

## Laboratory determination of chloride diffusion coefficient in an intact shale

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An experimental investigation of diffusive transport of a nonreactive solute (chloride) in saturated, intact Queenston Shale is described. Laboratory tests were performed by placing distilled water in contact with samples of shale having a high initial concentration of chloride in their pore water. Chloride was then permitted to diffuse out of the shale and into the distilled water reservoir for a period of up to 65 days. At the end of each test, the shale sample was sectioned to determine the variation in chloride pore-water concentration with depth through the sample. Fickian diffusion theory was then used to deduce the diffusion coefficient ( $D$ ). The experimental diffusion coefficient for chloride at a temperature of  $22 \pm 1^\circ\text{C}$  ranged from  $1.4 \times 10^{-6}$  to  $1.6 \times 10^{-6}$   $\text{cm}^2/\text{s}$ , which corresponds to a tortuosity ( $\tau$ ) ranging from 0.095 to 0.108. Based on pore size measurements and consideration of the ionic diameter of hydrated chloride, the "effective porosity" available for chloride diffusion is estimated to be greater than 75% of the total porosity calculated from the moisture content of the shale.

*Key words:* diffusion, chloride, rock matrix, Queenston Shale, laboratory study.

L'on décrit une étude expérimentale du transport par diffusion d'un soluté inerte (chlorure) dans le schiste argileux saturé et intact de Queenston. Des essais de laboratoire ont été réalisés en mettant de l'eau distillée en contact avec des échantillons de schiste argileux ayant une concentration initiale élevée de chlorure dans l'eau des pores. Le chlorure a pu ainsi diffuser en dehors du schiste dans le réservoir d'eau distillée pour une période allant jusqu'à 65 jours. À la fin de chaque essai, l'échantillon de schiste était sectionné pour déterminer la variation en fonction de la profondeur dans l'échantillon et de la concentration de chlorure dans l'eau des pores. La théorie de diffusion de Fick a alors été utilisée pour déduire le coefficient de diffusion ( $D$ ). Le coefficient expérimental de diffusion pour le chlorure à une température de  $22 \pm 1^\circ\text{C}$  s'étend de  $1,4 \times 10^{-6}$  à  $1,6 \times 10^{-6}$   $\text{cm}^2/\text{s}$ , ce qui correspond à une tortuosité ( $\tau$ ) de 0,095 à 0,108. En partant des mesures de la dimension des pores, et en considérant le diamètre ionique du chlorure hydraté, l'on estime que la «porosité effective» disponible pour la diffusion du chlorure est supérieure à 75% de la porosité totale calculée avec la teneur en eau du schiste.

*Mots clés :* diffusion, chlorure, matrice de la roche, schiste argileux de Queenston, essai de laboratoire.

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### Introduction

Contaminant migration through fractures is a major consideration when attempting to evaluate the potential impact of waste disposal sites or subsurface chemical repositories located in fractured media. The motivation for the present study arises from an attempt to understand the very limited distance of contaminant migration from two municipal waste landfill sites located in Burlington, Ontario. Both sites are located in and on fractured Queenston Shale in a groundwater recharge zone.

Any evaluation of the potential for groundwater contamination in fractured rock formations requires consideration of advective-dispersive transport along the rock fractures and diffusive transport from the fractures into the surrounding rock matrix. Matrix diffusion allows contaminants to be stored in micropores where they are essentially immobile relative to their potential migration along fracture planes. For reactive contaminants, matrix diffusion also serves to increase the amount of solid available for interaction, beyond that provided by the surface area of the fracture walls. The net effect of matrix diffusion is to retard the arrival of both reactive and nonreactive contaminants at any point along the fracture.

To mathematically model contaminant transport along fractures with diffusion into the rock matrix, it is necessary to know the diffusion coefficient of the contaminant in the rock matrix (e.g., see Grisak and Pickens 1980; Sudicky and

Frind 1982; Rowe and Booker 1988, 1989). For practical purposes, the diffusion coefficient of a contaminant in a saturated porous media is often estimated based on the diffusion coefficient for a nonreactive species. To date, a number of studies have been conducted involving the measurement of diffusion coefficient for simple, nonreactive species such as chloride ( $\text{Cl}^-$ ) and iodide ( $\text{I}^-$ ) in igneous rocks (e.g., see Wadden and Katsube 1982; Skagius and Neretnieks 1986). In these studies, one-dimensional steady state diffusion was established across thin (typically 1 cm) disk samples separating two compartments having a uniform but different concentration of the species of interest. The diffusion coefficient was then backfigured from the steady state flux measurements into the low-concentration compartment. The purpose of this paper is to illustrate the measurement of diffusion coefficient for chloride on samples of intact, saturated, Queenston Shale using a simple non-steady-state technique and much larger samples.

