LABORATORY DETERMINATION OF CHLORIDE DIFFUSION
COFFICIENT IN AN INTACT MUDSTONE

by

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ABSTRACT

An experimental determination of chloride diffusion coefficient in saturated, intact Bison mudstone is described. Laboratory tests simulating one dimensional diffusive transport were performed by placing distilled water directly above a sample of Bison Mudstone having a high initial concentration of chloride in its pore water. Chloride and other species naturally occurring in the pore water were then permitted to diffuse out of the sample and into the distilled water reservoir for a period of up to 34 days. At the end of the test, the sample was sectioned, and the chloride pore water concentration profile measured. Fickian diffusion theory was then used to deduce the diffusion coefficient (D). The diffusion coefficient for chloride at a temperature of 10° C ranged from 1.5 to 2.0 x 10^{-6} cm ^{2}/sec, from which a corresponding tortuosity factor (τ) ranging from .15 - .20 can be calculated.

Based on pore size measurements, double layer thickness and consideration of the hydrated ionic diameter of chloride, the "effective porosity" available for chloride diffusion is approximately equal to the total porosity calculated from the moisture content of the rock.

For comparison, an attempt was made to obtain the diffusion coefficient for bromide diffusing into the sample, simultaneous with chloride diffusing out. It was found, however, that the concentration profile obtained for bromide could not be fitted by the Fickian diffusion theory, due to interactions between bromide and other species naturally occurring in the rock sample.

KEY WORDS   Diffusion, Rock Matrix, Chloride, Bison Mudstone,
                   Laboratory Study

SUMMARY

The measurement of chloride diffusion coefficient on samples of intact, saturated mudstone using a simple non-steady state technique is presented. The chloride diffusion coefficient measured by this technique may be useful in modelling contaminant transport along fractures with diffusion into the rock matrix.

INTRODUCTION

The evaluation of contaminant transport from waste disposal sites or subsurface chemical repositories located in fractured rock requires consideration of advective-dispersive transport along the fractures and diffusive transport from the fractures into the surrounding rock matrix. Advective-dispersive transport along the fractures represents the dominant mode of contaminant migration from such facilities. The process of matrix diffusion allows contaminants to be stored in micropores where they are essentially immobile relative to their potential migration along fractures. 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 non-reactive contaminants at any point along the fracture (see Freeze and Cherry, 1979 for a general discussion).

In order to mathematically model contaminant transport along fractures with diffusion into the rock matrix, it is necessary to estimate the diffusion coefficient of the contaminant in the rock matrix (eg., see Rowe and Booker, 1989). For practical purposes, the diffusion coefficient of a species in a saturated porous media (D) may be estimated by the empirical expression,

$$D = \tau \times D_o \qquad\qquad [1]$$

where D_o is the diffusion coefficient of the species in pure aqueous solution, and τ is the tortuosity of the porous media. The

aqueous solution diffusion coefficient may be obtained from the literature (e.g, American Institute of Physics Handbook, 1972; Wilke and Chang, 1955). The tortuosity factor can be considered as a correction factor ($0.0 < \tau < 1.0$) which accounts for the fact that pathways for diffusion in a porous media are longer and more tortuous than in aqueous solution. Although only approximately true (see Quigley et. al., 1987), the tortuosity is often assumed to be a property of the porous media, depending on fabric and pore structure rather than the nature of the diffusing species. Hence, it is often estimated based on the results of laboratory diffusion experiments for simple non-reactive species such as chloride (Cl^-). According to Eqn. 1, the tortuosity factor obtained from laboratory diffusion tests for Cl^- might be useful to estimate the diffusion coefficient for any other species provided its diffusion coefficient in aqueous solution is known.

In a previous study (Barone et. al., 1990), a simple non-steady state technique was used to measure the chloride diffusion coefficient on samples of intact, saturated, Queenston Shale. The purpose of this paper is to present the chloride diffusion coefficient obtained (by the same technique) on samples of Bison Mudstone. Unlike the Queenston Shale, the Bison Mudstone shows a significant amount of moisture uptake at the end of the diffusion test. Hence, a second objective is to discuss this increase in moisture content, and its effect on the measured chloride diffusion coefficient. Finally, results of a slightly modified technique, designed to yield the matrix diffusion coefficient for chloride and bromide (Br^-) simultaneously on a single sample, are presented.

