

A comparative anion diffusion study on different argillaceous, low permeability sedimentary rocks with various pore waters

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ARTICLE INFO

Handling Editor: S. Stroes-Gascoyne

Keywords:

Clay

Porosity

Blue Mountain Fm

Queenston Fm

Ionic strength

ABSTRACT

Through-diffusion experiments with tritiated water (HTO) and $^{36}\text{Cl}^-$ as a function of pore water concentration (0.01–5 M) were performed on two Ordovician-age argillaceous rock samples from the Blue Mountain Fm and Queenston Fm shales of the Paleozoic intracratonic Michigan Basin in Canada. This study reveals that the effect of ionic strength on the anion-transport porosity is similar, and only the minimal anion excluded porosity is higher in the Blue Mountain Fm shale. The differences in rock sample mineralogy cannot explain this effect. It is hypothesized that the structure of the Blue Mountain Fm shale samples has led to pore space openings sufficiently small that they behave as interlayers. Such pores are defined as interlayer equivalent (ILE) pores. These ILE pores, as in the case of interlayer pores, can act to permanently limit the anion-accessible porosity. Pore-size distribution measurements provide further evidence of increased potential for ILE pores within the Blue Mountain Fm samples. A Donnan model, which includes consideration of both ILE and uncharged pores, is shown to describe the effect of molar concentration on the anion-accessible porosity in the argillaceous rocks investigated.

1. Introduction

Investigation of the transport properties of argillaceous rocks is an important research activity in the field of nuclear waste management, as such rock types are considered by many countries to have great potential as host materials for deep geologic repositories for radioactive waste. Safety analyses, targeted at the quantification of contaminant transport across deep geological formations, such as argillaceous rocks, require knowledge of the pertinent transport parameters (e.g., diffusion coefficients, anion-accessible porosity). These parameters depend on the mineralogy, microstructure and pore-water chemistry of the clay formation (Van Loon et al., 2004; Appelo et al., 2008; Houben et al., 2013; Xiang et al., 2013, 2016; Al et al., 2015). For neutral and positively-charged chemical species, the whole pore space of an argillaceous rock is available for transport (Altmann et al., 2012). In contrast, argillaceous rocks consist of clay particles composed of sheet silicates, which are negatively charged at their surfaces. Anions in the aqueous solution are repulsed by the negatively-charged clay mineral surfaces and, thus, are excluded from a portion of the pore space (Bolt and de Haan, 1979). Hence, the entire pore space of an argillaceous rock is not actually available for anion transport, i.e., the anion-accessible porosity is smaller than the total porosity (Muurinen, 1994). This effect is well

known as anion exclusion in soil and clay science (Van Loon et al., 2007).

The anion-exclusion effect depends on the extent of the electric double layer (Plecis et al., 2005; Wigger and Van Loon, 2017b). The electric double layer (EDL) occurs in the interface between the clay mineral surface and the pore solution, consisting of the permanent negatively-charged clay surface and the cations in the pore solution that balance the negative charge. It consists of a Stern layer, devoid of anions, and a diffuse layer, where the concentration of anions is lower than that of cations (Chagneau et al., 2015; Tournassat et al., 2016). The nature and properties of such layers are highly dependent on the type of clay mineral and the chemistry of the pore water. Previous experiments have demonstrated an increase of the anion-accessible porosity associated with increasing ionic strength (Muurinen et al., 1988; Muurinen, 1994; Lehtikoinen et al., 1995; Riebe and Bors, 2001; Leroy et al., 2006; Muurinen et al., 2007; Glaus et al., 2010; Tachi and Yotsuji, 2014; Wigger and Van Loon, 2017b). This observation is described by the Gouy-Chapman theory, where the charge distribution of ions is modelled as a function of distance from the clay surface using applied Maxwell-Boltzmann statistics. It shows that the electric potential decreases exponentially away from the surface (Schofield, 1947; Edwards et al., 1965; Bolt and de Haan, 1979; Wersin et al., 2008) and

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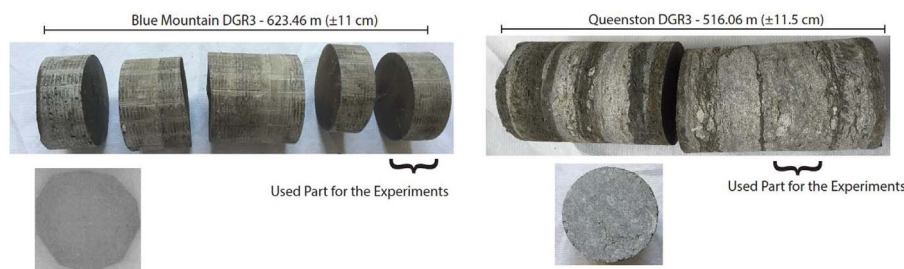


Fig. 1. Core photos representing the homogeneous Blue Mountain Fm sample (DGR3 – 623.46) and the heterogeneous Queenston Fm sample (DGR3 – 516.06).

the shielding-length, called the Debye length, varies with ionic strength (Appelo and Postma, 2005).