### Theoretical development

One-dimensional diffusive transport of a dissolved nonreactive species through a saturated porous medium may be approximated by Fick's second law:

$$[1] \quad \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2}$$

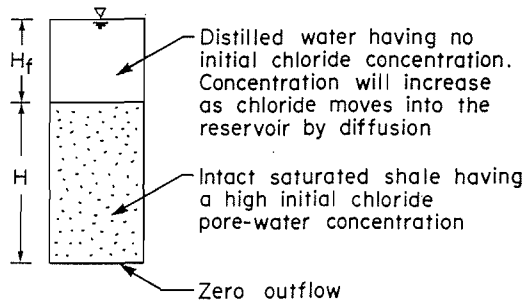


FIG. 1. Schematic diagram of the diffusion test.

where  $c$  is the concentration at time  $t$  and depth  $z$ , and  $D$  is the porous medium diffusion coefficient for the species. It should be noted that the concentration term ( $c$ ) refers to the mass of solute per unit volume of pore water accessible to the diffusing species. This is particularly important for very compact porous media such as shales where a portion of the pore water may not be accessible to the diffusing solute due to exclusion from the vicinity of the negatively charged clay surfaces and (or) due to pores not being large enough to accommodate the solute.

In the tests conducted by the authors, a volume of distilled water was placed in contact with a core sample of intact, saturated Queenston Shale as shown in Fig. 1. Chloride and other species naturally occurring in the pore water of the shale were then permitted to diffuse upwards through the specimen, across the interface, and into the distilled water reservoir. It can be shown (Rowe and Booker 1985) that the concentration of chloride  $c_T(t)$  in the reservoir at any time  $t$  is given by

$$[2] \quad c_T(t) = \frac{1}{H_f} \int f_T(t) dt$$

where  $H_f$  is the height of distilled water calculated as the volume of distilled water divided by the cross-sectional area of the core sample perpendicular to the direction of diffusion and  $f_T(t)$  is the mass flux across the boundary between the reservoir and the sample. The subscript "T" refers to the top of the sample. The mass flux  $f_T(t)$  can be further related to the chloride concentration gradient across the sample-reservoir boundary  $(\partial c(t)/\partial z)_T$  by Fick's first law:

$$[3] \quad f_T(t) = n' D \left( \frac{\partial c(t)}{\partial z} \right)_T$$

where  $n'$  is the material porosity available for chloride diffusion. As previously mentioned, in compact porous media such as shales, a portion of the pore water may not be available to the diffusing solute. Hence, the term  $n'$ , often referred to as the "effective" or "transport" porosity, may be lower than the total porosity ( $n$ ) calculated from the moisture content of the shale.

The base of the sample is sealed with an impermeable membrane so as to create a zero-flux base boundary condition, that is,

$$[4] \quad f_B(t) = n' D \left( \frac{\partial c(t)}{\partial z} \right)_B = 0$$

One-dimensional diffusion of chloride through the shale is thus described by [1]–[4]. The solution to these equations has been given by Rowe and Booker (1985) and has been

TABLE 1. Physical and chemical characteristics of the shale (average values)

Moisture content (%)	4.29
Specific gravity	2.83
Dry density (g/cm <sup>3</sup> )	2.55
Saturation (%)	100
Total Porosity (%)	10.8
Mineralogy (%)*	
Quartz	~26
Calcite	~13
Dolomite	~5
Feldspars	~4
Hematite	Trace
Illite	~40
Chlorite	~10
Vermiculite	Trace
Cation exchange capacity (mequiv./100 g dry wt.)	12.5
Pore-water species (g/L)	
Chloride	7.89
Sulphate	4.46
Sodium	6.17
Calcium	0.39
Magnesium	0.29
Potassium	0.06
Adsorbed species (mequiv./100 g dry wt.)	
Sodium	1.68
Potassium	3.06
Magnesium	2.13
Calcium	5.60

\*Based on X-ray diffraction analysis, cation exchange capacity, glycol retention, total potassium analysis, and gasometric analysis (for carbonates).

implemented in the computer program POLLUTE (Rowe *et al.* 1983). This approach permits accurate calculation of concentration in only a few seconds on a microcomputer and hence is well suited for use in interpretation of the experimental results provided that they are consistent with Fickian diffusion theory.

