

Diffusion and retention experiment in clay formation: An international field, lab and modelling exercise

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Due to their favourable hydraulic and retention properties, deep argillaceous formations are worldwide being considered as potential host rocks for deep geological disposal of radioactive waste. Combined laboratory and large scale *in situ* migration studies showed that diffusion is the main transport process for radionuclides in Opalinus Clay [1]. Retention of radionuclides, on the other hand, has been predominantly investigated by batch sorption measurements. This paper reports on a large scale, *in situ* experiment at an Underground Rock Laboratory in Switzerland. The objectives are threefold: (i) to obtain diffusion and retention data for moderately and strongly sorbing tracers, (ii) to improve diffusion data for rock anisotropy and (iii) to quantify effects of the borehole-disturbed zone for non-reactive tracers. The design has been validated by diffusion tests with non-sorbing and sorbing tracers [2, 3]. The injected tracers were tritium, I, Br, ²²Na, ⁸⁵Sr, Cs, ¹³⁷Cs, ¹³³Ba, ⁶⁰Co ¹⁵²Eu, and ⁷⁵Se (planned). These tracers were added as a pulse to the fluid circulating in a packer system allowing the tracer to diffuse into the clay formation. As part of the EU project FUNMIG an extensive modelling exercise accompanies this experiment in which four distinct reactive transport models are being benchmarked.

[1] E. Tevissen, J.M. Soler, Mont Terri Project. DI Experiment. Synthesis Report. Mont Terri Technical Report TR 2001-05, swisstopo, Wabern, Switzerland, 2003. [2] J.-M. Palut, Ph. Montarnal, A. Gautschi, E. Tevissen, E. Mouche. J. (2003) *Contaminant Hydrology* **61**, 203. [3] L.R. Van Loon, P. Wersin, J.M. Soler, J. Eikenberg, Th. Gimmi, P. Hernán, S. Dewonck, S. Savoye (2004) *Radiochimica Acta* **92**, 757.

An inelastic neutron scattering study of adsorbed water on rutile and cassiterite nanoparticles

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Water is ubiquitous on the surface of oxide nanoparticles, displaying varying degrees of deviation from bulk water structure and dynamics, and can exert a profound influence on the thermodynamic properties of the oxide [1-3]. The exceptionally large incoherent neutron scattering cross-section of hydrogen compared to other elements makes neutron scattering an attractive technique to study the structure and dynamics of surface water. We have used inelastic neutron scattering (INS) to investigate the structure and vibrational density of states (VDOS) of the surface water in two nanopowder oxides, TiO₂ (rutile) and SnO₂ (cassiterite). The INS spectra of the water adsorbed on the surface of 7 nm TiO₂ and 5-10 nm SnO₂ nanoparticles were measured at 4 K over the 0-550 meV range using the high-resolution medium energy chopper spectrometer (HRMECS) at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. INS spectra were also collected after the samples were heated at 373K to remove any loosely-bound layers of water. The results from this study show how surface confinement on the surfaces of rutile and cassiterite nanoparticles influences water vibrations. In addition, the VDOS derived from the INS spectra can be used to compute the heat capacity and entropy of the surface water [4]. We will present a comparison of INS measurements with calorimetric data that will provide additional insight into the structure and dynamics of water confined on the surface of TiO₂ and SnO₂ nanoparticles.

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[2] Predota *et al.* (2004) *J. Phys. Chem. B.* **108**, 12049.

[3] Boerio-Goates *et al.* (2006) *Nano Lett.* **6**, 750.

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