This study investigated the effect of different molar concentrations on the anion-transport porosity in two argillaceous, low-permeability sedimentary rocks from southern Ontario, Canada, using a well-established through-diffusion technique (Van Loon et al., 2003a,b, Van Loon and Mibus, 2015). The aim of this investigation is to obtain a better understanding of the anion-exclusion effect, and its dependence on molar concentrations, in such rock types.

2. Materials and methods

2.1. Sample description

Two different rock samples originating from Canada were used for this study: Blue Mountain Formation shale and fossiliferous, argillaceous limestone from the Queenston Formation (Fig. 1). The Queenston Fm sample was collected from a depth of 516.06 m, while the Blue Mountain Fm sample was collected at 623.46 m. The Blue Mountain Formation is very fine-grained and dark grey-green to black, soft, non-calcareous shale. The Queenston Formation is a red to maroon and green shale with 0.01 m–0.1 m thick interbeds of grey to dark grey, fossiliferous, very hard grey/blue carbonates (Armstrong and Carter, 2006). The mineralogy of the samples used in this study, as well as important physical properties, are summarized in Table 1.

Table 1

Mineralogy and physico-chemical properties of the Blue Mountain Fm and Queenston Fm samples.

Parameters	Blue Mountain Fm	Queenston Fm
Sample	DGR3-623.46	DGR3-516.06
Grain density [kg/dm ³]	2.67 ± 0.002	2.76 ± 0.001
Bulk dry density [kg/dm ³]	2.54 ± 0.03	2.68 ± 0.03
Water loss porosity [–]	0.15 ± 0.025	0.03 ± 0.006
^a CEC [meq/kg sample]	212 ± 0.5	66 ± 0.2
^b Mineralogy [wt.%]		
Phyllosilicates [wt.%]	66 ± 3	12 ± 3
Kaolinite	1	< 1
Illite	45	8
Chlorite	20	4
Other minerals [wt.%]	34 ± 3	88 ± 3
Calcite	3	70
Dolomite/Ankerite	< 1	12
Na-Plagioclase	< 1	0
K-Feldspar	2	1
Pyrite	2	< 1
Quartz	27	5

^a Measured by the Cs-method (Baeyens and Bradbury, 2004).

^b Analyzed as described in Mazurek et al. (2012).

2.2. Sample preparation

Cores from the Canadian rock formations, with a diameter of 0.075 m, were sliced perpendicular to the core axis into 0.005–0.006 m thick pieces using a diamond saw, without coolant. The slices were cut decagonal (diameter = ca. 0.065 m) with the same procedure and then embedded in an epoxy resin (Epofix, Struers GmbH). After hardening of the resin, the sample was placed on a lathe and the resin on the diametral (planar) ends removed.

2.3. Resaturation

The samples were mounted in a diffusion cell (Fig. 2), described in detail in Wigger and Van Loon (2017b). The diffusion cells were made of Ertalyte[®], an unreinforced polyester based on polyethylene terephthalate (PET-P), including implemented sintered titanium filters (diameter = 0.065 m; thickness = 0.0012 m; pore diameter = 1×10^{-5} m; porosity = 0.1; effective diffusion coefficient = 3.8×10^{-11} m²/s – Aldaba et al., 2014). The cell was connected, through tubing (inner diameter = 0.001 m), to two reservoirs containing synthetic pore water (Table 2), which was circulated using a 24-channel peristaltic pump (IPC, Ismatec, IDEX, United States). Weight measurements of both containers allowed detection of the occurrence of advective flow. In any case of detection of hydraulic gradients across the thin sample coupons, the experiments would have been aborted; however, there were no such occurrences over the course of this investigation.

To investigate the effect of different molar concentrations on anion diffusion, four sub-samples of Queenston Fm and Blue Mountain Fm were saturated with artificial pore water at varying molar concentrations with pure 0.01, 0.1, 1 and 5 M NaCl. The saturation process was monitored using ion chromatography (ICS50001, ThermoFischer) every second week. Due to the fact that the original pore water had a relatively high molarity (ca. 7 M), the pore waters in the sub-samples were replaced with the ‘fresh’ synthetic NaCl solutions over a period of one month. After four months, the pore solution compositions achieved chemical equilibrium. In a second experimental set, the Blue Mountain Fm samples were re-saturated with synthetic CaCl₂ solutions to gain insight into, and compare, the diffusion behavior of Cl[–] when different cations dominate, i.e., Na versus Ca. In the case of CaCl₂ saturation, the stable chemical conditions between the pore solution and the rock sample were reached faster than when NaCl was used. Thus, the re-saturation period for this aspect of the experiment was reached after two instead of four months. The final composition of the replacement pore waters, for each molar concentration investigated, is provided in Table 2.

2.4. Diffusion measurements

As soon as chemical equilibrium were reached, through-diffusion experiments were started. The biggest reservoir (source reservoir) was filled with 100 ml of the equilibrated pore solution and spiked with both tracers (³⁶Cl[–] and HTO), and the smaller reservoir (downstream

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