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LABORATORY DETERMINATION OF CHLORIDE DIFFUSION COEFFICIENT IN INTACT SHALE

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ABSTRACT

An experimental investigation of diffusive transport of a non-reactive solute (Cl^-) in saturated, intact Queenston Shale is described. Laboratory tests were performed by placing distilled water in contact with samples of shale which had a high initial concentration of chloride in the porewater. 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 porewater concentration with depth through the sample. Fickian diffusion theory was then used to deduce the diffusion coefficient (D). The experimental diffusion coefficient at a temperature of 22 $\pm$ 1°C ranged from 1.4 to 1.6×10^{-6} cm^2/sec and corresponds to a tortuosity (τ) ranging from .074 to .084.

INTRODUCTION

The evaluation of potential contamination of groundwater due to waste disposal sites constructed on fractured rock formations requires consideration of advective-dispersive transport along the fractures and diffusive transport into the adjacent solid matrix. The process of diffusion of a contaminant from the fractures into the rock matrix serves to slow the rate of advance of the contaminant front and for a conservative species such as chloride this represents the primary mechanism for attenuation.

To quantify the diffusive mass transport into the rock matrix, it is necessary to know the diffusion coefficient of the contaminant in the rock matrix. The purpose of this paper is to describe an experimental determination of the diffusion coefficient for chloride in intact samples of Queenston Shale taken from below the watertable.

THEORETICAL DEVELOPMENT

One-dimensional diffusive transport of dissolved non-reactive contaminants through a saturated porous medium may be approximated by Fick's second law viz.:

$$\frac{dc}{dt} = D \cdot \frac{d^2c}{dz^2} \qquad [1]$$

where c is the concentration of the contaminant at time t at depth z, and D is the diffusion coefficient which is often related to the diffusion coefficient in free solution D_o by an empirical parameter, τ, referred to as the "tortuosity"; i.e.,

$$D = \tau \cdot D_o$$

For practical purposes, the tortuosity factor is often considered a material constant, and conceived as the ratio of the net distance travelled in the porous medium to the length of the tortuous pathway followed by the contaminant while diffusing around the solid particles. However, experimental evidence would suggest that the "tortuosity" is not a true material constant; that is, it may vary somewhat from one contaminant to another (e.g. see Gillham et al., 1984; Rowe et al., 1988).

In the tests conducted by the authors, a volume of distilled water was placed in contact with a core sample of intact, saturated shale as shown in Fig. 1. Chloride which is naturally occurring in the porewater of the shale was then permitted to diffuse through the specimen and into the distilled water reservoir. Under these conditions 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

$$c_T(t) = \frac{1}{H_f} \int_0^t f_T(\tau)\, d\tau \qquad [2]$$

where H_f is the height of the 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 mass flux $f_T(t)$ can be further related to the chloride concentration gradient across the sample/reservoir boundary $(dc/dz)_T$ by Fick's first law, viz.

$$f_T(t) = nD \left(\frac{dc}{dz}\right)_T \qquad [3]$$

where n is the material porosity and the subscript T refers to the top of the sample.

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

$$f_B(t) = nD \left(\frac{dc}{dz}\right)_B = 0 \qquad [4]$$

One-dimensional diffusion of chloride through the shale is described by Eqs. 1-4. The solution to these equations has been given by Rowe and Booker (1985) and has been 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 Eqs. 1-4 (as implemented in the computer program POLLUTE), was then used to obtain a match to the experimental curve by varying the diffusion coefficient (while keeping other geometrical and material parameters constant). The diffusion coefficient which was judged to provide the "best fit" to the experimental data was selected as the experimental diffusion coefficient.

QUEENSTON SHALE

The Queenston shale used in this study was a reddish brown shale. Core samples (6.2 cm diameter) were obtained from a site 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 ground water level) in order to obtain saturated and relatively unweathered

shale. The extruded shale was immediately wrapped with wetted tissue, covered, and transported back to the laboratory for storage at 22° ± 1°C. Within one day after drilling, samples of the core ranging in depth from 11.45 m to 11.78 m below ground surface were cut with a diamond saw for use in the diffusion experiments. The samples were free of visual fractures and believed to be completely saturated.

Table 1 identifies average values for several physical and chemical properties. Figure 2 shows a standard scanning electron photomicrograph at a magnification of 400 for both a vertical and horizontal face of the shale core. The lack of any distinct layering suggests that the shale is quite isotropic in structure. Thus, although the diffusion tests were conducted in the vertical direction, the deduced diffusion coefficient would likely be applicable in any other direction. That is, there is no expected variation in tortuosity with direction. It should be noted, however, that Queenston shale at other sites (e.g. Niagara Falls, Ontario) does show distinct horizontal layering (Lee, personal communication).

