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Molecular scale understanding of Ni^{2+} and Zn^{2+} adsorption on swelling clay minerals

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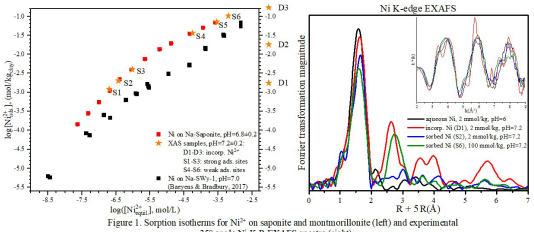

Figure 1. Sorption isotherms for Ni^{2+} on saponite and montmorillonite (left) and experimental 35° angle Ni-K P-EXAFS spectra (right).

Sorption of hazardous metals on clay minerals is a key process contributing to the safety of repository systems. The existence of high- and low-affinity adsorption sites on smectites edge surfaces, responsible for metals uptake has been revealed in previous studies [1,2]. The exact molecular nature of these adsorption sites has yet not been fully resolved.

Like the adsorption of Ni^{2+} on montmorillonite [1], Ni^{2+} on saponite shows a non-linear adsorption behavior, indicating the likely presence of multiple sorption sites (Fig.1). Based on the sorption isotherms obtained on saponite, self-oriented clay films with Ni loadings expected to represent sorption dominated by either strong or weak sites were prepared (S1-S6 in Fig. 1). Subsequently, polarized Ni K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy was conducted to analyze the structural arrangement surrounding the nickel atoms.

For low Ni^{2+} loading samples (below 4 mmol/kg), P-EXAFS results confirmed the existence of strong sorption sites. An increase of Ni loading (up to 40 mmol/kg) leads toa decreased Ni-Mg bond length and an increase of Ni-Si coordination number, indicating the formation of a secondary phase. The exact structure of the new phase is still under evaluation.

The molecular structure of cations adsorbed on the water-edge interfaces for the most stable surfaces ((010) and (110)) was modeled using ab initio MD, enabling us to obtain a theoretical estimation of the Gibbs free energies of Zn-Ni cation exchange reactions between weak and strong sites. Comparing the free energies obtained experimentally for montmorillonite with the ones calculated for saponite, indicates that Zn^{2+} shows higher affinity to strong sites than Ni^{2+}. Next, using linear combination fit method we aim to describe exact atomistic structure of Zn^{2+} and Ni^{2+} sorption complexes on saponite edges.

References:

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