THEORETICAL DEVELOPMENT

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

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} \qquad\qquad [\,2\,]$$

where c is the species concentration in the pore water at time t and depth z, and D is the porous media diffusion coefficient for the solute. It should be noted that the concentration term (c) refers to the mass of solute per unit volume of pore water which is accessible to the diffusing species. This is important for very dense porous media 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 being too small to accommodate the hydrated solute.

In the tests conducted by the authors, a known volume of distilled water was placed in contact with a core sample of intact, saturated Bison Mudstone as shown in Fig. 1. Chloride, and other species naturally occurring in the pore water of the mudstone were then permitted to diffuse upwards 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,

$$c_T(t) = \frac{1}{H_f} \int f_T(t)\,dt \qquad\qquad [\,3\,]$$

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, viz.

$$f_T(t) = n' \ D \left(\frac{\partial c(t)}{\partial z} \right)_T \qquad [\ 4\ ]$$

where n' is the porosity available for chloride diffusion within the sample. As previously noted, for very compact porous media , a portion of the porewater 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. 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.

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

$$f_B(t) = n' \ D \left(\frac{\partial c(t)}{\partial z} \right)_B = 0 \qquad [\ 5\ ]$$

One-dimensional diffusion of chloride through the mudstone sample is thus described by Eqs. 2 - 5. 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., 1990). 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 classical Fickian diffusion theory.

After allowing time for outwards diffusion (~31 days), the sample was sectioned and the chloride concentration profile with depth was determined. Program POLLUTE 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 which was judged to provide the "best fit" to the experimental profile was selected as the experimental chloride diffusion coefficient.

A second type of test, designed to simultaneously yield a diffusion coefficient for both chloride and bromide, involved spiking the distilled water reservoir with potassium bromide. For this case, diffusion of bromide into the sample is described by Eqs. 2 - 5, with the exception that the upper boundary condition (Eqn. 2) is taken as,

$$c_T(t) = c_o - \frac{1}{H_f} \int f_T(t) \, dt \qquad\qquad [\ 6\ ]$$

where, c_o is the Br^- concentration in the reservoir at the start of the test.

BISON MUDSTONE

Core samples of Bison Mudstone (5.3 cm diameter) were obtained from a site near Oklahoma City. Upon removal from the ground, the core samples were wrapped with aluminum foil and coated with paraffin wax in order to maintain their natural moisture content. On arrival at the University of Western Ontario Laboratory, the core samples were stored at 10° C prior to use. Typically, the diffusion tests were started 28-45 days after coring. All specimens chosen for diffusion testing were free of visual fractures.

A total of five specimens ($\approx$ 7cm in length) were selected for the diffusion tests (Sa #1 to 5). The depth below ground surface, geotechnical index characteristics, and mineralogy are summarized for each test sample in Table 1. The data given for moisture content represent average values obtained from 1 cm thick core sections cut directly above and below each test specimen. Specific gravity, dry density, and mineralogy were determined on a single sample from either directly above or below the test sample.

The degree of saturation for each sample was calculated based on dry density, moisture content, and specific gravity. The dry density was measured on approximately 5 grams of intact, freeze dried mudstone, using a Micromeritics Mercury Porosimeter. The degree of saturation calculated this way ranged from 98 - 100% for all samples except sample #4 which gave a value of 91%. The moisture content, specific gravity, and the degree of saturation were then used to calculate the total porosity (n).

For each test sample, the background concentrations for various dissolved and adsorbed inorganic species are summarized in Table

2. The values given represent average values based on the slices of core cut above and below the test sample. Dissolved concentrations were obtained by a single washing of 8 grams of oven dried, pulverized (<76 um) mudstone in 50 mL of distilled water. The mixture was agitated for about 15 minutes and centrifuged at 2,500 rpm for 30 minutes. 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. It was found that the supernatant concentrations obtained for chloride upon washing the pulverized mudstone for approximately 15 minutes was not significantly different than that obtained upon washing for 24 hours, indicating that the wash duration of 15 minutes was adequate.

