Available online at www.sciencedirect.com

ScienceDirect

Procedia Earth and Planetary Science 17 (2017) 57 – 60

Procedia
Earth and Planetary Science

15th Water-Rock Interaction International Symposium, WRI-15

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

Catherine Yu[a,b,1], Jean-Michel Matray[a]

[a]*IRSN, BP17 – 92262 Fontenay-aux-Roses Cedex, France*
[b]*Aix Marseille Université UMR 6635 CEREGE, BP80 F13545 Aix-en-Provence Cedex 4, France*

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 unaccessible 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.

Peer-review under responsibility of the organizing committee of WRI-15
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

* Corresponding author. Tel.: +33-(0)15-835-8603; fax: +33-(0)14-657-6258.
E-mail address: catherine.jiyu@irsn.fr

Peer-review under responsibility of the organizing committee of WRI-15
doi:10.1016/j.proeps.2016.12.029

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 equilibration[1]. 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 CO_2 partial pressure. This paper presents the acquisition of anions concentrations (Cl^-, Br^-, SO_4^{2-}) 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 N_2 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 ($NaHCO_3$ 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 (HYTEC[5] 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 from[2] 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