

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

F. GOUTELARD, Y. CHARLES AND E. TEVISSSEN

CEA/DEN/DPC bât. 450 91191 Gif sur Yvette Cedex France

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 likely 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 $D_{IS}^{\infty} = k T / 6 \pi \eta_s r_I$ with 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 properties 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. Effective diffusion coefficient increase by a factor 3 to 5.7 and 4 to 7.5 for HTO and $^{36}\text{Cl}^-$ 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 $^{36}\text{Cl}^-$ in these 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 Stokes-Einstein law, so assumptions previously cited aren't valid. Arrhenius type law 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.