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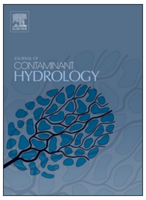

Effect of confining pressure on diffusion coefficients in clay-rich, low-permeability sedimentary rocks

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ABSTRACT

The effect of confining pressure (CP) on the diffusion of tritiated-water (HTO) and iodide (I^-) tracers through Ordovician rocks from the Michigan Basin, southwestern Ontario, Canada, and Opalinus Clay from Schlattingen, Switzerland was investigated in laboratory experiments. Four samples representing different formations and lithologies in the Michigan Basin were studied: Queenston Formation shale, Georgian Bay Formation shale, Cobourg Formation limestone and Cobourg Formation argillaceous limestone. Estimated in situ vertical stresses at the depths from which the samples were retrieved range from 12.0 to 17.4 MPa (Michigan Basin) and from 21 to 23 MPa (Opalinus Clay). Effective diffusion coefficients (D_e) were determined in through-diffusion experiments. With HTO tracer, applying CP resulted in decreases in D_e of 12.5% for the Queenston Formation shale ($CP_{max} = 12$ MPa), 30% for the Georgian Bay Formation shale (15 MPa), 34% for the Cobourg Formation limestone (17.4 MPa), 31% for the Cobourg Formation argillaceous limestone (17.4 MPa) and 43–46% for the Opalinus Clay (15 MPa). Decreases in D_e were larger for the I^- tracer: 13.8% for the Queenston shale, 42% for the Georgian Bay shale, 50% for the Cobourg Formation limestone, 55% for the Cobourg Formation argillaceous limestone and 63–68% for the Opalinus Clay. The tracer-specific nature of the response is attributed to an increasing influence of anion exclusion as the pore size decreases at higher CP.

Results from the shales (including Opalinus Clay) indicate that the pressure effect on D_e can be represented by a linear relationship between D_e and ln(CP), which provides valuable predictive capability. The nonlinearity results in a relatively small change in D_e at high CP, suggesting that it is not necessary to apply the exact in situ pressure conditions in order to obtain a good estimate of the in situ diffusion coefficient. Most importantly, the CP effect on shale is reversible (± 12%) suggesting that, for argillaceous rocks, it is possible to obtain D_e values that are representative of the in-situ condition by conducting measurements on re-pressurized samples that were obtained with standard drilling practices. This may not be the case for brittle rock samples as the results from limestone suggest that irreversible damage occurred during the pressure cycling.

1. Introduction

Studies targeted at the quantification of contaminant transport across deep geological formations such as shales and limestones require knowledge of the pertinent transport parameters, such as diffusion coefficients, at depth. The question arises whether measurements performed under laboratory conditions are representative of the in-situ values and to what degree effects from changes in the pore architecture due to stress relaxation, drilling/sample preparation or partial desaturation are reversible. In-situ determinations of effective diffusion coefficients (D_e) and tracer-accessible porosities (ϕ) of HTO, Cl^- and I^- were performed in Opalinus Clay of the Mont Terri Underground Rock Laboratory in northwestern Switzerland at a depth of 250–300 m below surface. The obtained values are compatible with laboratory determinations within error (Gimmi et al., 2014; Tevissen et al., 2004; Van Loon et al., 2004a; Wersin et al., 2004, 2008), suggesting that laboratory experiments with applied confining pressures similar to the in situ conditions are an effective alternative to in situ experiments. In contrast, Hendry et al. (2009) reported a slightly higher average D_e value from laboratory experiments under confining pressure (CP) than at field scale for a clay-rich medium, and attributed the difference to sample swelling. Further, Van Loon et al. (2003a, 2003b) conducted laboratory studies targeted at the effect of CP on D_e in the Opalinus Clay using tritiated water (HTO) and anionic halide (Cl^- and I^-) tracers with the through-diffusion (TD) method. They reported decreases in D_e of 17–30% with a pressure increase from 1 to 5 MPa for samples of the Opalinus Clay from the Mont Terri laboratory, and decreases in D_e of 16–32% over a CP range from 4 to 15 MPa for the Opalinus Clay from

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Benken (northeastern Switzerland, depth 550–650 m). In both cases greater decreases were reported for anionic tracers compared to HTO.

Similar to the Opalinus Clay in Switzerland, the Upper Ordovician shales (Queenston and Georgian Bay formations) and the underlying Cobourg Formation argillaceous limestone in the Michigan Basin of southwest Ontario, Canada, are under consideration as the host or confining units for a Deep Geological Repository (DGR) for low- and intermediate-level radioactive waste. The proposed repository would be located at the Bruce nuclear site where the upper Ordovician units occur at depth of 450–680 m below ground surface. The stratigraphy and hydrostratigraphy of Paleozoic rocks at the Bruce nuclear site are described by Beauheim et al. (2014), who conducted detailed hydraulic testing in boreholes, demonstrating that the horizontal hydraulic conductivity (K) of Upper Ordovician shale and limestone at the site is very low, ranging from 2×10^{-16} to 2×10^{-10} m/s. Diffusion measurements have been reported for the upper Ordovician units (Al et al., 2010, 2012, 2015; Cavé et al., 2009; Xiang et al., 2013), but these were conducted at ambient laboratory pressure and the reported D_e values may overestimate the in-situ values.