EXPERIMENTAL PROCEDURES

A schematic of an assembled diffusion cell is shown in Fig. 3. Each cell consisted 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 the 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 plexiglass cylinder and the upper part of the membrane folded over the top of the cylinder, forming a reservoir compartment directly above the sample. Upon placing a known volume of distilled water into the reservoir, the top of the cylinder was fitted with a polyethylene cap plate. The distilled water solution was mixed periodically so as to maintain a relatively uniform concentration throughout the reservoir depth. During the experimental period, the cells were kept at a laboratory temperature of 22° $\pm$ 1°C.

An estimate of the time required to establish a significant chloride profile within the shale was obtained by initially assuming $\tau = .01$. This gave a required diffusion time of about 45 days. At the end of each experiment, the shale sample was removed from the cell and sectioned into 8 segments using a diamond saw. Immediately, each slice was weighed and placed into a 105°C oven for approximately 48 hours. After heating, the average moisture content for each slice was determined. The vertical distribution of chloride concentration was measured by firstly pulverizing each slice until it passed a #200 sieve and then washing 10 grams of this oven dried, powdered, material with 100 ml of distilled water in 250 ml glass centrifuge tubes. Each mixture was agitated for 10 minutes and centrifuged at 2,500 rpm for 30 minutes. The supernatant was then directly analyzed for Cl^- concentration using a specific ion electrode attached to a multipurpose meter. Calculation of the Cl^- porewater concentration from that measured in the supernatant was performed using the following equation:

$$Cl^- \text{ porewater concentration } (g/L) = \frac{c_s \, v_s \rho}{m_s \, w}$$

where, c_s = Cl^- concentration measured in the supernatant (g/L)

v_s = volume of supernatant (0.1 L)

m_s = mass of oven dried soil used in the wash (10 g)

w = average moisture content for the slice after the diffusion experiment

ρ = density of water (g/L)

Background Cl^- and cation porewater concentrations were determined using the same wash technique as discussed above.

TESTS CONDUCTED

A total of three diffusion tests for the Queenston shale (referred to as models 1 to 3) were conducted. Model 1 was terminated after 45 days while models 2 and 3 were terminated after 65 days. Table 2 shows the section of core used for the diffusion models. It also indicates which samples were used to obtain background porewater concentrations and basic geotechnical properties pertinent to the analysis.

EXPERIMENTAL RESULTS AND INTERPRETATION

The experimental Cl^- diffusion profiles for each cell are shown in Figs. 4-6. As a check on the experimental technique, mass balance calculations for Cl^- were performed for each test upon completion. For all three models, better than 98% of the original Cl^- mass was recovered. The diffusion coefficient for each model was estimated by superimposing several calculated diffusion profiles

onto the experimental data. Calculated profiles were obtained using program POLLUTE by varying the diffusion coefficient. The coefficient judged to give the best fit to the experimental data was taken as the experimental diffusion coefficient.

The values of the experimental diffusion coefficient and the tortuosity obtained for each model are presented in Table 3. For an average laboratory temperature of 22°C, the experimental Cl^- diffusion coefficient varied from 1.4 to 1.6×10^{-6} cm^2/s, corresponding to a tortuosity factor ranging from .074 to .084. Although the experimental data showed some scatter about the best fit theoretical curves, the experimental diffusion coefficient appears to be consistent from one cell to another. The primary source of the scatter is thought to be associated with the wash extraction procedure. To provide a measure of the magnitude of uncertainty associated with the wash extraction, triplicate washes were performed for two slices from model 2. The results indicated a maximum uncertainty of $\pm$ .2 g/L in chloride pore water concentration. This relates quite well to the deviation of most points from the best fit theoretical curve.

Figure 7 shows the moisture content profiles for each model after the diffusion experiment as well as the background values. For all models, the final moisture content appears to be consistent with the initial background values.

Quigley et al. (1987) have indicated that phenomena such as the osmotic flow of water from low salt concentration to high salt concentration (i.e. from the distilled water reservoir into the sample) could potentially influence the concentration profile. However, the good theoretical fit to the experimental data suggests that for the experimental conditions and materials used, this phenomenon did not have a significant effect. Furthermore, osmotic flow of water

from the reservoir into the soil would be expected to induce an increase in moisture content which would be most notable near the reservoir/sample interface; this was not observed.

CONCLUSIONS

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 of the contaminant front and for a conservative species such as chloride, represents the primary source of attenuation. This paper has described a number of laboratory tests involving the diffusive migration of chloride in saturated, intact Queenston shale. A theoretical model was used to backfigure the diffusion coefficient (D) from the experimental results. Based on this study, it is concluded that:

(1) For the conditions examined in these tests, the experimentally obtained Cl^- concentration profiles in the shale samples were consistent with theoretical diffusion profiles, suggesting that phenomena such as osmotic water migration did not significantly influence the diffusion of chloride from the shale.

