



# Investigation of partial water saturation effects on diffusion in shale

Jacob A. Nunn<sup>a,\*</sup>, Yan Xiang<sup>b</sup>, Tom A. Al<sup>a,\*\*</sup>

<sup>a</sup> Department of Earth and Environmental Science, University of Ottawa, 25 Templeton St., Ottawa, ON, K1N 6N5, Canada

<sup>b</sup> Department of Earth Sciences, University of New Brunswick, Fredericton, NB, Canada

## ARTICLE INFO

### Keywords:

Diffusion  
X-ray radiography  
Nuclear waste management  
Partial saturation  
Gas saturation  
Sedimentary rock  
Archie's law  
Shale  
Low-permeability

## ABSTRACT

A new method for testing the effect of partially saturated conditions on aqueous diffusion was developed using samples from the Upper Ordovician Queenston Formation shale from the Michigan Basin of southwest Ontario, Canada. Effective diffusion coefficients ( $D_e$ ) were determined for iodide tracer on duplicate cm-scale samples from a core segment. Partially saturated conditions were created with a new gas-ingrowth method that takes advantage of the variability of  $N_2$  solubility with pressure. The method is designed to create partially saturated pores, quantify the level of partial gas/brine saturation within the tracer-accessible pore space, and measure  $D_e$  under fully porewater-saturated and partially gas-saturated conditions for the same sample. X-ray radiography is used with an iodide tracer for quantifying the degree of partial saturation and measuring  $D_e$ . The saturated  $D_e$  values range from  $2.8 \times 10^{-12}$  to  $3.1 \times 10^{-12}$  m<sup>2</sup>/s. Following generation of a gas phase in the pores (average gas saturations of 4–6.7%),  $D_e$  values decrease by 20–22% relative to the porewater-saturated condition, indicating that the tortuosity factor (ratio of constrictivity to tortuosity) is sensitive to saturation. The data suggest that a relatively small fraction of the pore space dominates the solute transport. The gas-ingrowth method was successful for generating partial gas saturation, but the distribution of the gas phase is non-uniform, with relatively high gas saturations near boundaries and lower saturations in the interior of the samples.

## 1. Introduction

Low-permeability sedimentary rocks are of scientific interest because they present barriers to the migration of fluids and contaminants, which is important in CO<sub>2</sub> sequestration, shale gas exploitation, and nuclear waste management (Al et al., 2015; Benson and Cole, 2008; Javadpour et al., 2007; Leung et al., 2014; Lindeberg and Bergmo, 2003; Mazurek et al., 2011; Russell and Gale, 1982). Diffusion is the dominant transport process in sedimentary formations when hydraulic conductivity (K) is less than about  $10^{-10}$  m/s. The role of diffusive transport and its effect on barrier performance requires reliable measurements of effective diffusion coefficients ( $D_e$ ) (Shackelford, 1991). Measurements of  $D_e$  have been conducted at the laboratory scale (cm) with several established techniques, including: through diffusion (Jacops et al., 2013; Rebour et al., 1997; Savoye et al., 2010; Van Loon et al., 2003a, 2003b; Xiang et al., 2016), in-diffusion (Cormenzana et al., 2003), out-diffusion (Waber and Smellie, 2008), radial diffusion (Van der Kamp et al., 1996; Van Loon et al., 2004), X-ray computed tomography (Agbogun et al., 2013a; b), and radiography (Cavé et al., 2009; Loomer et al., 2013; Tidwell et al., 2000; Xiang et al., 2013). Drilling and sample collection for laboratory-scale measurements may

cause thermo-mechanical disruption of cores, resulting in altered physical properties such as porosity and tortuosity. Attempts have been made to reproduce in-situ temperature and pressure conditions in the laboratory in order to determine the magnitude of these effects on diffusive transport (Savoye et al., 2011; Van Loon et al., 2003a, 2004, 2003b; Wise and Houghton, 1966; Xiang et al., 2016). In efforts to understand diffusive transport at a larger scale (10's to 100's of m), numerous researchers have employed measurements of naturally-occurring tracer distributions in rock porewater which, combined with solute-transport modelling and knowledge of paleohydrology, allows for estimation of  $D_e$  at the formation scale (Al et al., 2015; Bensenouci et al., 2011; Desaulniers et al., 1981; Gimmi et al., 2007; Hendry et al., 2004, 2013; Hendry and Harrington, 2014; Mazurek et al., 2011; Patriarache et al., 2004a, 2004b; Remenda et al., 1994).

