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Acquisition of anion profiles and diffusion coefficients in the Opalinus Clay at the Mont Terri rock laboratory (Switzerland)

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Abstract

Chloride, bromide and sulphate concentration profiles have been analysed through the Opalinus Clay of Mont Terri in the framework of the Deep Borehole Experiment. Aqueous leaching and out diffusion experiments were carried out to acquire anion concentrations and estimate pore diffusion coefficients. Out diffusion technique gave consistent values of chloride and bromide compared to the concentration profiles acquired so far at the tunnel level of the Mont Terri rock laboratory. Concentrations acquired by leaching experiments show a maximum chloride concentration of 16.1 ± 1.7 g/l at the basal part of Opalinus Clay which is higher than the value of 14.4 ± 1.4 g/l obtained by out diffusion at the same level. This excess of chloride is likely due to dissolution of Cl⁻ bearing minerals or release of Cl initially contained in inaccessible porosity. Bromide to chloride ratios are virtually the same as that of seawater, whereas sulphate to chloride ratios are significantly higher. Those latter are probably due to pyrite oxidation and dissolution of sulphate-bearing minerals occurring during sample collection and preparation. An anisotropy ratio of 2.4 was estimated for pore diffusion coefficient in the Opalinus Clay sandy facies.

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Keywords: Opalinus Clay; chloride; sulphate; bromide; diffusion coefficient

1. Background

The Deep Borehole experiment at the Mont Terri underground rock laboratory (Switzerland) gives the opportunity to evaluate, in a hydraulically undisturbed zone, the properties and processes that define the Opalinus Clay as a confining unit. The goal of the experiment is to develop and validate a methodology for assessing the

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containment properties of a thick argillaceous unit using the Opalinus Clay as an example. The experiment is based on the drilling of a 247.5 m long 45° inclined borehole (BDB-1) crossing the Opalinus Clay and its adjacent formations. The whole borehole was cored and drillcores were collected as quickly as possible after extraction. The acquisition of porewater geochemistry is a first step to model water and solutes fluxes across the formation. Indeed, porewater composition is an essential input parameter in transport models as fluid is the vector of potential radionuclide migration from a deep geological repository to its adjacent aquifers. Low permeability (10^{-15} to 10^{-12} m/s) and low gravimetric water content (3 to 6%) in clay media make it difficult to extract porewater by conventional methods such as pumping. Porewater extraction processes based on physical or chemical extraction include centrifugation, squeezing, leaching, advective displacement and diffusive equilibration¹. Geochemical modelling is an indirect approach to obtain the porewater composition by considering it as the result of water-rock interactions. The characterization of the geochemical system is based on selected properties of the rock and the solution: mineralogy, petrology, cation exchange properties, accessible porosity, mobile anions concentrations, and CO₂ partial pressure. This paper presents the acquisition of anions concentrations (Cl⁻, Br⁻, SO₄²⁻) as well as diffusive transport parameters provided by aqueous leaching and out diffusion experiments.

2. Material and methods

The rock sequence crossed by the borehole comprises four units. The top unit (Hauptrogenstein) consists in Dogger limestone (~37 m thick) and is followed by the Passwang Formation (~ 69 m thick) made of marls and limestones. The Opalinus Clay (~ 132 m thick) is a clayrock that can be subdivided into different facies (sandy, shaly and carbonate-rich sandy facies). BDB-1 borehole terminates in the topmost layers of the Liassic Staffelegg formation (~ 9 m thick) characterised by heterogeneous clay-rich rocks and sandstones. Core samples taken every 10 m along the borehole were sent to the IRSN laboratory for petrophysical, mineralogical and geochemical analysis.

Two methods were applied to acquire the halide profile along the BDB-1 borehole: aqueous leaching and out diffusion. Chloride, bromide and sulphate contents were determined by ionic chromatography using a Metrohm Advanced Compact IC 861 with an accuracy of 10%. Porewater concentrations were deduced from measured test solution concentrations using mass balance equations and assuming an anion accessible porosity of 55% of the water accessible porosity within the argillaceous formation^{2,4}. Aqueous leaching was carried out under N₂ in a glovebox, by diluting pore water solutes contained in powdered rock sample (< 100 µm) into milliQ water at a solid/liquid ratio of 0.5 for 2 h. Out diffusion experiments were performed at ambient conditions by immersing cuboid-shaped samples obtained with a diamond wire saw into synthetic solutions (NaHCO₃ added to milliQ water). Test solutions were regularly sampled until reaching a concentration equilibrium state.