After allowing time for a diffusion profile to develop, the shale sample was sectioned and the chloride concentration profile with depth was determined. The theoretical solution to [1]–[4] was then used to obtain a match to the experimental profile by varying the diffusion coefficient (while keeping other geometrical and material parameters constant). The diffusion coefficient that was judged to provide the "best fit" to the experimental profile was selected as the experimental chloride diffusion coefficient.

### Queenston Shale

Core samples of Queenston Shale (6.2 cm diameter) were obtained from the region between the Bayview Park and Burlington landfills, located in Burlington, Ontario. Core sampling at the site was started at a depth of approximately 9 m below ground surface (4 m below the groundwater level) in order to obtain saturated and relatively unweathered shale. The core samples were immediately wrapped with saran wrap, covered with wetted tissue, and transported back to the laboratory, where they were stored at a temperature of  $22 \pm 1^\circ\text{C}$ . Within 1 day of drilling, samples of the core ranging in depth from 11.45 to 11.78 m below ground sur-

TABLE 2. Pore size distribution for the shale\*

Pore diameter ( $\mu\text{m}$ )	% of total porosity	Method of analysis
300-30	4	Micromeritics mercury porosimeter
30-0.03	5	Micromeritics mercury porosimeter
0.030-0.006	32	Micromeritics mercury porosimeter
0.006-0.002	32	Quantachrome automated gas adsorption system
$\Sigma = 73\%$		

\*Obtained on approximately 10 g intact, freeze-dried shale.

face were cut with a diamond saw for use in the diffusion tests and for characterization of the rock. All diffusion test samples were free of visual fractures and were believed to be completely saturated.

The geotechnical index characteristics, mineralogy, pore-water chemistry, and adsorbed species concentrations are summarized in Table 1. The moisture content of the shale was determined on approximately 1 cm thick core sections by heating at 100°C for at least 48 h. Dry density was measured on 10 g of freeze-dried shale, using a Micromeritics mercury porosimeter. The moisture content, dry density, and specific gravity were then used to calculate the percentage saturation and total porosity. The percentage saturation calculated this way confirmed that the shale was completely saturated.

Measurement of background pore-water concentration for the various inorganic species involved pulverizing oven-dried shale to particles of <76  $\mu\text{m}$  diameter and washing 5 g of this pulverized material in 100 mL of distilled water. The mixture was agitated for 15 min and centrifuged at 2500 rpm for 30 min. The supernatant was then analyzed for the species of interest. Chloride concentration in the supernatant was determined by a specific-ion electrode, sulphate by ion chromatography, and the cations by atomic absorption spectrometry. Supernatant concentration was converted to pore-water concentration using the relationship

$$[5] \text{ pore-water concentration (g/L)} = \frac{cV\rho}{mw}$$

where  $c$  is the species concentration in the supernatant (g/L),  $V$  is the volume of supernatant (0.10 L),  $m$  is the mass of oven-dried sample used in the wash (5 g),  $w$  is the moisture content of the sample used in the wash, and  $\rho$  is the density of pure water at 22°C (1000 g/L). It should be noted that pore-water concentrations calculated using [5] represent the dissolved mass of the species per unit volume of "total" pore water. There is no correction applied to the moisture content ( $w$ ) to account for pore water not accessible to the dissolved species.

Measurement of the adsorbed concentration of sodium and potassium involved washing 2 g of air-dried, pulverized shale in 150 mL silver thiourea solution for about 24 h. The mixture was then centrifuged and the supernatant analyzed. With this technique, any adsorbed sodium or potassium on the clay exchange sites is effectively replaced by the silver ion from the wash solution. For calcium and magnesium,

use of silver thiourea resulted in incorrectly high concentrations in the supernatant owing to dissolution of calcite and dolomite. To overcome this problem, a wash solution containing 2 g/L potassium chloride in distilled water had previously been found by the authors to provide complete exchange of calcium and magnesium for potassium, with minimal dissolution of carbonates. The cation exchange capacity was taken as the sum of the adsorbed concentration of the four cations listed in Table 1.

Table 2 indicates the percentage of total porosity ( $n$ ) corresponding to various ranges in pore size. This data was obtained by two techniques: a Micromeritics mercury porosimeter capable of measuring volumes for pores ranging from 300 to 0.006  $\mu\text{m}$  in diameter, and a Quantachrome automated gas adsorption system capable of measuring volumes for pores ranging from 0.06 to 0.002  $\mu\text{m}$ . As indicated in Table 2, the total porosity is largely derived from pores 0.03-0.002  $\mu\text{m}$  in diameter. Furthermore, approximately 30% of the total porosity is derived from pores outside the range of measurement (i.e., >300  $\mu\text{m}$  and (or) <0.002  $\mu\text{m}$ ). For comparison of the range in pore size with the size of the diffusing species, the hydrated diameter of chloride and sodium is about 0.0007  $\mu\text{m}$  (Horvath 1985, p. 344). Based on this data (pore size and hydrated diameter), it is conceivable that some pores may be too small to accommodate the fully hydrated diameter of the diffusing species and will thus impede migration.

