Influence of Temperature on HTO and $^{36}Cl^-$ Diffusion in Bentonite and Callovo-Oxfordian clays

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The Callovo-Oxfordian formation at Bures in the Paris Basin (France) has been chosen as a potential host rock for deep radioactive waste disposal. Bentonite MX80 is proposed as buffer barrier surrounding the canisters. These materials have very low permeability and diffusion is like-ly to be the predominant mechanism transfer governing radionuclide migration. High level waste disposal will induce a temperature increase in these barriers. In a dilute solvent, this effect is described by the Stokes-Einstein law $D^{\infty}_{IS} = k\ T\ /6\pi\ \eta_S\ r_I$ whith D^{∞}_{IS} the diffusion coefficient of a solute I infinitely diluted, k the Boltzmann constant, T the temperature, r_I the ionic radius and η_s the viscosity of the solvent. The effective diffusion coefficient of solutes in porous media is linked to the diffusion coefficient in free-water, porosity, tortuosity and constrictivity. Moreover, the effective diffusion coefficients of halides are reduced by anionic exclusion. In compacted clays, the physical prop-erties of the interstitial water is strongly affected by liquid-solid interfaces. As a matter of facts, the use of Stokes-Einstein law in order to evaluate the effect of temperature on diffusion coefficients in such media is questionable.

In order to check the validity of Stokes-Einstein law for HTO and ^{36}Cl in compacted bentonite and Callovo-Oxfordian argillite, through-diffusion experiments have been carried out to quantify the effective diffusion coefficient for HTO and ^{36}Cl. After the permanent diffusion state is reached at 20 °C, the temperature is increased step by step (35-50-65-80°C). Two chemical conditions have been selected. Effect-ive diffusion coefficient increase by a factor 3 to 5.7 and 4 to 7.5 for HTO and $^{36}Cl^-$ respectively as temperature increases from 20°C to 80°C. Hysteresis phenomenon has been seen: effective diffusion coefficient at 20°C after and before heating are significantly different. Assuming that pore water viscosity is equal to bulk water viscosity and that formation factor is constant in the range investigated, validity of the Stokes-Einstein law for tritium and $^{36}Cl^-$ in theses porous medias has been analyzed. For tritiated H_2O, it hasn't been possible to clearly validate or invalidate the law, notably because of the hysteresis effect. Diffusion of ^{36}Cl does not follow the Stocke-Einstein law, so assumptions previously cited aren't valid. Arrhenius type low fit well the experimental data as soon as the diffusion coefficient at 20°C after heating is removed. Activation energies are coherent with literature data.

Reactive transport experiments and modelling of CO_2 sequestration in deep aquifers

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Reliable estimates of the capacity and sustainability of CO_2 geological storage sites require, among other things, rigorous modeling of CO_2-rock interactions. Central issues for this purpose are the characterization of the elementary reactions involved in aqueous CO_2-mineral interactions as well as the generation of comprehensive thermodynamic and kinetic data bases describing the rates of carbonate and silicate minerals dissolution and the rate of carbonate mineral precipitation under conditions of CO_2 pressure similar to those of deep geological injection. To validate at a centimetric scale the elementary mechanisms and values of parameters generated at the microscopic scale, we have performed CO_2 reactive transport experiments in porous limestones cores (Lavoux, France) using an externally heated (up to 100°C) single-pass plug flow percolation cell operating under N_2 confining pressure up to 60 bars. Analyses of reacting solutions (calcium, alkalinity) were combined with in situ pH and permeability measurements, and XR tomography of limestone cores before and after reaction. The input solution for these experiments was injected into the mixed flow reactor at a flow rate of 0.1 mL/min using a single-piston Gilson pump.

This study presents the first experimental results obtained with this new device. The limestones cores have a porosity of 20%, and permeabilities ranging from 10 to $20\text{x}10^{-12}$ m^2. X-Ray diffraction (XRD) and optical microscopy indicated that the samples are essentially pure calcite. All experiments were performed at 25°C using 0.1 M NaCl input solutions equilibrated with a CO_2 pressure of 10 bars. The in situ measured pH of the input solution was 3.4, whereas the in situ outlet pH ranged from 7.5 to 8. The outflow solution was supersaturated with respect to calcite. The positive feedback between fluid transport and mineral dissolution causes complex reaction front morphologies such as fingers or wormholes for fluid flows of 0.1 mL/min and 10 bar of P_{CO2}.

DIAPHORE reactive transport code, developped by IFP (French Petroleum Institute) was used to model the temporal evolution of reactive surface areas, porosities and chemical composition of the oulet solutions.