

2.1.P07**Molecular models of the external surfaces of kaolinite and the dynamics of the clay-water interface**

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An atomic level understanding of mineral-water interactions is important for the evaluation and prediction of numerous properties for clays and other minerals, especially in the treatment of environmental waste. In particular, the behavior of water at the clay-water interface controls many processes including solvation, sorption, precipitation, and growth. Our ability to understand these complex processes is provided by a few experimental and analytical methods such as X-ray absorption, vibrational, and NMR spectroscopies. However, due to complexities in the structure, composition, and nano-size of clays, and the inherent uncertainties of the experimental methods, it is important to apply theoretical molecular models to obtain a fundamental understanding and interpretation of these phenomena. We have recently developed a general force field [1] suitable for the simulation of hydrated and multicomponent mineral systems, including kaolinite. Interatomic potentials for CLAYFF were derived from parameterizations incorporating structural and spectroscopic data from a variety of simple hydrated compounds. A flexible water model is used to describe the water and hydroxyl behavior.

The structure and dynamics of various saturating amounts of water within an expanded kaolinite were examined using NVT molecular dynamics and the CLAYFF forcefield. No constraints on atomic positions were imposed, thereby allowing relaxation of all atoms at the interface. Kaolinite is characterized by the layering of gibbsite and siloxane sheets that ultimately provide two distinctive external basal surfaces with relatively hydrophilic and hydrophobic behavior, respectively. Analysis of the equilibrium trajectories indicates contrasting behaviors in coordination number, hydrogen bonding, and orientational order for the water molecules at these two surfaces. Water molecules exhibit ordering up to 8 or 9 Å from either of the surfaces.

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Reference

- [1] Cygan R.T., Liang J.-J., and Kalinichev A.G. (2004) *JPC B* **108**, in press.

2.1.P08**Cu adsorption kinetics onto illite surfaces: A flow-through reactor study**

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Adsorption of heavy metals is a key factor in several environmental systems. The current work tries to address this problem in relation to the fixation mechanisms of base metals in sediments percolated by landfill leachate-polluted surface waters [1]. It was verified that illite constitutes a common clay mineral in such sediments and that Cu is the most anomalous metal present.

The Silver Hill Mt1 illite was obtained from the CMS repository of special clays. The illite sample was washed and particles with 0.4 to 20 µm dimensions were separated for the study. The sample was pre-treated for the oxidation of organic matter, and dissolution of carbonates and oxides. Measured N₂ BET surface area is 38.04±0.03 m²/g. For the adsorption experiments, a continuous stirred flow-through reactor with 0.2 µm filter membranes was used. All system variables were kept constant, with Cu concentrations varying from 50–150 µM in the input solution during each experimental run. Experiments were performed at pH 4.5, 5.5, and 6.5, and ionic strength 10⁻⁴ M and 10⁻³ M KClO₄, as a proxy to the nearly pristine and contaminated surface and ground waters. Experiments lasted until a steady output Cu solution was achieved. Output solution was regularly sampled and analysed for Cu by AAS.

The Cu-rich input solution was fed into the reactor at the start of each experimental run. The loaded illite immediately started to adsorb Cu, and soon after a steady-state was achieved in the reactor for a couple of hours. Apparent rates of adsorption varied between 3.1×10⁻⁸ and 6.2×10⁻⁸ moles s⁻¹ at these steady-state conditions. Some of the time-dependent adsorption curves were integrated and showed a nearly constant total amount of adsorbed Cu, which was used as an estimate for the site density of the illite. The density of sites varied between 6.90×10⁻⁵ and 7.11×10⁻⁵ moles/g. Cu adsorption kinetics increases with increasing pH, but at pH>5.5 we gathered evidence for Cu precipitation, probably as a chloride phase. However this effect is attenuated with increasing ionic strength, thus indicating that salt effects may be of the utmost importance in Cu fixation in sediments, as one should expect in the highly polluted landfill leachate waters. Besides, these waters are heavily loaded with organic material, with special emphasis on the volatile fatty acids. These aspects are still under investigation.

Reference

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