(2) The diffusion coefficients obtained from three tests were in good agreement indicating the repeatability of the experimental procedure.

(3) The diffusion coefficient for chloride at a temperature of 22° $\pm$ 1°C ranged from 1.4 to 1.6×10^{-6} cm^2/s with a corresponding tortuosity, τ, ranging from .074 to .084.

ACKNOWLEDGEMENTS

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TABLE 1. TYPICAL PHYSICAL AND CHEMICAL PROPERTIES OF THE SHALE (Average Values)

Moisture Content, %	4.29
Specific Gravity	2.83
*Porosity, %	10.8
Pore Water Chemistry, g/L	
Chloride	7.900
Sodium	6.200
Calcium	.390
Magnesium	.290
Potassium	.060

* calculated assuming 100% saturation

TABLE 2. CORE SECTION USED FOR THE DIFFUSION EXPERIMENTS

DEPTH BELOW GROUND SURFACE (m)		SAMPLE THICKNESS (cm)	SAMPLE #	SAMPLE USE	BACKGROUND Cl^- POREWATER CONCENTRATION (g/ℓ)	BACKGROUND GEOTECHNICAL PROPERTIES MOISTURE CONTENT	POROSITY*
11.45		3.0	B.G.4	Background	7.55	4.15%	10.5%
		7.1	3	Model 3			
		3.0	B.G.3	Background	7.79	4.56%	11.4%
		7.1	2	Model 2			
		3.0	B.G.2	Background	8.74	4.43%	11.1%
		7.1	1	Model 1			
		3.0	B.G.1	Background	7.50	4.00%	10.2%
11.78							

* Calculated porosity assuming 100% saturation

TABLE 3. SUMMARY OF EXPERIMENTAL DIFFUSION COEFFICIENTS FOR Cl^-

Model #	Experimental Diffusion Coefficient at 22°C (cm^2/s)	Tortuosity* Factor
1	1.4×10^{-6}	.074
2	1.6×10^{-6}	.084
3	1.5×10^{-6}	.079

* Tortuosity factor calculated using $D_{o_{Cl^-}} = 1.90 \times 10^{-5}$ cm^2/s at 22°C (American Institute of Physics Handbook, 1972)