Supernatant concentration was converted to pore water concentration using the relationship:

$$\text{pore water concentration (g/L)} = \frac{c_s \, V \, \rho}{m \, w} \qquad [\,7\,]$$

where, c_s = species concentration in the supernatant (g/L)
  V = volume of supernatant (L)
  m = mass of oven dried sample used in the wash (g)
  w = moisture content of slice prior to oven drying
  ρ = density of pure water at 22°C (1,000 g/L)

It should be noted again that pore water concentrations calculated using Eqn. 7 represent the dissolved "free" mass of the species per unit volume of "total" pore water.

The adsorbed cation concentrations (Table 2) were measured by washing 1.5 g of air dried, powdered material in 50 mL Silver

Thiourea solution (pH =7.0) for about 24 hours. With this technique, any adsorbed cations on the clay exchange sites are replaced by the silver ion from the wash solution (Chabbra, 1975). The mixture was then centrifuged and the supernatant analyzed for the cations by atomic absorption spectrometry.

EXPERIMENTAL PROCEDURES

As shown in Figure 1, the diffusion model consists of a hollow plexiglass cylinder with an inside diameter of 6.7 cm and length of approximately 11 cm. The diffusion test specimens (≈7cm in length) were cut from core sections using a oil lubricated diamond saw, and immediately wiped free of oil using ethanol. Each test specimen was then coated along its sides with silicone seal and fitted with a tight rubber membrane extending from the bottom to about 5 cm above the top of the specimen. The rubber membrane serves to prevent drying along the sides and allows for the containment of a reservoir on the top of the specimen. Placement of the silicone seal along the sides of the sample helps to ensure a good seal along the membrane/sample interface. To prevent drying through the bottom , a circular piece of rubber membrane material was cut to the same diameter as the specimen and adhered to the bottom using a silicone seal bond. The specimen 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. The top of the cylinder was then fitted with a polyethylene cap plate and the entire model transferred to a controlled environmental chamber where it was

maintained at a constant temperature of 10° C for a period of about 31 days. During this period the reservoir solution was mixed periodically so as to maintain a relatively uniform concentration throughout the reservoir depth.

At the end of each test, the rock sample was removed and sectioned into 6 segments using an oil lubricated diamond saw. Immediately, each slice was wiped free of oil using ethanol, weighed, and placed into a 100°C oven for at least 48 hours for determination of average moisture content (w). The vertical distribution of chloride concentration was measured by pulverizing each oven dried slice to < 76 μm and then washing the chloride out using the distilled water wash technique previously described.

Calculation of the Cl⁻ pore water concentration from that measured in the supernatant was performed using Eqn. [7], taking the "w" term as the moisture content measured for the slice at the end of the diffusion test. The resultant Cl⁻ concentration profile with depth, was then fitted using program POLLUTE, taking the "effective" porosity (n') as equal to the total porosity distribution obtained at the end of the test. The diffusion coefficient judged to provide the "best fit" to the experimental profile was selected as the experimental chloride diffusion coefficient.

For the test in which the distilled water reservoir was spiked with reagent grade potassium bromide, the bromide concentration profile at the end of the test was obtained using Eqn. 7 and the same wash technique used for chloride. The only difference was that the bromide concentration in the wash supernatant was measured by

ion chromatography. The theoretical analysis of the bromide profile was also conducted using Program POLLUTE, taking the "effective" porosity equal to the total porosity distribution at the end of the test.

TESTS CONDUCTED

A diffusion test was conducted on each of the five specimens described in Table 1. For sample #5 the reservoir solution contained 2.2 g/L potassium bromide to permit determination of diffusion coefficient for bromide diffusing into the sample simultaneously with chloride diffusing out. Table 3 shows those details of each test, which are pertinent to the theoretical analysis.

EXPERIMENTAL RESULTS AND INTERPRETATION
Moisture Content After Diffusion

For each specimen, the moisture content profile at the end of the diffusion period is shown on Figure 2. Also shown are the initial profiles inferred from moisture contents measured on the background slices above and below the test sample.

