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Contribution of the diffusive exchange method to the characterization of pore-water in consolidated argillaceous rocks

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Abstract

Consolidated argillaceous rocks, potential host rocks for nuclear waste disposal, display particular properties (low water content, very small pore size) that require specific methods, especially for the characterization of their pore-water. The diffusive exchange method was applied to the claystone of Tournemire by taking into account the effect of swelling or micro-cracks induced by drilling. The good agreement of diffusion parameters with those obtained from the through-diffusion method showed that the extent of this disturbance was low. This method led to stable isotope content values in pore-water in good agreement with those measured in the fracture fluids located in the vicinity, validating the method. On the contrary, the vacuum distillation technique gave a systematic depletion in heavy isotopes of water, probably induced by an incomplete extraction of pore-water. For the chloride tracer, the determination of the accessible porosity on each sample allowed the estimate of chloride concentration of pore-water to be improved, by taking into account all the petrophysical heterogeneities.

Keywords: Argillite; Diffusion; Chloride; Stable isotopes

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1. Introduction

One of the very few methods that can provide information about fluid flow and solute transport in porous media with low hydraulic conductivities and water content is based on the study of

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natural-tracer distribution (in particular ^{18}O, ^{2}H and Cl^{-}) in pore-water (Toulhoat et al., 1996; Hendry and Wassenaar, 1999; Harrington et al., 2001). Such an approach was applied to consolidated argillaceous formations (e.g. Opalinus clay, Tournemire Toarcian shales) that are studied for the feasibility of deep radioactive-waste disposal. Interpretations of natural-tracer profiles in such media generally led to consider diffusion as the main mechanism (e.g., Rübel et al., 2002; Patriarche et al., 2004b). In this case, tracer profiles represent the result of large-scale (some hundred meters) and long-term (several millions years) natural experiments. They complement diffusion experiments performed in laboratories (Rebour et al., 1997; Van Loon et al., 2003a, 2004a; Melkior et al., 2005) or underground facilities (Palut et al., 2003; Van Loon et al., 2004b). In laboratories, a through-diffusion method requires samples with thickness less than 1 cm (Boving and Grathwohl, 2001; Van Loon et al., 2003b) while in underground facilities such as Mont Terri, penetration depth of the quickest artificial tracers (tritiated water) did not exceed 1 m after one year (Palut et al., 2003; Wersin et al., 2004). The understanding of natural-tracer profiles is essential for the upscaling of these laboratory experiments. They can bring important information about long-term transport process, required for performance assessment.

However, the particular properties of consolidated argillaceous rocks (very low water content, 2% to 5% by wet weight for Tournemire shales; the small pore size, few nm; and the charged clay surfaces) make the determination of tracer concentrations in pore-water difficult (see Sacchi et al., 2001). For instance, Moreau-Le Golvan et al. (1997) evaluated, the vacuum distillation technique which is widely used to determine the stable isotope content of pore-water on Tournemire shale samples. They showed that water extraction is influenced by temperature, sample grain sizes, and by the time that a crushed sample is in contact with the atmosphere. They concluded that these parameters might have a significant influence, especially on the ^{18}O content of extracted water. Rübel et al. (2002) showed from a study on Opalinus clay samples, that the distillation technique induces a systematic depletion in heavy isotopes with regard to a vapour exchange equilibration method.

The determination of the chloride concentration of pore-water also poses problems, especially with regard to the localisation of the chloride reservoirs in rock, their accessibility, and the estimation of the chloride-accessible porosity. In a study on Tournemire shales, Patriarche et al. (2004a) found that the amount of extracted chloride always corresponded to less than 20% of the total chlorine concentration of rock, whatever the method they used (leaching, diffusion). It also depended on the sample grain size, especially for the leaching method. The authors suggested that different reservoirs of chloride, more or less accessible, exist in the rock and can be located (1) in some pores enclosing water with high chloride concentration, (2) in the vicinity of cation compensation sites, near argillaceous layers and (3) mainly in some minerals (apatite, fluid inclusions in carbonates). Thus, the very low efficiencies of leaching and diffusion experiments could be explained considering that most of chlorine is fixed into minerals, and only dissolved chloride is able to diffuse. The determination of the chloride concentration of pore-water from the amount of extracted chloride also requires the knowledge of the chloride-accessible porosity, called “geochemical porosity” by Pearson (1999). This porosity is lower than total porosity, due to the anionic exclusion mechanism, which is enhanced in argillaceous media where pores are very small and negative charges on clay surfaces tend to repulse anions (Bolt, 1982). The value of chloride-accessible porosity is generally either not considered in the calculations (Motellier et al., 2003; Gaucher et al., 2004) or derived from an indirect determination, increasing the uncertainty on the chloride concentration estimates (Patriarche et al., 2004a).

Unlike other methods, such as vacuum distillation, vapour exchange equilibration, leaching, squeezing or core degassing, the determination of natural-tracer contents from the diffusive