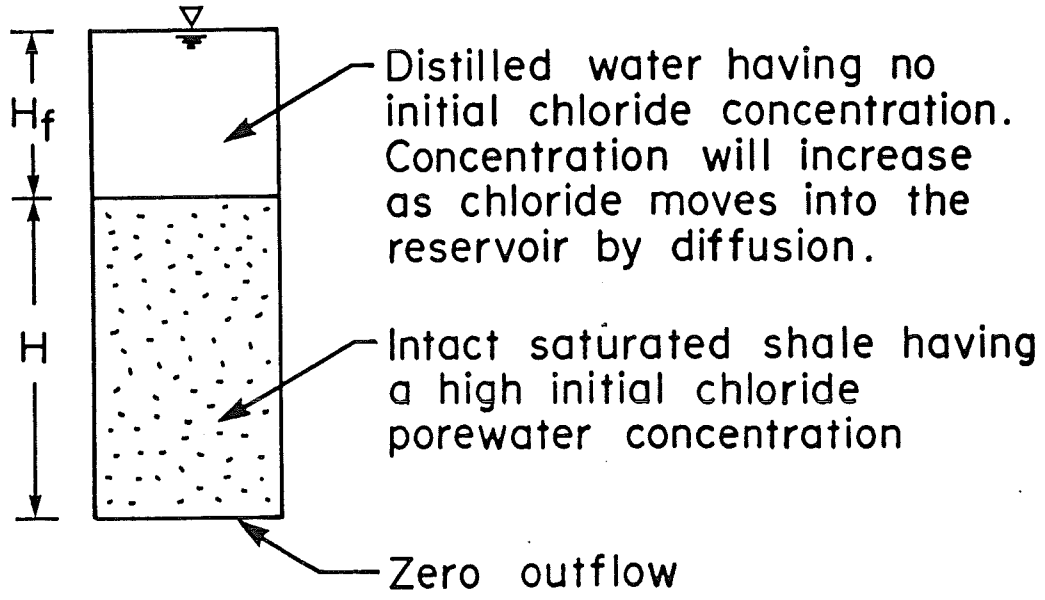
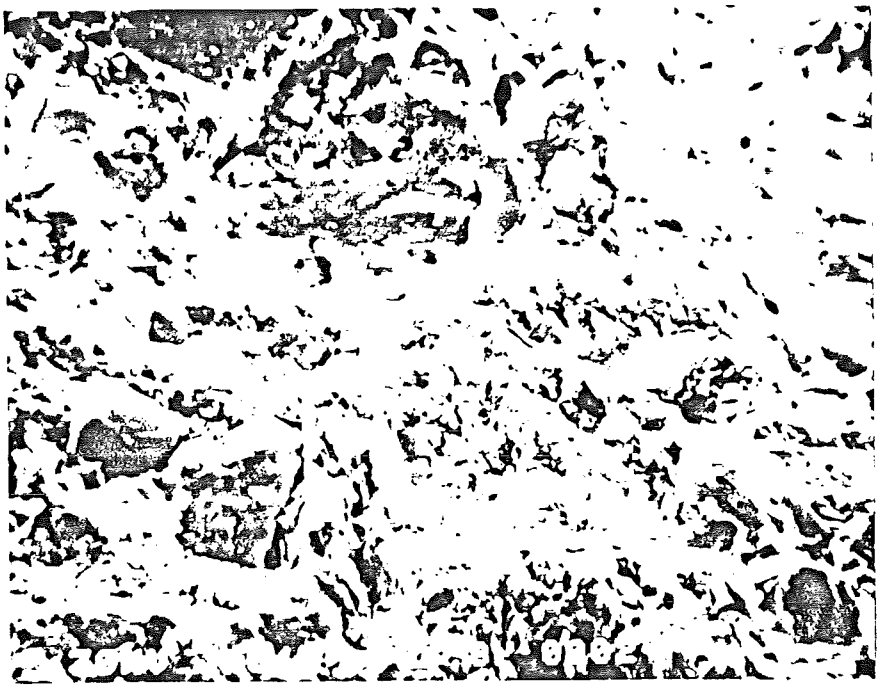
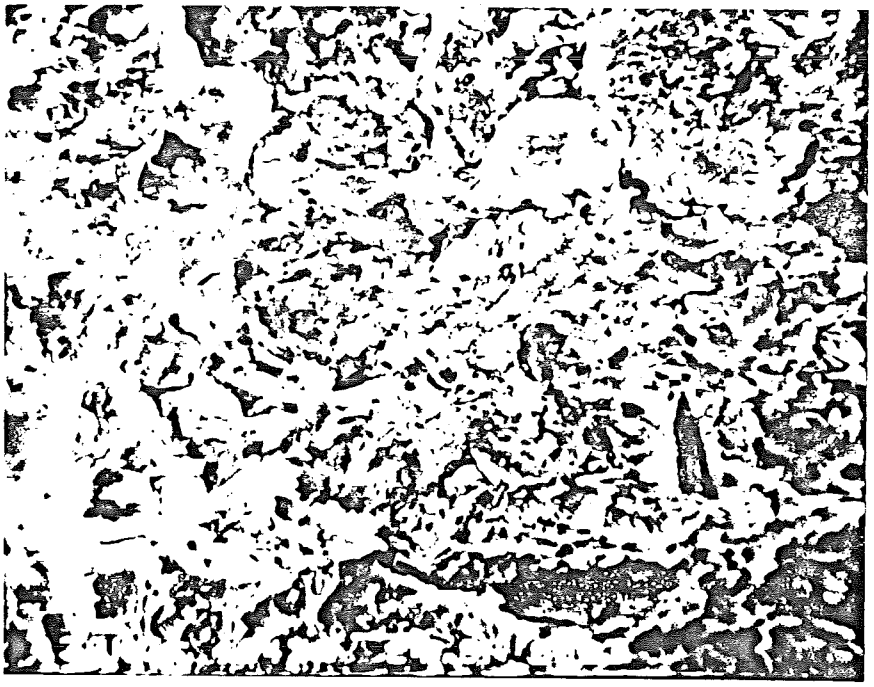


FIGURE 1 SCHEMATIC DIAGRAM OF THE DIFFUSION TEST



(a)



(b)

SCALE: 1 cm = 24.8 μm

FIGURE 2 SCANNING ELECTRON PHOTOMICROGRAPH OF THE SHALE (MAGNIFICATION X400) FOR a) VERTICAL SURFACE, b) HORIZONTAL SURFACE