### Experimental procedures

A schematic drawing of an assembled diffusion model is shown in Fig. 2. Each model consists of a hollow Plexiglas cylinder with an inside diameter of 6.7 cm and length of approximately 11 cm. An intact 6.2 cm diameter core sample, 7.1 cm in length, was fitted with a tight rubber membrane extending from the bottom to about 5 cm above the top of the sample. The rubber membrane serves to prevent drying along the sides and allows for containment of a reservoir on the top of the sample. To prevent drying through the bottom of the specimen, a circular piece of rubber membrane material was cut to the same diameter as the sample and adhered to the bottom using a silicone seal bond. The sample was then placed within the Plexiglas cylinder and the upper part of the membrane folded over the top of the cylinder, forming a reservoir compartment directly above the sample. The diffusion period commenced upon placement of a known volume of distilled water into the reservoir. The top of the cylinder was then fitted with a polyethylene cap plate and the entire model maintained at a laboratory temperature of 22  $\pm$  1°C for a period of up to 65 days. During the experimental period, the distilled water solution was mixed periodically so as to maintain a relatively uniform concentration throughout the reservoir depth. At the end of each experiment, the shale sample was removed and sectioned into eight segments using an oil-lubricated diamond saw. Following this, each slice was immediately wiped free of oil, weighed, and placed into a 100°C oven for at least 48 h. After heating, the average moisture content ( $w$ ) for each slice was determined. The vertical distribution of chloride concentration was measured by pulverizing each slice to particles <76  $\mu\text{m}$  in diameter and then washing 5 g of this oven-dried, powdered material once only with

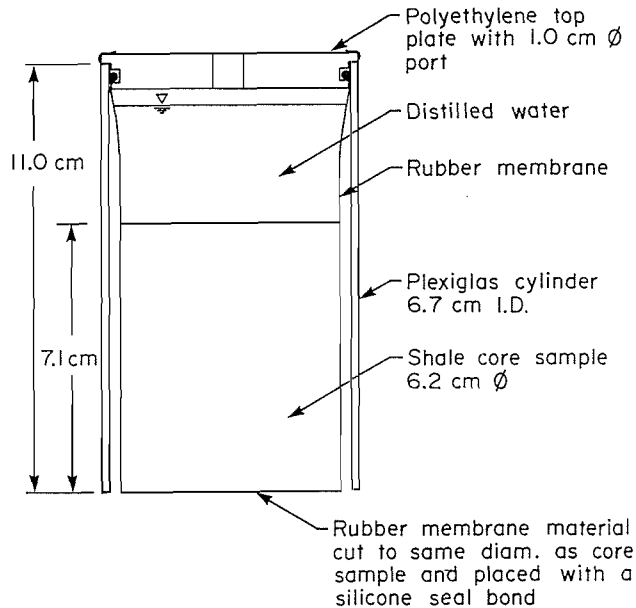


FIG. 2. Schematic diagram of an assembled diffusion model.

100 mL of distilled water in a 250 mL glass centrifuge tube. Each mixture was agitated for 15 min and centrifuged at 2500 rpm for 30 min. The supernatant was then directly analyzed for  $\text{Cl}^-$  concentration using a specific-ion electrode attached to a multipurpose meter. It was found that the supernatant concentration obtained upon washing the pulverized shale for approximately 15 min was not significantly different from that obtained upon washing for 24 h, indicating that a wash duration of 15 min was adequate.

Calculation of the  $\text{Cl}^-$  pore-water concentration from that measured in the supernatant was performed using a modified form of [5]:

$$[6] \text{ pore-water concentration (g/L)} = \frac{cV\rho}{mw'}$$

where  $w'$  is the moisture content available to the diffusing chloride ions. Various values of  $w'$  ranging from  $0.8w$  to  $w$  (which corresponds to an "effective" porosity ranging from  $0.8n$  to  $n$ ) were considered, and the  $\text{Cl}^-$  diffusion coefficient calculated for each case.