Comparison of the initial and final profiles suggests that some moisture uptake had occurred in each test. The increase in moisture content may be attributed to: initial negative pore pressures resulting from the relief of in situ total stresses, osmotic water migration from the reservoir into the sample, and the swelling of clay double layers. Firstly, the relief of total stress upon sampling may have produced an initial negative pore pressure

throughout the specimen. When the specimen is exposed to water, as in the tests conducted, the negative pore pressure would be relieved by moisture uptake, resulting in an increase in moisture content throughout the entire sample. Secondly, osmotic water migration from the reservoir into the sample may have occurred in response to the initially low total ion concentration of the reservoir solution relative to the bulk pore fluid. Finally, the decrease in total ion concentration of the bulk pore fluid (due to diffusion into the reservoir) may have led to swelling of the clay double layers. The net effect of this mechanism would be an increase in repulsive pressure between the clay particles (e.g., see Mitchell, 1976), and subsequent swelling of the sample. It should be noted however, that the absence of a more dominant moisture content increase near the sample/reservoir interface (where the depletion of pore water ions is largest), suggests that the influence of this mechanism is probably small in comparison to the previous two.

Considering each test sample to be completely saturated at the end of the diffusion test, the percentage volume change corresponding to the moisture content increase was calculated. Samples #1 - 3 yielded a percentage volume change ranging from 0.50 - 0.56%. Since samples #1 - 3 were taken from similar depths (Table 1) and have similar pore water chemistries (Table 2), the swelling mechanisms should lead to similar volume changes which is the case. For sample #4, the percentage volume change (1.6%) was significantly higher. This may be explained by the greater sample depth and higher pore water concentrations for sample #4, which

would augment stress relief swelling and osmotic water migration into the sample, respectively. Furthermore, sample #4 was drier than the rest of the samples and probably in a state of greater water deficiency (see Table 1). For sample #5, which was tested using a reservoir solution of 2.2 g/L KBr rather than pure distilled water, the percentage volume change (0.23%) was the least, despite the similarities in depth and pore water chemistry with sample #4. Although part of the increases in moisture content were probably suppressed in the upper part of this sample by the more saline reservoir, potassium diffusing into the sample may also have contributed. Adsorption of lesser hydrated potassium onto the exchange sites at the expense of sodium (as will be illustrated later) would cause the clay double layers to contract, thus inhibiting swelling.

For the diffusion tests conducted, the significance of sample swelling lies in its effect on the observed concentration profile , and in turn, the measured diffusion coefficient for the species of interest. This will be discussed in the following section.

Concentration Profiles and Determination of Diffusion Coefficient For Chloride

The Cl^- concentration profiles obtained from the wash technique are presented for each test on Fig. 3. Also presented are the initial Cl^- concentration profiles inferred from top and bottom background slices. To establish the test method variability in the Cl- pore water concentration measurements, a wash extraction was performed on three powdered samples from selected slices of samples

·#2 and #4. The spreads in values are indicated by means of a range bar. This exercise indicated a maximum uncertainty of about ± 6%. As a check on the experimental technique, the percentage recovery of Cl⁻ (i.e., the ratio of Cl⁻ mass recovered at the end of the test to the total Cl⁻ mass at the start of the test) was calculated. The Cl⁻ mass at the start of the test was inferred from the background Cl⁻ concentrations above and below the test sample. For all tests, the deviation from 100% recovery was within ± 3%.

The chloride pore water concentration data shows a significant decrease with respect to the background concentration, as a result of diffusion upwards into the distilled water reservoir. In order 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.

Values of experimental diffusion coefficient and corresponding tortuosity factor obtained for each sample are presented in Table 5. For a temperature of 10° C, the experimental Cl⁻ diffusion coefficient varied from 1.5 to 2.0 x 10^{-06} cm ^{2}/s which corresponds to a tortuosity ranging from 0.15 - 0.20. It should be noted that the tortuosity factor (i.e., $[D / D_o]_{Cl}^-$) was calculated taking D_o as 0.99 x 10^{-05} cm^2/s. This value of D_o represents an approximate aqueous diffusion coefficient for both Na^+ and Cl^- at 10°C when diffusing together from a source solution containing about 0.3 Molar NaCl (American Institute of Physics Handbook, 1972).