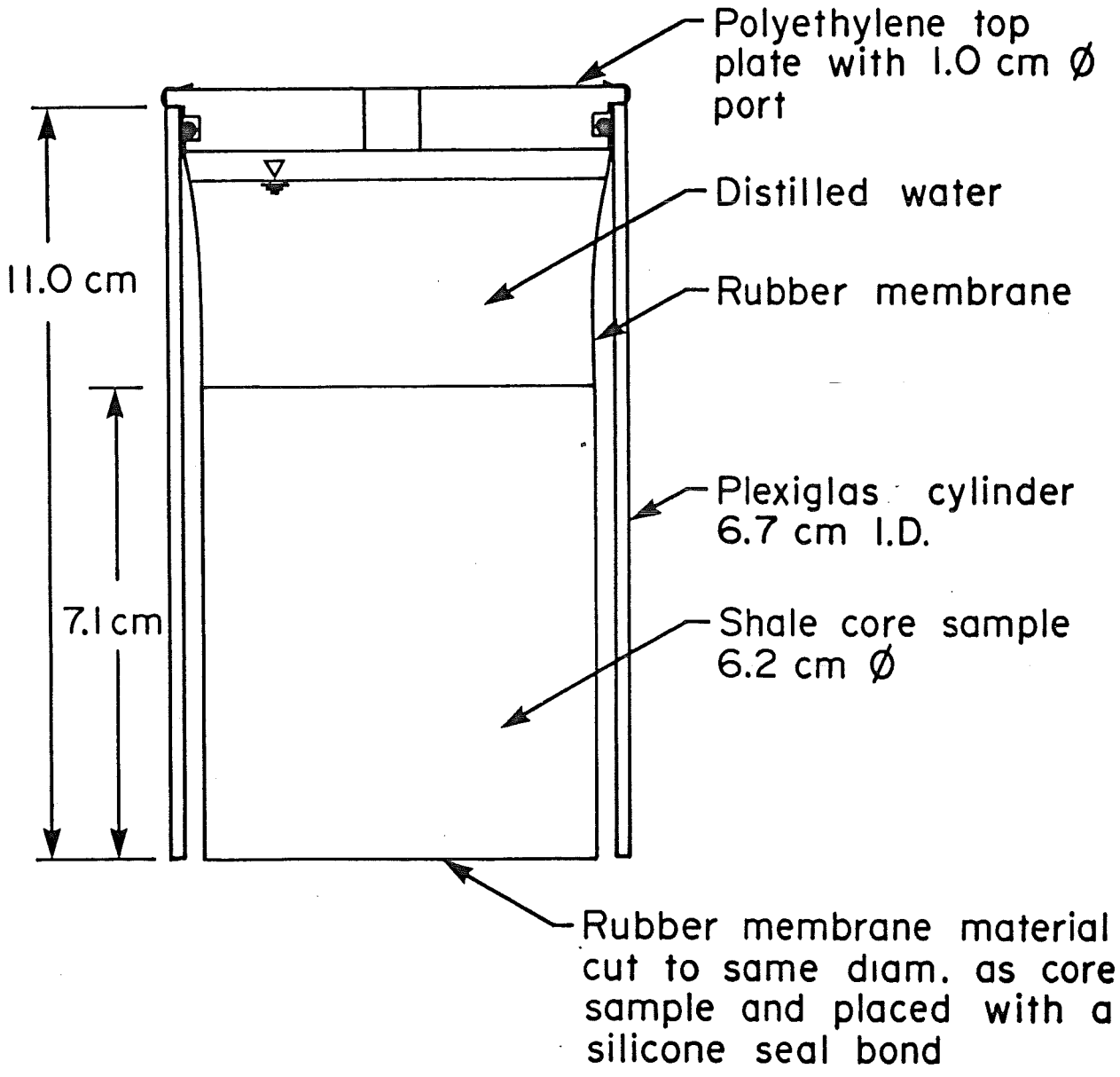


FIGURE 3 SCHEMATIC DIAGRAM OF AN ASSEMBLED DIFFUSION MODEL

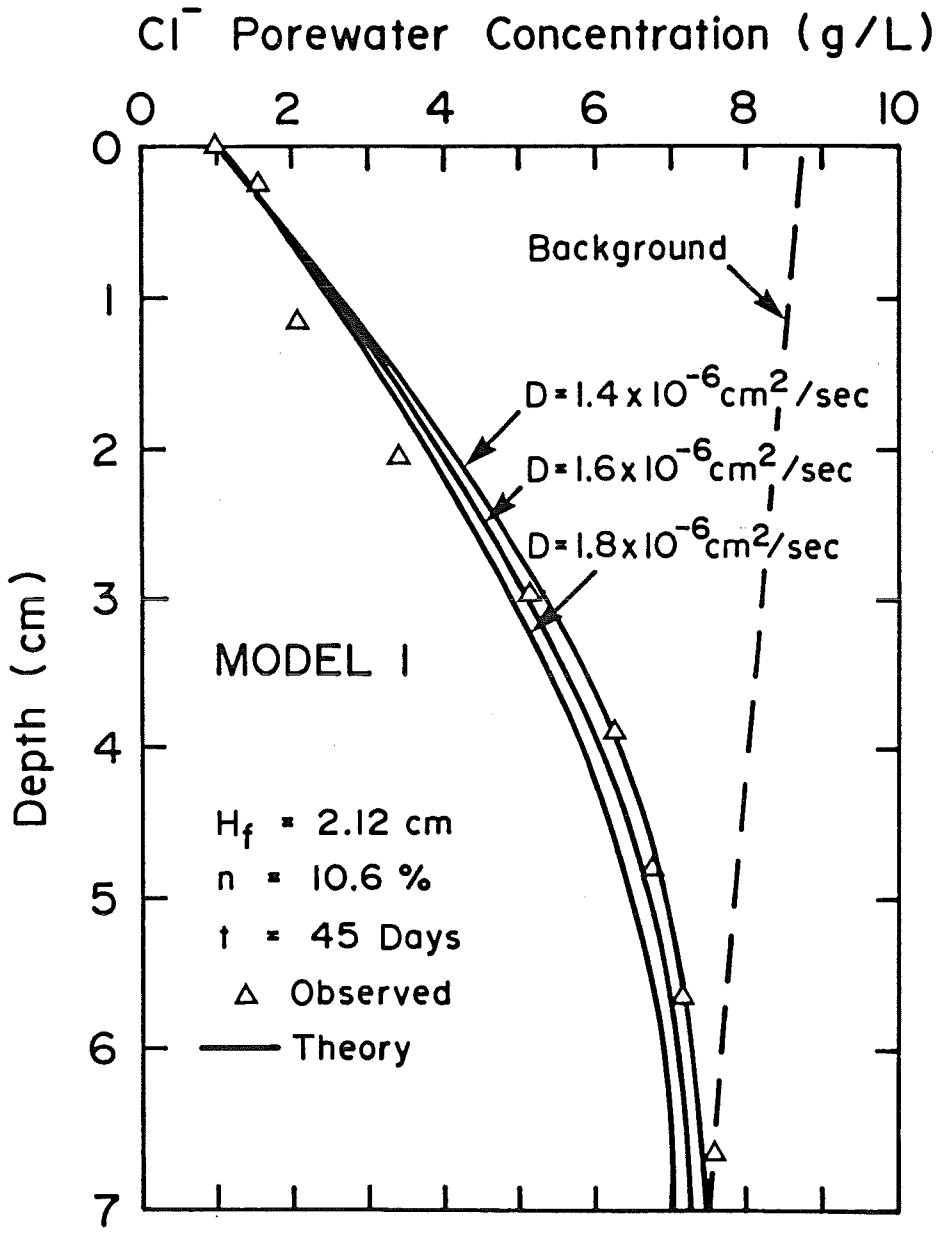


