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Mechanism of Zn adsorption on montmorillonite inferred from atomistic simulations, P-EXAFS-spectroscopy and sorption experiments

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The uptake of heavy metals by clay minerals such as montmorillonite and illite is an important process controling the migration of contaminants in the geosphere. The 2-site protolysis non electrostatic surface complexation and cation exchange (2SPNE SC/CE) sorption model [1] has been used over the past decade or so to quantitatively describe sorption of metals with valences from II to VI on montmorillonite [2]. One of the main assumptions in this model is that there are two broad categories of edge sorption sites; the so called strong (>SSOH) and weak (>SW1OH) sites. Because of their different sorption characteristics, it was expected that the coordination environments of the surface complexes on the two site types should be different. The aim of this study is to identify the nature of (>SSOH) and (>SW1OH) sites at an atomistic level combining sorption measurements, P-EXAFS spectroscopy and atomistic simulations.

Two different montmorillonites were chosen for the experimental part of this study: Milos (Island of Milos, Greece) and STx-1 (Gonzales County, Texas, USA). As a reference for Zn substituted for Al in the clay octahedral sheet a MILOS sample was prepared without adding any Zn. Milos was chosen because it contains 1.8 [mmol/kg] Zn incorporated into the structure, compared to only 0.3 [mmol/kg] for STx-1. Compared to the foreseen added Zn loadings of ˜2 mmol/kg and ˜30 mmol/kg, respectively, the quantity of incorporated Zn in the STx-1 is quite low and thus does not impair the EXAFS signal form the adsorbed species. In a first step Zn isotherm data on two montmorillonites, Milos and STx-1, were measured and modelled using the 2SPNE SC/CE sorption model. The results were used to define the most favourable experimental conditions under which Zn sorption was either dominated by the strong (>SSOH, ˜2 mmol kg-1) or by the weak sites (>SW1OH, ˜40 mmol kg-1). Highly oriented self-supporting films of montmorillonite were prepared to measure P-EXAFS spectra of Zn complexes adsorbed at low (˜2 mmol kg-1), and medium Zn loadings (˜30 mmol kg-1) as well as Zn incorporated in the montmorillonite structure. The molecular structure of potential Zn complexes on the (010), (110), (130) and (100) edges of montmorillonite were derived based on ab initio molecular dynamics and geometry optimization runs. These optimised molecular structure were used to calculate theoretical EXAFS spectra. The molecular mechanism of Zn uptake on montmorillonite was then derived comparing the measured and calculated EXAFS spectra.

The analysis of the measured EXAFS spectra [3] and simulation results [4] suggests that Zn preferentially substitutes for Al(III) in the trans-symmetric sites of the octahedral layer. At low loading Zn is incorporated into the outermost trans-octahedra on (010) and (110) edges. At medium loading Zn forms mono- and bi-dentate inner-sphere surface complexes attached to the octahedral layer of (010) and (110) edge sites. The maximal site density of inner-sphere sorption sites inferred from molecular simulations agrees well with site capacities of surface complexation sites derived from macroscopic studies and modeling.

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