Except for sample #4, which showed the greatest swelling, the

test specimens provided a diffusion profile which could be adequately fitted by the theoretical model, suggesting that the observed swelling had little effect on the concentration profile developed at the end of the test. For these samples, the scatter of the chloride data about the best fit theoretical curve appears to be random and representative of the uncertainty in the wash extraction procedure used. The experimental data from sample #4, however, show a distinct trend of deviation from the theoretical curves which can not be explained in terms of uncertainty in Cl^- concentration. For this test, the measured concentrations for the upper half to two thirds of the sample fall below the theoretical values. It is considered that this deviation from the theoretical diffusion profiles is primarily due to swelling of the specimen, which contributes to a decrease in the chloride concentration within the sample. For example, based on Equation 7, an increase in moisture content from 9% (background) to about 11% as noted for sample #4 would result in a 20 % decrease in Cl^- pore water concentration. In so doing, the moisture content increase would have influenced the diffusion process itself, since diffusion is driven by the concentration gradient. Since this additional dilution of chloride pore water concentration is not accounted for by the theoretical model, there is a poor agreement between the theoretical curves and the measured concentration data. Hence, a Cl^- diffusion coefficient is not reported for this sample.

As previously indicated, the measured Cl^- concentration profiles and the theoretical analysis are based on the assumption that the entire moisture content and hence the total porosity is

available to the diffusing Cl^- ions (i.e., n' = n in Eqn. 4.). To assess the validity of this assumption, consideration is given to the distribution of pore size within the rock in comparison to the hydrated diameter of a Cl^- ion. As determined by a Micromeritics Mercury Porosimeter, the distribution of pore sizes in the range 300 - .006 μm in diameter is shown for Sample #2 on Figure 4. The distribution shows a sharp pore size mode centred at about .03 μm. Based on this data as well as pore size data obtained from a Quantachrome Automated Gas Adsorption System (capable of measuring pore sizes in the range .06 - .002 μm), the percentage of total porosity corresponding to various ranges in pore diameter is indicated in Table 6. The data shows that the total porosity is largely derived from pores .06 -.002 μm in diameter, and that approximately 10% of the total porosity is derived from pores outside the range of measurement (i.e., > 300 μm and/or <.002 μm). Considering that the hydrated diameter of chloride is only about .0007 μm (Horvath, 1985, p. 344), it would seem reasonable to assume that essentially all of the total pore spaces are large enough to accommodate the fully hydrated diameter of chloride. Since the rock contains some smectite (eg., see Table 1), consideration is also given to the possibility that some pores may consist mostly of clay double layer water from which chloride would be expelled. Based on the theory outlined by Mitchell (1976), the double layer thickness for a sodium saturated smectite in a solution having a total ion concentration of 0.3 Molar is about .0007 μm. For a calcium saturated smectite, the double layer thickness would be about .0003 μm. Since these thicknesses are

small relative to the range in pore size, it seems that essentially all of the moisture content and thus the total porosity is available to the diffusing Cl^- ions.

Bromide Concentration Profile and Determination of Bromide Diffusion Coefficient

Figure 5 shows the bromide concentration profile obtained for sample #5, which was tested using a reservoir solution of 2.2 g/L KBr in distilled water. The initial Br^- concentration obtained on background slices cut above and below the sample was below the detection limit of the wash technique (i.e., < .03 g/L). Therefore, the initial background concentration profile for Br^- was considered to be zero. As a check on the experimental methods, the percentage recovery for Br^- at the end of the test was calculated as 95%. As for chloride, calculation of the bromide concentration data involved the assumption that essentially all of the moisture content is available to the Br^- ions. Since Br^- has a hydrated diameter similar to that of Cl^-, the previous discussion suggesting the validity of this assumption for Cl^- would also apply for Br^-.

The Br^- concentration profile given in Fig. 5 shows that Br^- migration has extended to the bottom of the sample. In order to maintain charge balance, the diffusion of Br^- into the rock is coupled with the inward diffusion of K^+, despite the fact that the initial K^+ concentration in the source reservoir (0.73 g/L) is less than the initial K^+ pore water concentration (2.10 g/L, Table 2). This is indicated by the decrease in K^+ concentration in the reservoir, from an initial value of 0.73 g/L to a value of 0.17 g/L

at the end of the test (see Table 4).