The main objectives of this study were to determine the magnitude and reversibility of the confining pressure effect on D_e for a variety of sedimentary rock samples of differing lithology within the Michigan Basin in Canada, and for the Opalinus Clay from the Schlattingen borehole in northeastern Switzerland (for reference see Al et al., 2015; Clark et al., 2013; Mazurek et al., 2015; Wersin et al., 2013).

2. Materials and methods

2.1. Sample descriptions

2.1.1. Michigan Basin samples

The rock cores were obtained during a drilling and coring program through an 860 m thick sedimentary sequence at the Bruce nuclear site on the eastern flank of the intracratonic Michigan Basin, near Tiverton, Ontario (Intera, 2011). Drilling, sampling and preservation methods were designed to minimize alteration of porewater composition and physical disturbance of the core (Briscoe et al., 2010; Pinder, 2009; Sterling, 2010). The samples used in this study were prepared from drill core segments sampled from boreholes DGR2 and DGR3, approximately 1 km apart. The 76 mm diameter rock cores were preserved by vacuum-sealing, first in plastic bags, and then in aluminum-lined plastic bags, immediately (10–45 min) after drill core retrieval. They were shipped to the laboratory in coolers with ice packs (Briscoe et al., 2010; Sterling, 2010). Four rock types were selected for this study: Queenston Formation shale, Georgian Bay Formation shale, Cobourg Formation limestone and Cobourg Formation argillaceous limestone. The rock samples are from between 472 and 682 m below ground surface, with estimated vertical in situ stress of 12.0 to 17.4 MPa (Table 1). The lithology and mineralogy of these geologic units were described in Xiang et al. (2013) and Koroleva et al. (2009). Data for the uniaxial compressive strength (UCS) perpendicular to the bedding plane (Gorski et al., 2009, 2011) and elastic modulus (NWMO, 2011) are presented in Table 1.

Four diffusion samples were prepared for use in this study from segments that had been preserved as described above and stored in a refrigerator for approximately two years after they were drilled. Individual samples were prepared from the Queenston (DGR3-472.56) and the Georgian Bay shales (DGR2-593.53), and two from the Cobourg Formation but these are not considered duplicates because one (DGR3-682-1) was selectively cut from limestone and a second (DGR3-682-2) was cut from argillaceous limestone (Table 1). In order to avoid damage from swelling, samples from the Queenston and Georgian Bay shales were drilled with air. Limestone and argillaceous limestone samples were drilled with water.

2.1.2. Opalinus Clay

The Opalinus Clay samples were collected from a borehole at Schlattingen in northeastern Switzerland (Mazurek et al., 2015; Wersin et al., 2013). The 102 mm diameter core segments were 100–150 mm long. They were vacuum-sealed in plastic bags and then in aluminum-lined plastic bags and shipped to the laboratory in coolers with ice packs. Samples SLA-857.80 and SLA-929.22 are grey shales with well-defined, mm-scale light to dark grey layering parallel to the bedding plane. The clay content, UCS (perpendicular to bedding plane) and elastic moduli presented in Table 1 are based on reported values from the Opalinus Clay with burial depths between 400 and 900 m, including samples from Benken and Schlattingen (Giger and Marschall, 2014). In comparison to the Michigan Basin samples, Opalinus Clay has a higher proportion of smectite (invariably as illite/smectite mixed layers). Therefore, the Opalinus Clay samples swell and disintegrate in

Table 1
Sample descriptions and in situ vertical pressures.

Sample ID	DGR3-472.56	DGR2-593.53	DGR3-682-1	DGR3-682-2	SLA-857.80	SLA-929.22
Formation	Queenston	Georgian Bay	Cobourg	Cobourg	Opalinus Clay	Opalinus Clay
Lithologic type	Red shale	Grey shale	Limestone	Arg. limestone	Grey shale	Grey shale
Depth (m)[a]	472.56	593.53	681.89	681.99	857.80	929.22
In situ vertical stress (MPa)[b]	12.0	15.1	17.4	17.4	21.2	23.0
Minimum CP (MPa)	0.6	0.6	0.6	0.6	0.25	0.25
Maximum CP (MPa)	12	15	17.4	17.4	15	15
Mineralogy (wt%)[c]						
Illite	39	40	–	9	13	12
Ill/smectite					27	25
Chlorite	10	19	–	2	5	4
Kaolinite	–	–	–	–	15	14
Calcite + dolomite	39	21	–	85	15	12
Quartz	10	16	–	3	21	20
Porosity (−)[d]	0.086	0.092	0.013	0.013	0.116	0.110
UCS (MPa)[e]	44	35	72	72	31	31
Elastic modulus (GPa)[e]	15	9	32	32	9	9

[a] Depth below ground surface measured to the centre of the 20–30 cm long core segments.

[b] Estimated using bulk wet density of 2.6 g/cm^3 for Michigan Basin (Gorski et al., 2009) and 2.52 g/cm^3 for Opalinus Clay samples (Giger and Marschall, 2014).

[c] Data reported in Koroleva et al. (2009) for adjacent, but representative samples from the Michigan Basin. Data for Opalinus Clay samples from Wersin et al. (2016).

[d] Porosity determined gravimetrically with drying at 105 °C.

[e] Data for uniaxial compressive strength, normal to bedding, and elastic modulus are from Gorski et al. (2009, 2011) and NWMO (2011) respectively for Michigan Basin formations; data for Opalinus Clay from Benken and Schlattingen (depth from 400 and 900 m) are from Giger and Marschall (2014). The reported values do not account for cm-scale variations in mineralogy such as those that distinguish Cobourg limestone from Cobourg argillaceous limestone.