### Tests conducted

A total of three diffusion tests for the Queenston Shale (referred to as models 1-3) were conducted. Model 1 was terminated after 45 days, while models 2 and 3 were terminated after 65 days. The times at which the tests were terminated were selected based on an initial theoretical simulation of the diffusion test, using program POLLUTE, for the maximum and minimum likely values of the diffusion coefficient. The results of the analysis provided an indication of the minimum and maximum times to run the test such that a non-steady-state  $\text{Cl}^-$  diffusion profile would extend through the entire length of the sample. Table 3 shows the section of core used for the diffusion tests. It also indicates which samples were used to obtain background pore-water concentrations and basic geotechnical properties pertinent to the analysis.

### Experimental results and interpretation

Figure 3 shows the moisture content profile obtained for each model at the end of the diffusion period. Also shown are initial moisture contents obtained from background slices cut from the core immediately above and below the test sample. In all models, the final moisture content appears to be consistent with the initial background values, indicating little or no net uptake of water due to matrix suction and (or) osmosis. The significance of this type of bulk water movement lies in its effect on the observed concentration profile for the species of interest. For example, diffusion tests conducted by Kemper and van Schaik (1966) on samples of  $\text{Na}^+$ -saturated bentonite, showed that osmotically induced bulk water movement (as noted by a change in soil moisture content) could affect the concentration profile of diffusing species such that the profile cannot be entirely described by conventional Fickian diffusion theory. For the samples tested herein, the absence of any significant moisture uptake at the end of the test may be related to the calcite content of the shale ( $\sim 13\%$ ). As noted by Lo *et al.* (1978), calcite may act as a cementing agent tending to inhibit swelling. From free-swelling tests in distilled water, Lo *et al.* (1978) concluded that various southern Ontario shales (including Queenston Shale) exhibit essentially no swelling when the calcite content exceeds about 15%.

Assuming that the entire moisture content of the shale is available to  $\text{Cl}^-$  (i.e.,  $w' = w$  in [6]), the  $\text{Cl}^-$  concentration profiles obtained from the wash technique are presented for each model in Figs. 4-6. Also shown for each model is the inferred background  $\text{Cl}^-$  concentration profile based on the measured  $\text{Cl}^-$  concentration obtained on the background slices cut from above and below the test sample (see Table 3). The data shows a significant decrease in chloride concentration with respect to the background concentration, as a result of diffusion upwards into the distilled water reservoir. To maintain electroneutrality, the upward migration of chloride into the distilled water reservoir is coupled predominantly by the upward migration of sodium. This is indicated in Table 4, which shows the concentration of various species in the distilled water reservoir at the end of each test. As a check on the experimental technique, the percentage recovery of  $\text{Cl}^-$  (i.e., the ratio of  $\text{Cl}^-$  mass recovered at the end of the test to the total  $\text{Cl}^-$  mass at the start of the test) was calculated. The  $\text{Cl}^-$  mass at the start of the test was inferred from the background  $\text{Cl}^-$  concentrations above and below the test sample. For all three models, the deviation from 100% recovery was within  $\pm 3\%$ .

The diffusion coefficient for  $\text{Cl}^-$  was estimated by superimposing several calculated diffusion profiles onto the experimental data as shown in Figs. 4-6. Calculated profiles were obtained using program POLLUTE by varying the diffusion coefficient. Since the entire moisture content ( $w$ ) was assumed to be available to the diffusing chloride ions, the "effective" porosity ( $n'$ ) used in the theoretical analysis was taken as the average of the total porosity ( $n$ ) measured for the background samples above and below the test specimen (see Table 3).

The diffusion coefficient judged to give the best fit to the experimental data was taken as the experimental diffusion coefficient. Values of experimental diffusion coefficient obtained for each model are presented in Table 5. For an

TABLE 3. Core section used for the diffusion experiments

Depth below surface (m)	Sample thickness (cm)	Sample no.	Sample use	Moisture content (%)	Total porosity (%)	Cl <sup>-</sup> concentration (g/L)
11.45	3.0	B.G.4	Background	4.15	10.5	7.55
	7.1	3	Model 3			
	3.0	B.G.3	Background	4.56	11.4	7.79
	7.1	2	Model 2			
	3.0	B.G.2	Background	4.43	11.1	8.74
	7.1	1	Model 1			
	3.0	B.G.1	Background	4.00	10.2	7.50
11.78						

