

Molecular scale understanding of Ni²⁺ adsorption on swelling clay minerals

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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 not been fully resolved.

Similar to the adsorption of Ni²⁺ on montmorillonite [1], Ni²⁺ on saponite shows a non-linear adsorption behavior, which, by analogy, suggests the existence of strong and weak sorption sites (Fig.1). Based on the sorption isotherms obtained on saponite, self-oriented clay films were prepared, with Ni loadings corresponding to adsorption dominated by strong and weak sites, and then polarized Ni K-edge EXAFS spectra were recorded.

For samples with low Ni²⁺ loadings (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 to decreasing in Ni-Mg bond length and an increase in Ni-Si coordination number, indicating the formation of a secondary phase. The exact structure of the new phase is still under evaluation, but this solid phase will certainly mask Ni sorbed to weak sites.

The molecular structure of cations adsorbed on the water-edge interfaces for the most stable surfaces was modeled using ab initio MD, which enable us to obtain a theoretical estimation of the free energies of Zn-Ni cation exchange reactions between weak and strong sites on (100) and (130) edges of saponite. Theoretical values obtained for Zn-Ni exchange are equal to 13.5±0.4 and 5.50±0.03 kJ/mol for (100) and (130) surfaces, respectively. These results are in a good agreement with experimental results for montmorillonite (9.1 kJ/mol) – a trustworthy proxy and suggest a stronger affinity of Zn to strong sites than Ni.

[1] Dähn, Baeyens & Bradbury (2011), *Geochimica et Cosmochimica Acta* 75, 5154-5168.

[2] Bradbury & Baeyens (1997), *Journal of Contaminant Hydrology* 27, 223-248.

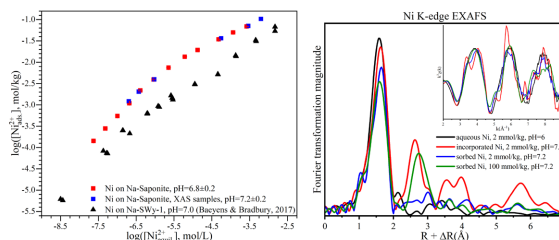


Figure 1. Sorption isotherm for Ni²⁺ on saponite and montmorillonite (left) and experimental 35° angle Ni-K EXAFS spectra (right).