Water contents were recalculated from laboratory measurements (weighing, drying, density measurements) considering a full saturation state for all samples. This correction was implemented due to the fact that desaturation of samples during core drilling and sample handling can lead to an overestimation of calculated porewater concentrations. In addition to the determination of porewater contents, out diffusion enabled to give rough estimates of the pore diffusion coefficient by modelling the experiment with a transport code (HYTEC⁵ in this study).

3. Results and discussion

3.1. Chloride, bromide and sulphate profiles

Calculated porewater concentrations obtained from aqueous leaching and out diffusion are reported in Figure 1, along with the values extrapolated from² for chloride and formerly acquired at the tunnel level. Chloride and bromide values obtained by aqueous leaching are systematically higher compared to out diffusion results though the two methods reveal a similar curved profiles with increasing chlorinity towards the basal part of Opalinus Clay (up to 16.1 g/l). Previous studies also concluded to maximum values for chloride content (from 13.6 to 14.4 g/l) found at the limit between the Opalinus Clay and the Staffelegg formation. Higher values of halides given by aqueous leaching compared to out diffusion are likely due to mineral dissolution or release of elements initially contained in unaccessible porosity. Out diffusion results for halides are consistent with those acquired so far at the Mont Terri tunnel level. Sulphate profiles (Fig. 1c) show very high concentrations, especially for out diffusion experiments

which were conducted in ambient conditions. Artificial increase of sulphate contents can be induced by artefacts linked to experimental procedures: pyrite oxidation during the sample preparation or equilibration process, and dissolution of sulphate-bearing minerals such as gypsum or celestite^{2,4}.

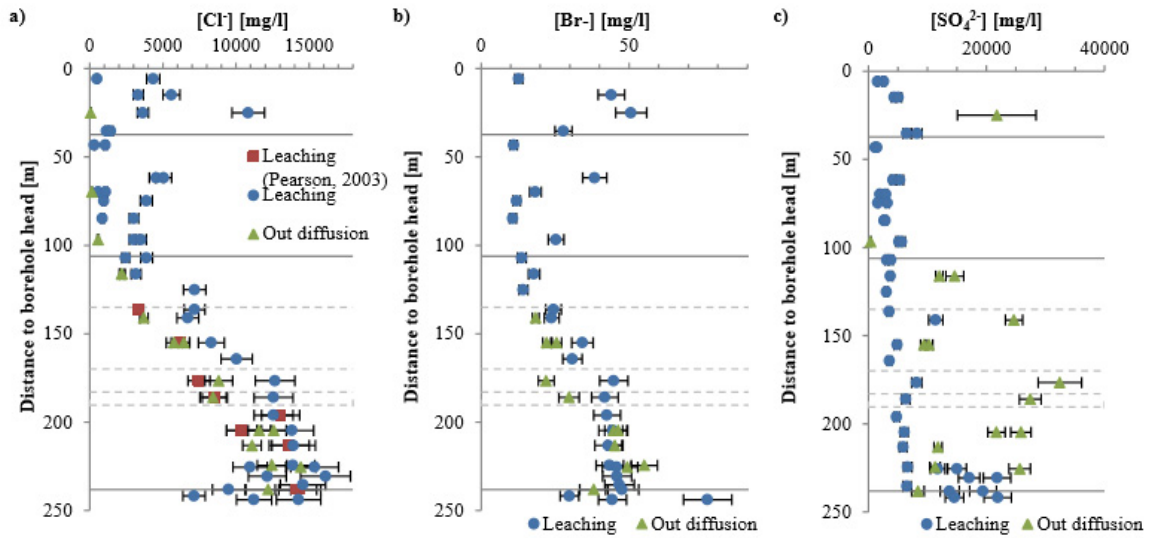


Fig. 1. Anion profiles acquired by leaching and out diffusion experiments for (a) chloride, compared to extrapolated leachate values from² obtained at the tunnel level; (b) bromide; and (c) sulphate.

The halide concentration ratios are consistent with a marine origin of the Opalinus clay porewater (Fig. 2). Sulphates being most probably a reactive solute in our experimental setup, sulphate to chloride ratios are considerably higher than that of seawater.