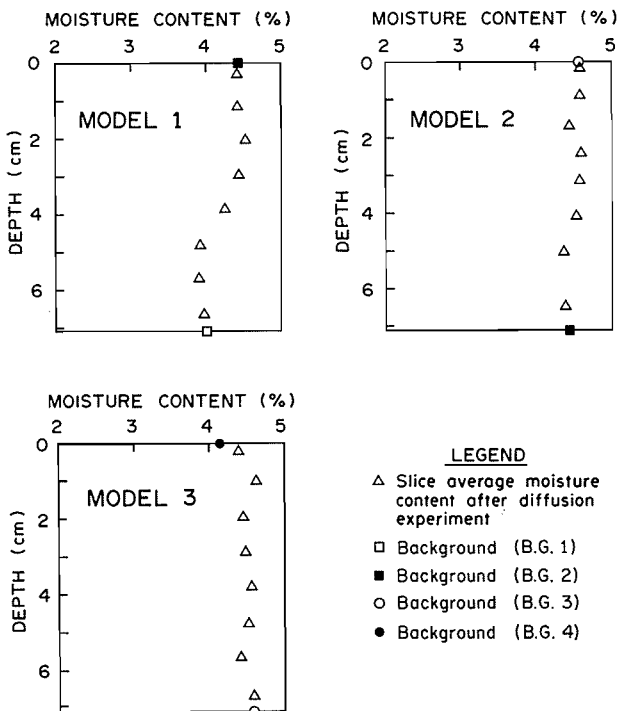


FIG. 3. Moisture content variation with depth after diffusion.

average laboratory temperature of 22°C, the experimental Cl<sup>-</sup> diffusion coefficient varied from  $1.4 \times 10^{-6}$  to  $1.6 \times 10^{-6}$  cm<sup>2</sup>/s. The primary source of scatter with respect to the best-fit theoretical curve is thought to be associated with the wash extraction procedure. To provide a measure of the magnitude of uncertainty associated with

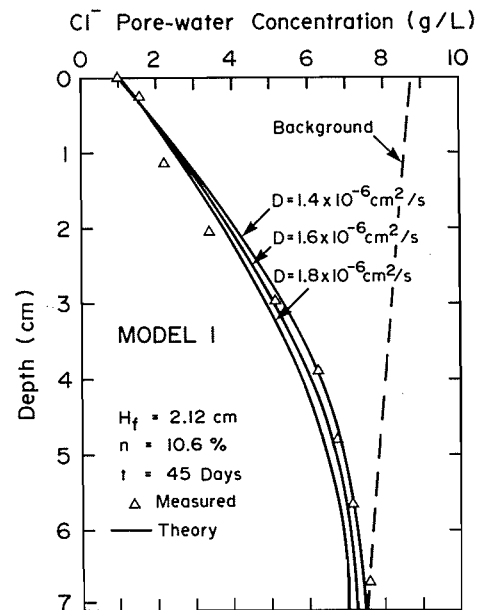


FIG. 4. Chloride pore-water concentration variation with depth for model 1.

the wash extraction, triplicate washes were performed for two slices from model 2. The results indicated a maximum uncertainty of  $\pm 0.2$  g/L in chloride pore-water concentration. This relates quite well to the deviation of most points from the best-fit theoretical curve.

Chloride pore-water concentration profiles recalculated for model 2 on the assumption that 80 and 90% of the entire shale moisture content is available to Cl<sup>-</sup> (i.e.,  $w' = 0.8w$  and  $w' = 0.9w$  in [6]), are shown in Figs. 7 and 8, respec-

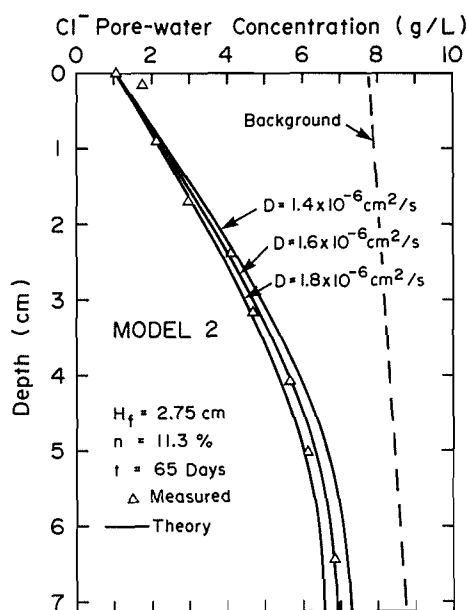


FIG. 5. Chloride pore-water concentration variation with depth for model 2.

