td>Not shown</td>
</tr>
</tbody>
</table>

Table 2: Model Parameters

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Surface Complexation Model</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Goethite</td>
<td>Dzombak and Morel HFO DLM</td>
<td>This Study</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>Mathur and Dzombak Goethite DLM</td>
<td>This Study</td>
</tr>
<tr>
<td>HMO</td>
<td>Dzombak and Morel HFO DLM</td>
<td>This Study</td>
</tr>
<tr>
<td>Alumina</td>
<td>Dzombak and Morel HFO DLM</td>
<td>This Study</td>
</tr>
</tbody>
</table>

Surface Complexation Modeling

Figure 13: Model data from this study (HMO), and Montmorillonite only from Mathur and Dzombak (2009). Goethite & Montmorillonite DLM (Schaller, et al., 2009) all parameters in Table 2.

Conclusions

• Binary systems containing goethite have sorption near 100% below pH -4
• 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 shift the sorption edge indicating the models require further calibration or that mineral-mineral interactions are affecting sorption behavior.

Acknowledgements

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References

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Richard et al., 2010, GCA 75: 7000
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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 mixing ~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

Figure 14: Adsorption of Cr(VI) on goethite as a function of time ~100% enriched at pH <6, ~90% sorbed at pH >7 - 9.

Figure 15: Sorption data from this study (HMO), and Montmorillonite only from Mathur and Dzombak (2009). Goethite & Montmorillonite DLM (Schaller, et al., 2009) all parameters in Table 2.

Future Work

• Compare SCM predictions for mixtures with HMO, kaolinite and montmorillonite to experimental data & verify model calibrations
• Complete edge experiments on mixtures of all minerals based on equal surface area of atmosphere, 0% pCO2 and 5% pCO2 with 0.1 M HFO and 0.01 M NaNO3 and compare with SCM predictions.

Figure 16: Sorption data from this study (HMO), and Montmorillonite only from Mathur and Dzombak (2009). Goethite & Montmorillonite DLM (Schaller, et al., 2009) all parameters in Table 2.