FIGURE 4 CHLORIDE PORE WATER CONCENTRATION VARIATION WITH DEPTH FOR MODEL 1

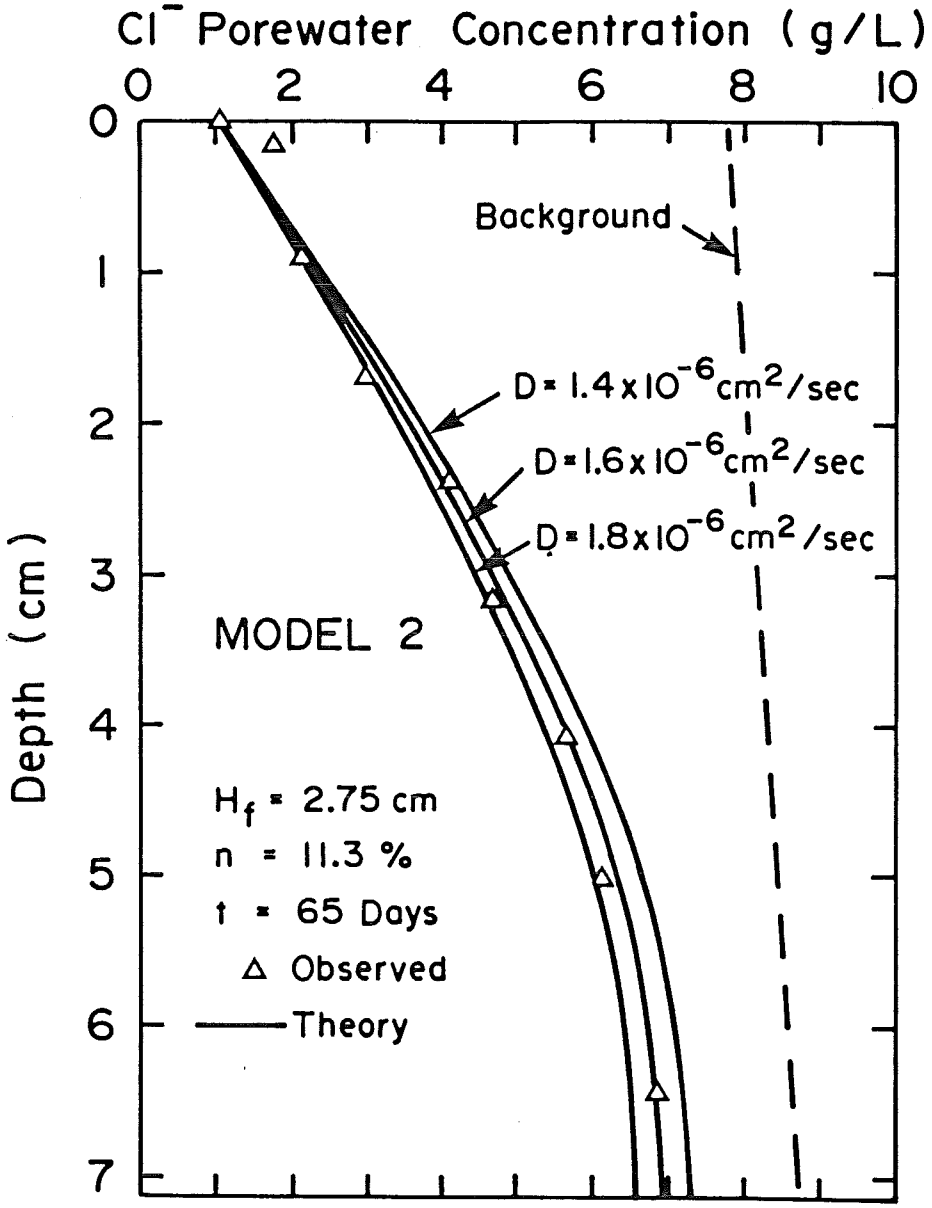