TABLE 4. Reservoir concentrations at the end of each test

Model no.	Concentration, g/L (mequiv./L)					
	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>
1	1.00	0.19	0.57	0.058	0.019	0.040
	(28.2)	(3.9)	(24.8)	(2.9)	(1.6)	(1.0)
2	1.08	0.23	0.55	0.060	0.020	0.050
	(30.5)	(4.8)	(24.0)	(3.0)	(1.6)	(1.3)
3	1.08	0.23	0.63	0.077	0.027	0.050
	(30.5)	(4.8)	(27.4)	(3.9)	(2.2)	(1.3)

tively. The calculated Cl<sup>-</sup> concentration profiles were then fitted using program POLLUTE, setting the "effective" porosity equal to 0.8n and 0.9n. In each case, the resulting diffusion coefficient is the same as that obtained assuming w' = w. The fact that the three cases considered (i.e., w' = w, 0.9w, and 0.8w) yield the same diffusion coefficient indicates that with the experimental technique adopted in these specific tests, determination of the diffusion coefficient for a nonreactive species does not seem to require knowledge of w' and hence "effective" porosity. However, it should be noted that when mathematically modelling advective transport of a nonreactive species along a fracture with diffusion into the rock matrix, an estimate of the "effective" matrix porosity is essential (see Rowe and Booker 1989). Based on the data presented in Table 2 and consideration of the hydrated diameter of chloride and sodium, the effective porosity of the Queenston Shale with respect to the diffusion of sodium and chloride is expected to exceed 0.75n. In other words, at least 75% of the pore sizes are large enough to accommodate fully hydrated Na<sup>+</sup> and Cl<sup>-</sup>.

This diffusion coefficient for Cl<sup>-</sup> in the shale (D) may be related to the Cl<sup>-</sup> diffusion coefficient in aqueous solution (D<sub>0</sub>) by the expression

$$[7] \quad D = \tau D_0$$

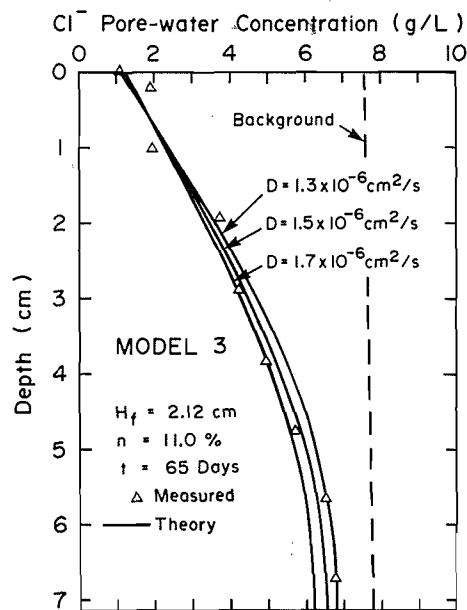


FIG. 6. Chloride pore-water concentration variation with depth for model 3.

TABLE 5. Summary of experimental diffusion coefficients for Cl<sup>-</sup>

Model no.	Experimental diffusion coefficient at 22°C (cm <sup>2</sup> /s)	Tortuosity factor
1	1.4 × 10 <sup>-6</sup>	0.095
2	1.6 × 10 <sup>-6</sup>	0.108
3	1.5 × 10 <sup>-6</sup>	0.101

where  $\tau$  ( $0 < \tau < 1.0$ ) is the "tortuosity factor" for the porous medium. Based on [7], approximate values of tortuosity factor for the tests conducted (see Table 5) ranged from 0.095 to 0.108. These values of  $\tau$  were determined using  $D_{0, \text{Cl}^-} = 1.48 \times 10^{-6} \text{ cm}^2/\text{s}$ , which is the aqueous diffusion coefficient of both Na<sup>+</sup> and Cl<sup>-</sup> at 25°C when diffusing together from a source solution containing 0.25 M NaCl (Stokes 1950). A concentration of 0.25 M NaCl was selected, since it is representative of the initial Cl<sup>-</sup> and Na<sup>+</sup> pore-water concentrations for the diffusion test specimens. Although only approximately true (e.g., see Quigley *et al.* 1987), the tortuosity is often assumed to be a property of the porous medium, depending on fabric and pore structure rather than the nature of the diffusing species. If this is the case (for practical purposes), then based on [7], knowledge of the tortuosity factor allows the diffusion coefficient for other species to be estimated from their values of D<sub>0</sub>. Measured values of D<sub>0</sub> for a variety of species can be obtained from the literature (e.g., American Institute of Physics Handbook 1972; Wilke and Chang 1955).

