

EXPERIMENTAL EVALUATION OF A RETENTION MODEL FOR MAJOR GROUNDWATER ELEMENTS ON THE TOURNEMIRE ARGILLITE

P. Jacquier¹, C. Beaucaire¹, A.L. Vuillaume², Ch. Wittebroodt², J. Ly¹, J. Page¹, S. Savoye², H. Pitsch²

1. CEA – Commissariat à l’Energie Atomique, Saclay, DEN/DANS/DPC/SECR/L3MR, Bât. 450, 91191 Gif-sur-Yvette, France (philippe.jacquier@cea.fr, catherine.beaucaire@cea.fr, jacques.ly@cea.fr, jacques.page@cea.fr)
2. IRSN - Institut de Radioprotection et de Sécurité Nucléaire, BP n°17, 92262 Fontenay-aux-roses, France (charles.wittebroodt@irsn.fr, sebastien.savoye@irsn.fr, helmut.pitsch@irsn.fr)

Introduction

This work deals with the behaviour of Tournemire argillite towards major elements. Rock samples come from the IRSN Tournemire experimental facility, located in Aveyron, Southern France. Their “intrinsic” ion-exchange properties, i.e. the concentrations of the different types of adsorption sites and the associated selectivity coefficients for H, Na, K, Ca and Mg were previously determined (Jacquier et al., 2004). This set of data constitutes a retention model which enables to describe the behaviour of major cations and H⁺ during water-rock interaction. The objective of the present study is to estimate the robustness of this model by comparing experimental data derived from several types of leaching experiments carried out on Tournemire samples with the corresponding calculated data.

Experimental concept

The occurrence of pyrite in the argillite led us to adopt two types of experimental protocols, since pyrite oxidation may drastically change the chemistry of leachates by producing a large amount of sulphate and decreasing pH. So, the first approach consisted in carrying out leaching experiments in a glove box with very low oxygen content (~1 ppm of O₂) in order to limit oxidation disturbances as much as possible. CO₂ partial pressure was also fixed at a value close to 10^{-2.4} atm which is assumed to meet the *in situ* condition (Beaucaire et al., 2007).

Conversely, in the second approach, the O₂ content of the glove box atmosphere was fixed close to 1000 ppm in order to estimate the effect of an oxidising disturbance on the leachate chemistry. In this case, CO₂ was not injected into the glove box, allowing pCO₂ to evolve freely.

In both protocols, four solid/liquid ratios, i.e. 0.04, 0.25, 0.6 and 1 g/g were investigated in order to cover a large range of chemical conditions. The concentrations of major dissolved cations (Na⁺, K⁺, Ca²⁺, Mg²⁺) and anions (Cl⁻, SO₄²⁻, HCO₃⁻/CO₃²⁻) were monitored at several times’ steps, i.e. 24 hours, 7 and 21 days. The adsorbed cationic populations on the argillite samples were also determined by cation displacement with Ni-ethylenediamine.

Results and modelling

Among the elements monitored during these experiments, different behaviours may be distinguished:

- Cl behaves as a mobile element, meaning that it is not controlled by an equilibrium with secondary minerals. In such leaching experiments, mobile elements diffuse out of the matrix porosity and their concentrations in the external fluid increase in proportion to the solid/liquid ratio. The case of SO₄ is more complex because, in sedimentary rocks, at least three different reservoirs exist: matrix porosity, sulphide- and sulphate-bearing minerals. In the present study, the SO₄ behaviour cannot be accounted for by considering a single source;

- Ca and Mg are quickly constrained by carbonates, regardless of the liquid/solid ratio;
- other elements such as Na and K are released in solution following the ion-exchange equilibria with surface minerals.

Finally, it is possible to compare the measured concentrations of major elements in the leachates with theoretical concentrations derived from the ion exchange properties of the rock and the dissolution precipitation equilibria of selected mineral phases like carbonates. Calculated concentrations are generally in good agreement with measured ones, whatever the amount of oxygen and even when the partial pressure of CO₂ is not fixed (See for example figure 1). So, we can consider that the retention model built up for the Tournemire argillite is sufficiently robust to describe the chemical reactivity of the argillite. Therefore, it is possible to calculate the chemical composition of the pore-water present in the Tournemire argillite in “equilibrium” conditions, as well as the composition of fluids resulting, for example, from an oxidizing disturbance.

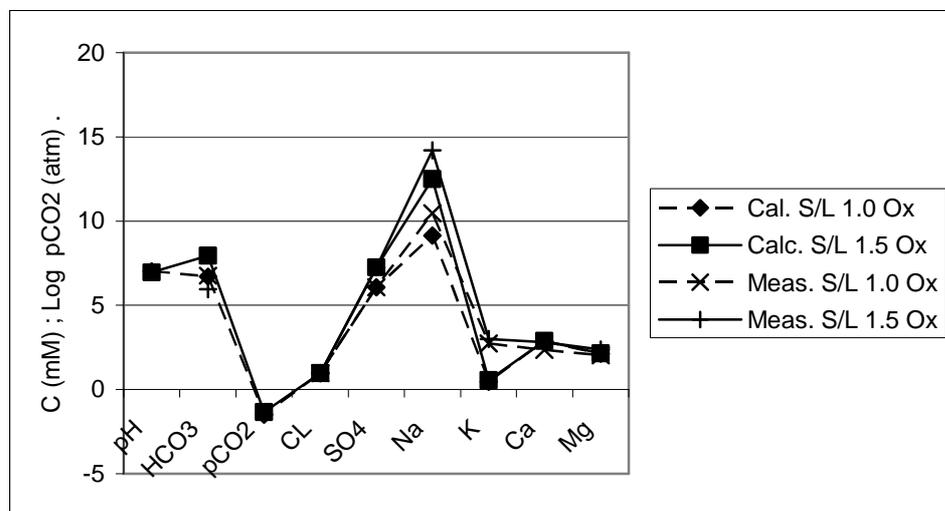


Figure 1: Comparison of calculated concentrations with measured ones in leaching experiment, with O₂ ~ 1000 ppm and pCO₂ not fixed, for two solid/liquid ratios (1.0 and 1.5 g/ml).

References

- Jacquier P., Ly J. and Beaucaire C. (2004): The ion-exchange properties of the Tournemire argillite I - Study of the H, Na, K, Cs, Ca & Mg behaviour. *Applied Clay Science* 26, 163-170.
- Beaucaire C., Michelot J.-L., Savoye S. and Cabrera J. (2007): Groundwater characterization and modelling of water-rock equilibria in the argillaceous formation of Tournemire (Aveyron, France). Submitted to *Applied Geochemistry*.