Comparison of the theoretical curves and experimental data on Figure 5, indicates that the measured Br$^-$ pore water concentration for the top three slices falls below the theoretical curves by an amount which can not be explained by the uncertainty in Br$^-$ pore water concentration. It is believed that the deviation between experimental and theoretical profiles is primarily due to interactions between Br$^-$ and cations naturally occurring in the sample pore water. In explanation, as K$^+$ migrates into the sample with Br$^-$, it adsorbs onto the clay exchange sites at the expense of Na$^+$ (see Fig. 6). The desorbed Na$^+$ must then help provide charge balance for Br$^-$ diffusing towards the base of the sample. However, because Na$^+$ experiences an upward concentration gradient (much stronger in magnitude than that for Br$^-$), some of the Br$^-$ which is coupled with Na$^+$ would be driven back up into the reservoir. This would reduce the net Br$^-$ flux into the sample, and in turn would reduce the Br$^-$ pore water concentration relative to that predicted by the theoretical model. For this reason, a diffusion coefficient for Br$^-$ is not given.

SUMMARY AND CONCLUSION

This paper has illustrated the direct measurement of chloride diffusion coefficient on samples of intact Bison Mudstone using a simple nonsteady state technique. For the conditions examined in these tests, it is concluded that the diffusion coefficient for chloride at a temperature of 10° C ranged from 1.5 to 2.0 x 10^{-6} cm^2/s which corresponds to a tortuosity, τ, ranging from .15 -.20.

Based on pore size measurements, thickness of clay double layers, and the hydrated ionic diameter for chloride, the "effective" porosity of the Bison Mudstone with respect to the diffusion of chloride is considered to be approximately equal to the total porosity determined from moisture content.

Comparison of the moisture content profiles before and after the diffusion test, indicated that some moisture uptake had occurred in all samples. For four out of the five samples tested, the measured increase in moisture content corresponded to a percentage volume change ranging from 0.23 - 0.56%. Since the Cl^- concentration profiles for these samples was adequately fitted by the Fickian diffusion theory, it is suggested that the volume change did not significantly affect the developed diffusion profile at the end of the test. For one sample, however, the percentage volume change (1.64%) was significantly larger than the others. The additional influx of water for this sample decreased the Cl^- pore water concentration by an amount which was significant relative to the dilution generated by Cl^- diffusion up into the reservoir. This resulted in a lack of agreement between the observed Cl^- concentration profile and the theoretical profiles. A diffusion coefficient for this specimen was not given.

Finally, for a single test, the distilled water reservoir was spiked with 2.2 g/L of KBr in an attempt to determine the diffusion coefficient and corresponding tortuosity factor for Br^- diffusing into the sample, simultaneously with Cl^- diffusing out. For this case, the Br^- concentration profile at the end of the test could not be fitted by the theoretical model due to interactions between

Br- and other naturally occurring cations diffusing out of the sample.

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APPENDIX II. NOTATION

c = species concentration in the pore water

c_o = species concentration in the reservoir at the start of the test

c_s = species concentration in the wash supernatant

c_T = species concentration in the reservoir

D = species diffusion coefficient in the porous media

D_o = species diffusion coefficient in pure aqueous solution

f_T, f_B = mass flux of the dissolved species across the top and bottom of the sample, respectively

H_f = equivalent height of distilled water above the sample

m = mass of oven dried sample used for measuring Cl^- pore water concentration

n = total porosity of the porous media

n' = porosity available for dissolved species diffusion (effective porosity)

t = time

V = volume of the wash supernatant

w = moisture content

z = depth

τ = tortuosity of the porous media

ρ = density of pure water at 22° C

TABLE 1   PHYSICAL CHARACTERISTICS AND COMPOSITION OF THE MUDSTONE (Average Values)

	SAMPLE #				
	1	2	3	4	5
Depth Below Ground Surface (m)	44.1	44.8	43.0	85.2	95.8
Moisture Content, %	10.46	10.70	12.18	9.00	11.14
Specific Gravity	2.73	2.81	2.81	2.77	2.76
Dry Density, gm/cm^3	2.11	2.17	2.09	2.17	2.09
Degree of Saturation, %	98	100	99	91	99
Total Porosity, %	22.56	23.12	25.69	21.50	23.70
Mineralogy, %					
Quartz	28	12	17	36	34
Calcite	1	2	2	–	–
Dolomite	8	12	7	6	5
Na Feldspar	8	4	3	4	7
Illite	34	37	40	30	25
Chlorite [1] / Smectite	21	33	31	24	29
Cation Exchange Capacity (meq/100g solids)	27	35	41	44	43