### Summary and conclusion

The prediction of contaminant migration through a saturated, fractured rock formation requires consideration of advective-dispersive transport along the fractures and diffusive transport into the adjacent rock matrix. This phenomenon of matrix diffusion serves to slow the rate of advance

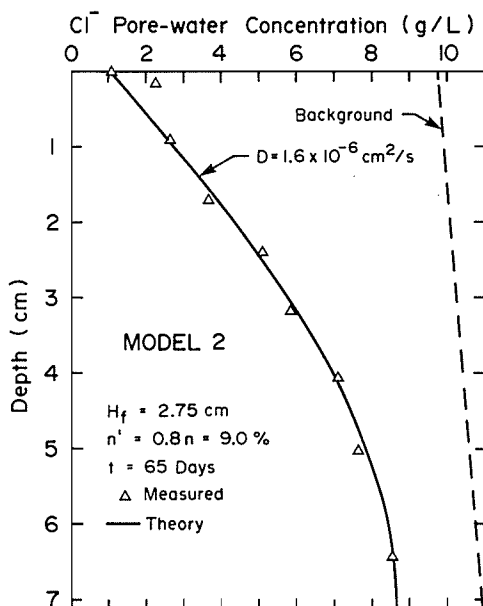


FIG. 7. Chloride concentration profile for model 2 assuming 20% of the total pore fluid is inaccessible to hydrated  $\text{Cl}^-$  ( $w' = 0.8w$ ).

of the contaminant front, and for a conservative species such as chloride, represents the primary source of attenuation. To quantify the diffusive transport of a contaminant from fractures into the rock matrix, it is necessary to know the diffusion coefficient of the contaminant in the rock matrix. This paper has illustrated the direct measurement of chloride diffusion coefficient on samples of saturated, intact Queenston Shale using a simple non-steady-state technique. For the conditions examined in these tests, it is concluded that the diffusion coefficient for chloride at a temperature of  $22 \pm 1^\circ\text{C}$  ranged from  $1.4 \times 10^{-6}$  to  $1.6 \times 10^{-6} \text{ cm}^2/\text{s}$ , which corresponds to a tortuosity,  $\tau$ , ranging from 0.095 to 0.108. Based on pore size measurements and consideration of the hydrated ionic diameter for sodium and chloride, the effective porosity of the Queenston Shale with respect to the diffusion of sodium and chloride is estimated to exceed 75% of the total porosity determined from moisture content. For the tests conducted, there was no increase in moisture content of the unconfined shale sample. This simplifies the problem, resulting in easy theoretical fitting of the observed concentration profile.

Finally, it is recognized that for a given porous medium, the diffusion coefficient of chloride may vary somewhat depending on the nature of interactions between chloride and its codiffusing ions (e.g., see Barone *et al.* 1989). For the test method described,  $\text{Cl}^-$  is allowed to diffuse out of the rock matrix and into the distilled water reservoir, along with other naturally occurring species in the shale pore water. It must be realized that the interactions between  $\text{Cl}^-$  and the codiffusing ions under such conditions may not be representative of the situation whereby  $\text{Cl}^-$  is diffusing from a fracture solution (i.e., leachate) into the rock matrix. As an example, for the latter case,  $\text{Cl}^-$  diffusing into the rock matrix may be slowed down by desorbed cations diffusing out of the rock matrix. Hence, for the purpose of modelling the diffusive transport of  $\text{Cl}^-$  from a fracture

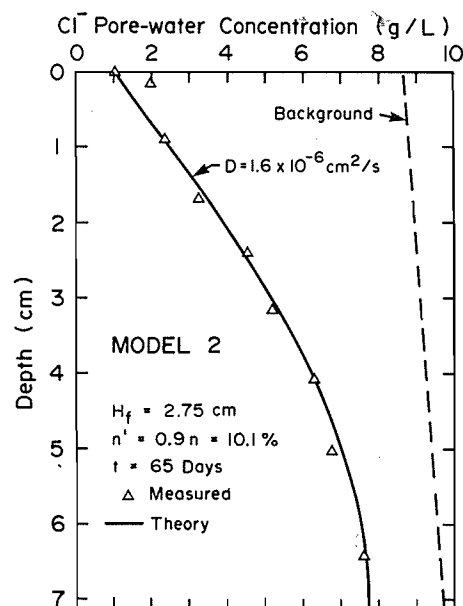


FIG. 8. Chloride concentration profile for model 2 assuming 10% of the total pore fluid is inaccessible to hydrated  $\text{Cl}^-$  ( $w' = 0.9w$ ).

solution into the rock matrix, the diffusion coefficient obtained from this type of test serves only as an approximate value, particularly where the nature of interactions between  $\text{Cl}^-$  and codiffusing ions is significantly different from that observed for the diffusion test.

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