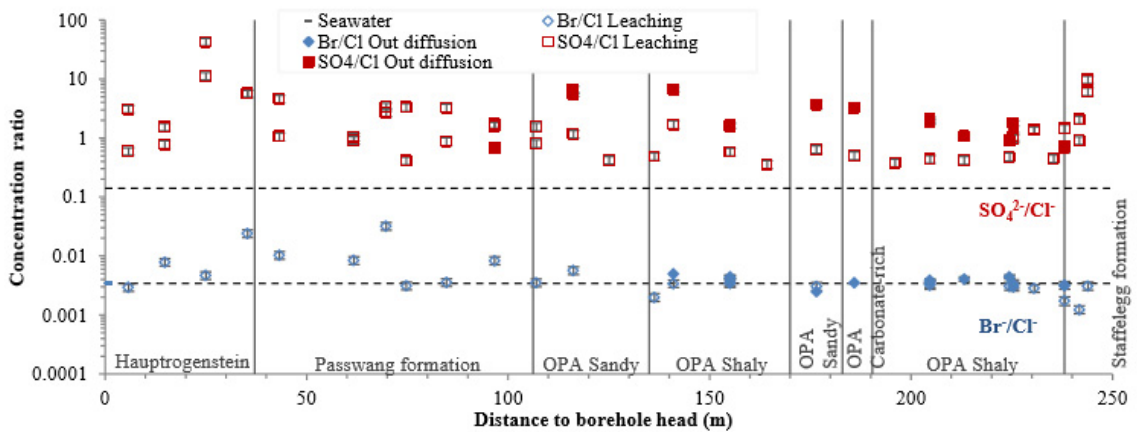


Fig. 2. Anion concentration ratios acquired by leaching and out diffusion experiments as a function of distance to BDB-1 borehole head and compared to marine ratios.

3.2. Pore diffusion coefficients

Out diffusion experiments were modelled using the transport code HYTEC and assuming that diffusion is dominating the solutes transport through the rock samples. Sample swelling prevented the possibility to get proper

values of diffusion coefficients for each of the tested samples. Estimated pore diffusion coefficients for chloride in a sandy facies of the Opalinus Clay are presented in Figure 3. With an imposed accessible porosity of 5.4%, pore diffusion coefficients were respectively estimated to $5 \cdot 10^{-10}$ m²/s and $1.2 \cdot 10^{-9}$ m²/s for diffusion perpendicular and parallel to bedding. These values correspond to an anisotropy ratio of 2.4, which is lower than the value of 4 reported by⁶. The discrepancy could be due to sample heterogeneity or different experimental procedures, added to uncertainties due to cracks induced by sample unconfining and swelling.

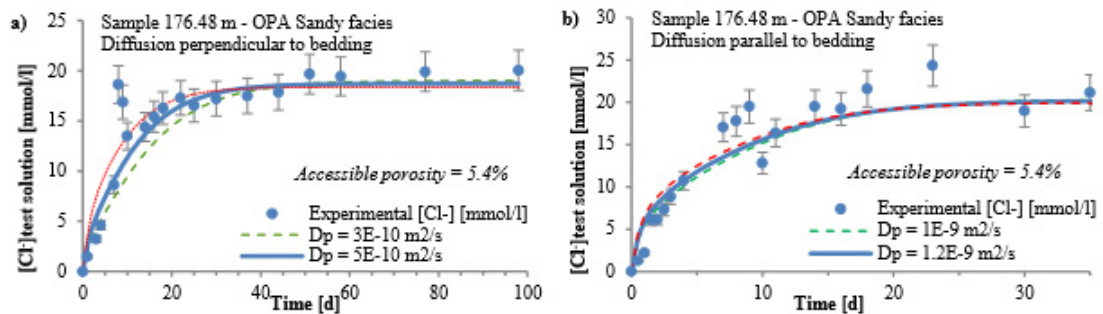


Fig. 3. Model fits of estimated pore diffusion coefficient for chloride based on the time series obtained during the out diffusion experiment on a sample located in the sandy facies of Opalinus Clay. (a) Diffusion perpendicular to bedding; (b) diffusion parallel to bedding. Best fits are represented by thick blue lines.

4. Conclusions

Concentrations acquired by leaching experiments are higher than the ones obtained by out diffusion with a maximum chloride concentration of 16.1 ± 1.7 g/l at the basal part of the Opalinus Clay. Bromide to chloride ratios are virtually the same as that of seawater, whereas sulphate to chloride ratios are significantly higher, probably due to pyrite oxidation and dissolution of sulphate-bearing minerals. A low anisotropy ratio of 2.4 was estimated for pore diffusion coefficient in the sandy facies of Opalinus Clay.

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