The majority of laboratory-scale investigations have been conducted on fully saturated samples, but under in-situ conditions, partial saturation is expected in some circumstances. Examples include organic-rich sedimentary rocks that contain CH<sub>4(g)</sub> at concentrations in excess of solubility, resulting in exsolution and displacement of porewater, as well as tunnelling excavations, which can lead to partially saturated conditions in the Excavation Damaged Zone (EDZ) (Matray et al., 2007;

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [jnunn061@uottawa.ca](mailto:jnunn061@uottawa.ca) (J.A. Nunn), [tom.al@uottawa.ca](mailto:tom.al@uottawa.ca) (T.A. Al).

Nagra, 2008). Investigations by Savoye et al. (2010, 2012, 2014, 2017) provide the most comprehensive assessment of the effect of partial saturation on solute diffusion in clay-rich rocks. They measured  $D_e$  for various tracers in the Callovo-Oxfordian claystone under partially saturated conditions using the through diffusion method and demonstrated that partial gas saturation leads to a decrease in  $D_e$  for solutes in the aqueous phase. For iodide, the tracer which is used for the present study, they observed a decrease in the effective diffusion coefficient of Iodide ( $D_{e-I}$ ) by a factor of 50 under conditions of 19% gas saturation. Additional examples of diffusion studies on partially saturated geologic materials include Badv and Faridfarid (2005) Conca and Wright (1992), Hamamoto et al. (2009), Hamamoto et al. (2010), Mehta et al. (1995), Olesen et al. (2000), Porter et al. (1960) and Rowell et al. (1967).

The Upper Ordovician shales (Queenston, Georgian Bay and Blue Mountain formations) of the Michigan Basin in southwest Ontario, Canada, have been studied extensively at the Bruce nuclear site, where the 200-m thick, low-permeability shale sequence has the necessary properties to act as natural geologic barrier for a proposed Deep Geological Repository (DGR) for low- and intermediate-level radioactive waste (CEAA, 2015).

Elevated  $CH_4(g)$  concentrations have been measured in these shales (Clark et al., 2013), and it has been suggested that a gas phase of up to 10% may be present (Intera, 2011). The porewater in the shales has very high salinity, up to halite saturation (Al et al., 2015), and dewatering methods, such as that employed by Savoye et al. (2010, 2012, 2014, 2017), would lead to salt precipitation that could occlude pores and influence  $D_e$ . The objectives of this work were to 1) develop a novel gas-ingrowth method for generation of a gas phase by manipulating pressure to control  $N_2(g)$  solubility; and 2) measure the degree of gas saturation in the pore space using a non-destructive X-ray radiography technique (Cavé et al., 2009); 3) quantify the change in  $D_e$  for  $I^-$  that results from the generation of partial gas saturation in samples of shale from the Michigan Basin.

## 2. Material and methods

### 2.1. Sample description

The samples used in this study are from the Ordovician Queenston Formation shale. The duplicate samples were collected from a 76-mm-diameter drill core segment at a depth of 472 m in borehole DGR-3 located at the Bruce nuclear site in southwest Ontario, Canada. Representative physical and mineralogical properties of the Queenston shale are provided in Table 1.

### 2.2. Measurement of diffusion coefficients and porosity

#### 2.2.1. Sample preparation and apparatus

Samples for diffusion measurements were prepared in duplicate using a diamond coring bit to drill sample cores from the original 76-mm core sample. The samples (20-mm diameter and 20–23 mm length) were drilled normal to bedding, using air to cool the bit. Natural porewater in the Queenston shale is near saturation with respect to halite (Al et al., 2015; Clark et al., 2013) so any evaporation during sample preparation could result in halite precipitation and occlusion of the pores. In order to prevent this from affecting the porosity and diffusion measurements, a new approach was used whereby samples were initially resaturated in a closed chamber containing an open vessel with deionized water. The water chemical potential gradient between the deionized water and the sample porewater causes water transfer to the rock porewater via the vapor phase. Resaturation is accomplished by vapor-phase diffusion, and at the point when water droplets began to accumulate on the surface of the rock, the samples were fully immersed in a synthetic pore water (SPW; Table 2) formulated for the Queenston shale using methods modified after the approach of Cavé et al. (2009) and Xiang et al. (2013). The samples were immersed in SPW under

**Table 1**  
Representative physical properties of the Queenston Formation shale, including porosity, diffusivity, hydraulic conductivity and mineralogy.

