



Diffusion, sorption, and retardation processes of anions in bentonite and organo-bentonites for multibarrier systems

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The low permeability, high cation exchange capacity (CEC) and plasticity of bentonites favor their use in multibarrier systems of waste deposits [1]. Bentonites have a high CEC but their ability to sorb anions is very low. There is, however, need for retardation of anions and organic pollutants in many applications. Bentonites, modified with certain organic cations, have the capacity to sorb anions and non-polar organic compounds in addition to cations. Investigations on organically modified clays address a wide variety of applications including immobilization of pollutants in contaminated soils, waste water treatment and *in situ* placement for the protection of ground water [2]. Many experiments on anion and cation sorption of organo-clays were conducted in the batch mode which does not reflect solid-liquid ratios and material densities in barrier systems. Diffusion experiments on compacted clays allow the evaluation of transport processes and sorption of pollutants at conditions relevant for repositories. For organo-clays only few diffusion studies are published e.g. [3] measured the diffusion of tritium and [4] the diffusion of H₂O in bentonite and organo-bentonites.

The organic cation hexadecylpyridinium (HDPy) was added to Wyoming bentonite (MX-80) in amounts corresponding to 2-400 % of the CEC. The uptake of organic cations was determined by the C-content, XRD and IR-spectroscopy. Wettability was analyzed by the contact angle. Physical, chemical and mineralogical properties of clays were characterized. Diffusion experiments were carried out *in situ* in a cell attached to the ATR-unit of a FTIR-spectrometer. For H₂O-diffusion the compacted organo-clays are saturated first with D₂O, afterwards H₂O is supplied to the surface at the top of the clay platelet. Anion-diffusion was conducted with NO₃⁻-solution instead of H₂O only having characteristic IR band positions at 1350 cm⁻¹. Three different concentrations (0.25M, 0.5M and 1M) were used. Additional batch experiments with NO₃⁻ will support the understanding of sorption behavior of the anions.

All hydrophilic samples have a higher retardation capacity, indicated by diffusion coefficients of 2.44 x 10⁻¹¹ m/s² for original bentonite and ≤2.1 x 10⁻¹¹ m/s² for hydrophilic organo-clays. For hydrophobic organo-clays the H₂O diffusion can be higher and is increased at high bulk density (1-1.5 g/m³) up to 2.76 x 10⁻¹⁰ m²/s. Experiments with NO₃⁻ at bulk density of 1.5 g/m³ reveal that the apparent diffusion coefficients of nitrate are with results up to 5.61 x 10¹² m²/s distinctively lower than free diffusion of nitrate in pure water (6.46 x 10¹⁰ m²/s at experimental conditions) and nitrate diffusion in natural bentonite (2.63 x 10¹¹ m²/s). The measurements allow the interpretation of the different sorption mechanisms, retardation capacity and diffusion behavior of the analyzed clays at different anion concentrations. Ongoing molecular dynamic simulations will contribute understanding of diffusion processes in organo-clays including the conditions at the interface of the clay minerals and in solution.

References:

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