FIGURE 5 CHLORIDE PORE WATER CONCENTRATION VARIATION WITH DEPTH FOR MODEL 2

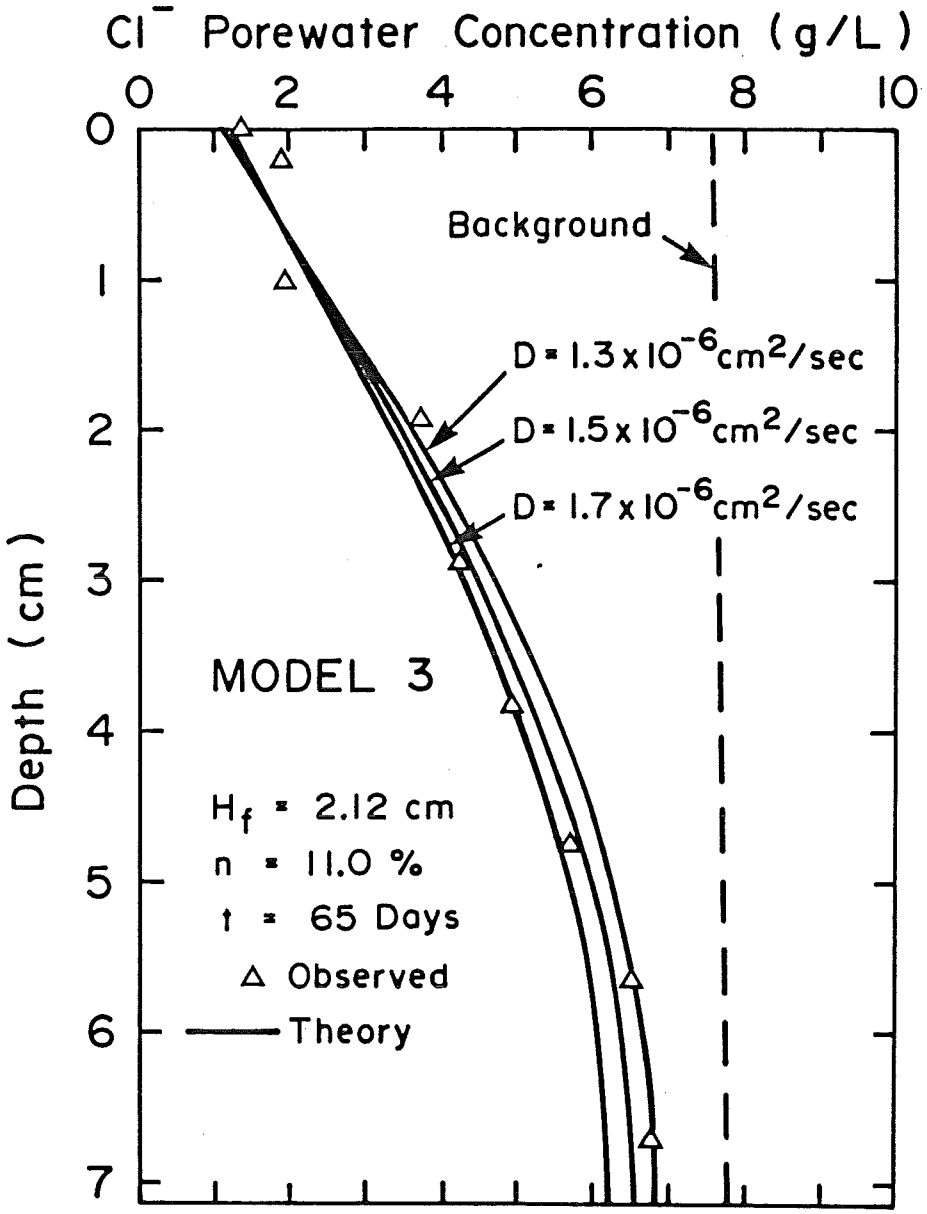


FIGURE 6 CHLORIDE PORE WATER CONCENTRATION