

2.3.P01**Competitive adsorption of phosphate and organic acids: A quantitative and spectroscopic approach**

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During the past years extensive research has been made in the field of mineral surfaces and the adsorption of various inorganic and organic ligands to those surfaces. One inorganic ligand that is of great importance to plant growth and survival is orthophosphate, a nutrient that is unavailable for uptake when adsorbed to a mineral surface. As a response to phosphate depletion, roots have been noticed to excrete small carboxylic acids, which are thought to compete with phosphate for the sites on the minerals and hence make the phosphate available for uptake by the plant.

Goethite is a mineral found in many of the Earth's climate zones. It is well characterised and easily synthesised which, in combination with its abundance in soils, makes it an ideal model compound to work with in laboratory studies.

The aim of the present work was to gain further knowledge about the phosphate-goethite system and to explore the competition between phosphate and some organic acids. The aim was also to investigate the competition among the acids. Previous work done in this area show that oxalate is a more powerful adsorbate than malonate onto the surface of goethite [1], but the different adsorption efficiencies among the other acids remain, to our knowledge, unexplored. In order to meet the research objectives, a combination of quantitative adsorption data and molecular spectroscopic data were collected. The work was made in series of batch experiments, measuring ligand adsorption as a function of pH and ligand concentration. In-situ ATR-FTIR spectroscopy has been extensively used to evaluate the speciation and adsorption mechanisms of phosphate and the carboxylic acids (malonate, oxalate, citrate and hexa-mellitate). In addition, UV-spectroscopy, scintillation counting and atomic absorption spectroscopy have been used to gain quantitative adsorption and dissolution data.

References

- [1] Axe K. Spectroscopic Studies of Oxalate and Malonate at the Water-Mineral Interfaces, *PhD thesis* (2002) Umeå University, Sweden.

2.3.P02**Determination of effective diffusion parameters in compacted kaolinite**J. MIBUS¹, M. LAMBARKI² AND R. KUECHLER¹¹ Forschungszentrum Rossendorf, Dresden, Germany
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(M.Lambarki@lih.rwth-aachen.de)**Introduction**

Clay minerals are main components of many soils, sediments, pelitic rocks, as well as fracture filling material in crystalline rocks. Furthermore, clays are used in geo-engineering, particularly to design hydraulic and geochemical barriers in contaminated sites, landfills or underground repositories for toxic or nuclear wastes. Due to the low permeability of clay molecular diffusion is the main transport mechanism of dissolved or colloidal substances at natural hydraulic gradients. This process has to be studied to assess the long-term behavior of geoen지니어ed barrier systems.

Experimental

In order to determine effective transport parameters in kaolinite diffusion experiments with a conservative tracer were performed. Kaolinite from Hirschau (Germany) was filled in a diffusion cell (cross sectional area 78.6 cm², layer thickness 1.8 cm), compacted to a dry density of 1.1 g cm⁻³ and fixed between two filter plates. The through-diffusion of tritiated water (HTO) was observed applying a tracer reservoir with a starting activity of 4·10⁵ Bq in 180 mL. The tracer activities of the high and the low concentration side were measured in intervals by liquid scintillation counting.

Modelling

An analytical solution of the one dimensional transport equation was developed to determine the diffusion coefficient and the effective porosity. Two variable boundary conditions accounted for the changing concentrations in the transient phase.

Results and Conclusions

A diffusion coefficient of $D_e = 3.2 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and an effective porosity of $\epsilon = 0.6$ were determined from the measured concentration versus time. These results are compared with stationary diffusion experiments using reactive tracers (Cu^{2+} , Zn^{2+} , Pb^{2+} , AsO_4^{3-}) and natural sealing material (loess loam) and kaolinite (Hamad, 2003). For instance, in loess loam D_e was found to be 2.47, 3.04, and $4.14 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for Cu, Pb, and Zn, respectively. These results indicate that the diffusion parameters in the natural and the engineered barrier material are in the same order of magnitude.

Reference

- [1] Hamad, Y.(2003) *Mitt. Ing. u. Hydrol.* RWTH Aachen.