

Adsorption of Metals and Oxyanions on Mineral Assemblages

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Trace metal contamination of near surface aquatic systems has created a need for accurate predictive models of inorganic contaminant speciation and transport in the natural environment. Thermodynamically-based surface complexation models (SCMs) can successfully describe adsorption of single metals and oxyanions on a diverse suite of pure substrates, including bacteria, amorphous and crystalline solids. Application of SCMs to better understand metal fate and mobility in natural systems requires models that can correctly predict adsorption in mixed mineral assemblages and over broad ranges of pH, ionic strength, pCO₂ and metal loading.

Adsorption edges for Cd, Co, Pb, and Cu have been measured as a function of pH (~3-10), ionic strength (0.001-0.1 M NaNO₃) and solid loading (~2-5 g/L solid; 10⁻⁶ to 10⁻⁴ M metal) on pure kaolinite (KGa-1b), silica, and hydrous ferric oxide (HFO). Adsorption of the metals on synthetic mixtures of kaolinite, quartz and HFO are well predicted using diffuse layer models (DLMs) developed from data for the pure endmember systems under similar conditions. However, for systems of pure solids and for synthetic mineral assemblages, the DLM approach often fails to correctly capture adsorption trends over broad ranges of ionic strength and solid loading. This is a significant problem which should be recognized and explicitly addressed if SCMs developed for single solids are to be applied to natural systems.

Redox-sensitive sorbates, such as Cr(VI), pose another challenge in developing SCMs that can correctly predict speciation in complex natural systems. Cr(VI) sorption on γ -alumina, a substrate which does not promote Cr(VI) reduction, is rapid and reversible. Single adsorption edges (pH ~4-10) measured at constant ionic strength (0.001 to 0.1 M NaNO₃), pCO₂ (0-2.5%) and loading (10⁻⁴ to 10⁻⁵ M Cr(VI) on 5 g/L solid) are well described using constant capacitance, double layer or triple layer models. However, none of the SCMs correctly describes Cr(VI) sorption over broad ranges in pH, ionic strength and pCO₂. Likewise, Cr(VI) sorbs quickly and reversibly on hydrous manganese oxide, and single edges are well described using the SCM approach. On clay minerals, however, development of SCMs is much more problematic due to slow and irreversible sorption, which likely reflects reduction of Cr(VI) to Cr(III) by organic matter or Fe(II) in the clay mineral lattices. On untreated kaolinite, Cr(VI) sorption at pH 3 is extremely slow, failing to reach a steady state even after 2 weeks of reaction time. Although sorption is rapid on untreated montmorillonite (Swy-2), on both kaolinite and montmorillonite, Cr(VI) fails to desorb at pH 10, even after several days. On kaolinite treated with HCl, hydroxylamine HCl or hydrogen peroxide, Cr(VI) sorption reaches steady state much more quickly, and more sorption occurs at pH 3-7 compared to the untreated kaolinite. These data point to the need for spectroscopic data to constrain SCMs describing Cr(VI) sorption on clay minerals.

Secondary Mineral Phases in a Uranium Mill Pilot Study

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Introduction

The uranium milling process at Cameco's Key Lake operation in northern Saskatchewan, Canada leaches untargeted elements of concern (EOC; e.g., arsenic, molybdenum, selenium, iron, radium-226) that have the potential to adversely impact local groundwaters and surface waters. [1] Studies at similar uranium milling operations indicate As concentrations are controlled by Fe oxide mineral phases such as ferrihydrite. [2-5] The environmental impact of EOCs in the Key Lake mill waste solution (raffinate) is mitigated by neutralizing the pre-discharge mine tailings with slaked lime, resulting in the formation of secondary As-, Mo-, Se-, and Fe-bearing mineral phases as well as co-precipitation of ²²⁶Ra phases. This serves to control EOC concentrations at very low levels in the tailings porewater.

As part of an ongoing investigation into the long-term stability of EOCs in the Deilmann Tailings Management Facility (DTMF) at Key Lake, secondary mineral phases formed during the neutralization process must be characterized and the controls on the aqueous phase concentrations of EOCs defined for a variety of ore blends. A pilot-scale model of the Key Lake mill neutralization circuit was thus developed (Figure 1) to assist in quantifying the redistribution of EOCs during the milling process. Secondary precipitates and supernatants in the physical model are separated and analyzed using ICP-MS, XRD, and Raman spectroscopy. The results are compared to geochemical modeling of the mill neutralization process.

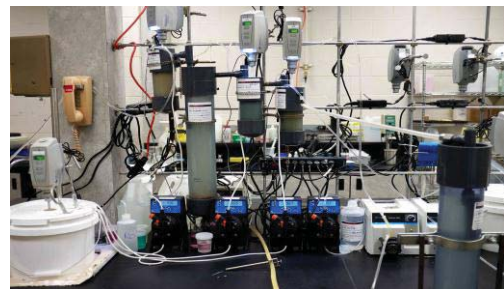


Figure 1: EOCs are removed from the raffinate by precipitation with slaked lime and thickener settling at pH set points.

Conclusions

A comparison of EOC percent removal efficiencies from the pilot-scale model and the Key Lake milling process indicates that the model successfully reproduces conditions in the mill.

[1] Liu & Hendry (2011) *Appl. Geochem.* **26**, 2113-2120. [2] Jia *et al.* (2006) *Environ. Sci. Technol.* **40**, 3248-3253. [3] Mahoney *et al.* (2007) *Appl. Geochem.* **22**, 2758-2776. [4] Moldovan, Jiang & Hendry (2003) *Environ. Sci. Technol.* **37**, 873-879. [5] Moldovan, Hendry & Harrington (2005) *Appl. Geochem.* **39**, 4913-4920.