VARIATION WITH DEPTH FOR MODEL 3

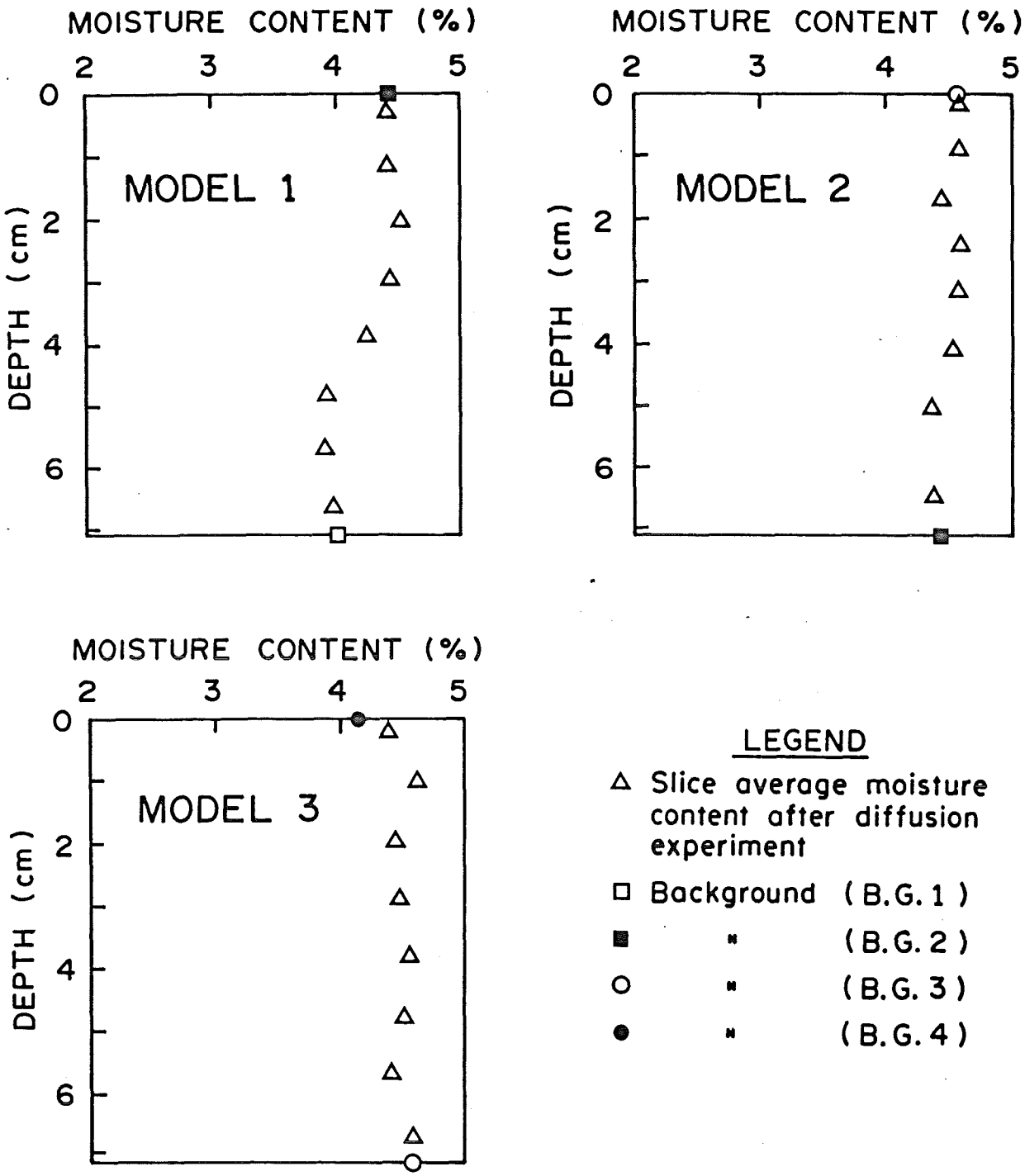


FIGURE 7 MOISTURE CONTENT VARIATION WITH DEPTH AFTER DIFFUSION