DIFFUSION OF TRITIATED WATER AND IONS THROUGH THE TOURNEMIRE ARGILLITE (FRANCE) IN PRESENCE OF ALKALINE FLUIDS

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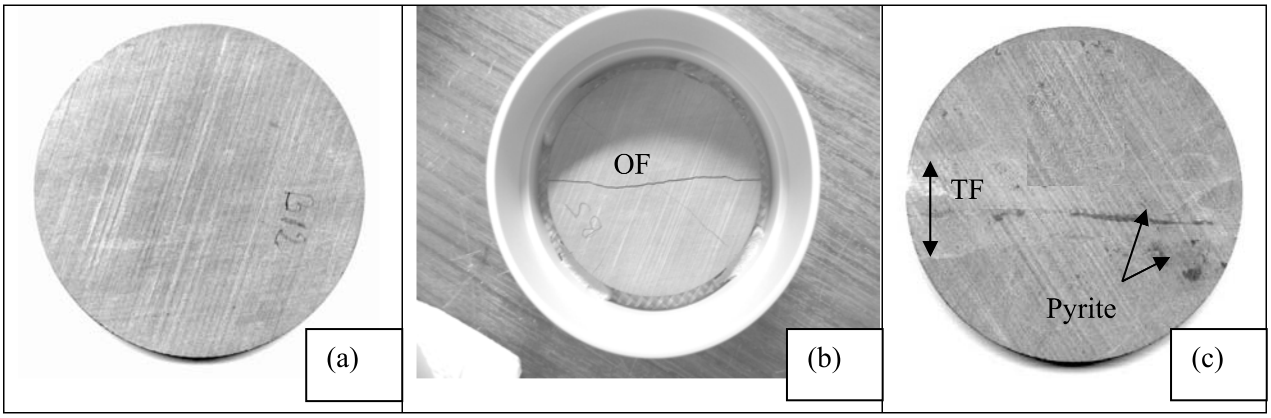
High-pH plumes arising from cementitious leachates are known to alter the mineral assemblage of clayey formations selected to play the role of natural barriers for radioactive waste repositories. Dissolution of constitutive minerals such as smectite and precipitation of secondary phases such as feldspar and zeolite have been reported [1, 2]. These mineral changes are suspected to have a significant effect upon diffusive transport properties, either enhancing or decreasing the mudrock ability for radioelement confinement. For instance, experiments performed under alkaline conditions have shown a decrease in water diffusion fluxes and an increase in cation fluxes [3].

This study was designed to provide better understanding of the phenomena that govern diffusion processes during the transition between site and alkaline conditions. Experiments involving the use of "through-diffusion" cells were performed to mimic the proceeding of an alkaline plume through different types of clayey materials from the Tournemire experimental site (France). Three kinds of sliced rock material were investigated for the diffusion of both water and major cations (sodium, potassium, calcium and magnesium): i) an unfractured sample, ii) a sample with an opened fracture and iii) a sample with a large tectonic fracture.



Photographs of sliced samples (Ø = 6.3 cm) used in the through diffusion cells and displaying: (a) no fractures; (b) an opened fracture (OF); (c) a large tectonic fracture (TF).

An equilibration procedure was required to i) (re-)saturate the rock with water and ii) force its equilibration with a synthetic solution prior to diffusion experiments. It was performed by renewed contacting of the clayey samples with the synthetic background solution every two weeks. The procedure was to be stopped when the composition of the withdrawn solution was similar to that imposed by the synthetic solution, i.e. re-equilibration between the rock and the solution was completed. Once the equilibration steps completed, tritiated water (HTO) considered as a reference species was introduced in the upstream reservoir in order to deduce the HTO diffusion coefficient through each sample. The process for alkaline water diffusions was then somewhat different from the so-called “through-diffusion” process designed to determine the transport parameters of a diffusing species in steady chemical conditions throughout the system (reservoirs + sample). In the experiments presented here, the initial solutions in the upstream and downstream reservoirs were different. Steady chemical conditions were maintained in the upstream reservoir filled with cementitious alkaline solutions (pH 13.5) while the downstream reservoir, initially filled with a synthetic site solution, was left free of any particular constraint. Hence, the composition of the downstream solution was expected to evolve until it reached that of the input alkaline solution, eventually forcing the whole system to equilibrate with it. At last, tritiated water was introduced in the upstream reservoir in order to deduce the evolution of diffusion coefficients for HTO after alkaline fluid diffusion. Microscopic investigations of the solid before and after alteration by the diffusion experiments were also performed for assessing the role of mineral alteration on diffusion processes.

Monitoring of the pH and the concentrations of the major cations showed rapid evolution in the downstream reservoirs. pH and alkaline cations concentrations increased until reaching the values prescribed by the composition of the alkaline solution. Alkaline-earth cations evolved quite differently: their concentrations drastically dropped, probably due to precipitation of carbonate phases.

Diffusion coefficients for HTO decreased of around 30% during the alkaline diffusion process. The pH and the concentrations of major cations were satisfactorily fitted by a geochemical model (PhreeqC…) that combines retention (via cation exchange on a multi-site ion exchanger), dissolution/precipitation of various phases (clays, carbonates,…) and transport (as Fick’s laws description). An evaluation of diffusion coefficients for hydroxyle and the studied cations was proposed.

No significant differences could be observed between the zones displaying no fractures or an opened fracture, showing that the discontinuities induced by the excavation works were readily sealed by the swelling property of the clayey rock when fully hydrated. The tectonic fractured- zone slice showed larger heterogeneity than the two previous samples: it was assumed that the occurrence of calcite and pyrite veins in this zone plays a role in the diffusion processes inasmuch as these minerals reduce both porosity and cation exchange capacity of the stone rock.

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