Porosity, Diffusion and Hydraulic Conductivity				
Water-accessible porosity $\phi_w^a$	Iodide-accessible porosity $\phi_I^a$	Effective-diffusion of HTO (perpendicular to bedding) $D_{e-HTO}^a$ m <sup>2</sup> /s	Effective-Diffusion of Iodide (perpendicular to bedding) $D_{e-I}^a$ m <sup>2</sup> /s	Hydraulic Conductivity $K_h^b$ m/s
0.058–0.11	0.044–0.094	$4.8 \times 10^{-12}$	$1.20 \times 10^{-12}$ – $3.4 \times 10^{-12}$	$3.0 \times 10^{-14}$
Mineralogy (wt %)				
	DGR2 <sup>c</sup>	DGR3 <sup>d</sup>	DGR4 <sup>d</sup>	
Quartz	4.0–12.0	23.5–34.1	18.5	
K-feldspar	< 2	1.4–3.2	1.3	
Plagioclase	< 2	1.2–1.9	1.9	
Calcite	8.0–57.0	6.1–14.6	31.6	
Dolomite/ankerite	7.0–31.0	6.6–11.4	7.6	
Clay minerals	29.0–53.0	41–45.2	36.6	
Illite/mica <sup>e</sup>	–	58.2–60.9	60.1	
Illite/smectite <sup>e</sup>	20–39	9.7	11.9	
Chlorite <sup>e</sup>	9.0–14.0	29.1–39.1	24.5	
Kaolinite <sup>e</sup>	< 1	3	3.5	
Pyrite	–	2.2	0.5	
Hematite	–	0.12	2.1	
Organic C	< 0.1–0.3	–	0.13	

<sup>a</sup> Xiang et al. (2013).

<sup>b</sup> Beauheim et al. (2014).

<sup>c</sup> Koroleva et al. (2009).

<sup>d</sup> Jackson (2009).

<sup>e</sup> Values are expressed as wt% of the clay fraction.

**Table 2**  
Composition of SPW and iodide tracer solution (SPW-T) used in diffusion experiments.

	SPW	SPW-T
Density (kg/L)	1.22	1.32
Element	mol/kgw	mol/kgw
Na	2.61	2.61
K	0.11	0.11
Ca	1.91	1.91
Mg	0.27	0.27
Cl	7.05	6.05
Br	0.06	0.06
Sr	0.02	0.02
I	0.00	1.00

vacuum for four weeks prior to the start of experiments. Water-accessible porosity ( $\phi_w$ ) measurements were conducted on the rock material remaining after subcoring using the method described by Xiang et al. (2013). It is a gravimetric method that accounts for the porewater salinity and requires oven drying at 105 °C.

A diffusion cell (Fig. 1) was specially designed to prevent expansion of the sample under the increased pressures experienced during nucleation and expansion of a gas phase in the pores (see below). An initial confining pressure of 0.83 MPa was applied to the samples using a calibrated relationship between vertical load and torque on the threaded end caps of the diffusion cell, similar to the approach employed by Van Loon et al. (2003a, 2003b). This confining pressure was intended to prevent expansion and damage to the sample during nucleation and growth of a gas phase, and it has no relationship to the confining pressure that affects the Queenston shale in natural subsurface conditions (12 MPa, Xiang et al., 2016). The cell was constructed with Delrin<sup>®</sup>, a form of polyoxymethylene thermoplastic, which was

Download English Version:

<https://daneshyari.com/en/article/8863026>

Download Persian Version:

<https://daneshyari.com/article/8863026>

[Daneshyari.com](https://daneshyari.com)