[1]   interlayered with illite

TABLE 2   CHEMICAL CHARACTERISTICS OF THE MUDSTONE (Average Values)

	Sample #				
	1	2	3	4	5
Porewater Species, (g/L)					
Chloride	2.69	1.50	1.64	5.17	5.35
Sulphate	4.62	4.52	4.53	5.20	5.52
Sodium	4.64	4.00	4.09	5.83	6.28
Calcium	<0.06	<0.06	<0.05	<0.04	<0.03
Magnesium	0.17	0.26	0.20	0.32	0.38
Potassium	0.93	1.75	1.29	1.85	2.10
Sum of Porewater Species Molar Concentrations	0.36	0.32	0.31	0.51	0.55
Adsorbed Species (meq/100g dry wt)					
Calcium	11.33	14.55	14.60	18.10	16.95
Magnesium	8.07	9.90	10.73	15.50	15.20
Sodium	4.42	6.95	7.68	6.94	7.00
Potassium	2.92	3.73	7.80	3.05	3.60

TABLE 3   SPECIFIC DETAILS PERTINENT TO THE THEORETICAL ANALYSIS
           OF EACH TEST

Sample #	Sample Height (cm)	H_f (cm)	Test Duration (days)	Background Cl^- Concentration (g/L)	Total Porosity (%)
1	7.1	3.0	31	2.90 ; 2.48	22.5 ; 22.7
2	7.0	3.1	34	1.48 ; 1.51	23.3 ; 23.0
3	7.0	3.1	32	1.76 ; 1.52	26.1 ; 25.2
4	7.0	3.1	31	5.04 ; 5.30	21.4 ; 22.0
5	5.7	3.6	31	5.06 ; 5.63	24.6 ; 22.7

[1] measured on a core section taken directly (above ; below) the
     test sample

TABLE 4 RESERVOIR CONCENTRATIONS AT THE END OF EACH TEST

Sample #	Cl⁻	Br⁻	SO₄⁼	Na⁺	Ca²⁺	Mg²⁺	K⁺
			Concentration, g/L (meq/L)				
1	0.38 (10.72)	— —	0.42 (8.75)	0.44 (19.13)	<0.01 (<0.50)	<0.01 (<0.82)	<0.01 (<0.25)
2	0.23 (6.49)	— —	0.34 (7.08)	0.32 (13.91)	<0.01 (<0.50)	<0.01 (<0.82)	<0.01 (<0.25)
3	0.30 (8.46)	— —	0.43 (8.96)	0.40 (17.39)	<0.01 (<0.50)	<0.01 (<0.82)	<0.01 (<0.25)
4	0.82 (23.13)	— —	0.44 (9.17)	0.62 (26.96)	0.02 (1.00)	<0.01 (<0.82)	<0.01 (<0.25)
5	0.80 (22.50)	1.33^1 (16.68)	0.44 (9.17)	0.89 (38.70)	0.04 (2.07)	0.01 (1.15)	0.17^2 (4.44)

[1] initial Br⁻ concentration (@ t=0) = 1.50 g/L

[2] initial K⁺ concentration (@ t=0) = 0.73 g/L

TABLE 5 SUMMARY OF EXPERIMENTAL DIFFUSION COEFFICIENTS FOR Cl^-

Sample #	Experimental Diffusion Coefficient @ 10° C (cm^2/s)	Tortuosity Factor
1	1.5×10^{-06}	0.15
2	1.5×10^{-06}	0.15
3	2.0×10^{-06}	0.20
4	not determined	-
5	2.0×10^{-06}	0.20

TABLE 6 PORE SIZE DISTRIBUTION FOR THE BISON MUDSTONE*

Pore Diameter (μm)	% of Total Porosity	Method of Analysis
300 - .06	~10 %	Micromeritics Mercury Porosimeter
.06 - .006	~66 %	"
.006 - .002	~14 %	Quantachrome Automated Gas Adsorption System
	$\overline{\Sigma = 90 \%}$	

* obtained on freeze dried mudstone

Polyethylene top
plate with 1.0 cm Ø
port

Distilled water

Rubber membrane

11.0 cm

Plexiglass cylinder
6.7 cm I.D.

~7 cm

Mudstone core sample
5.3 cm Ø

Rubber membrane material
cut to same diam. as core
sample and placed with a
silicone seal bond
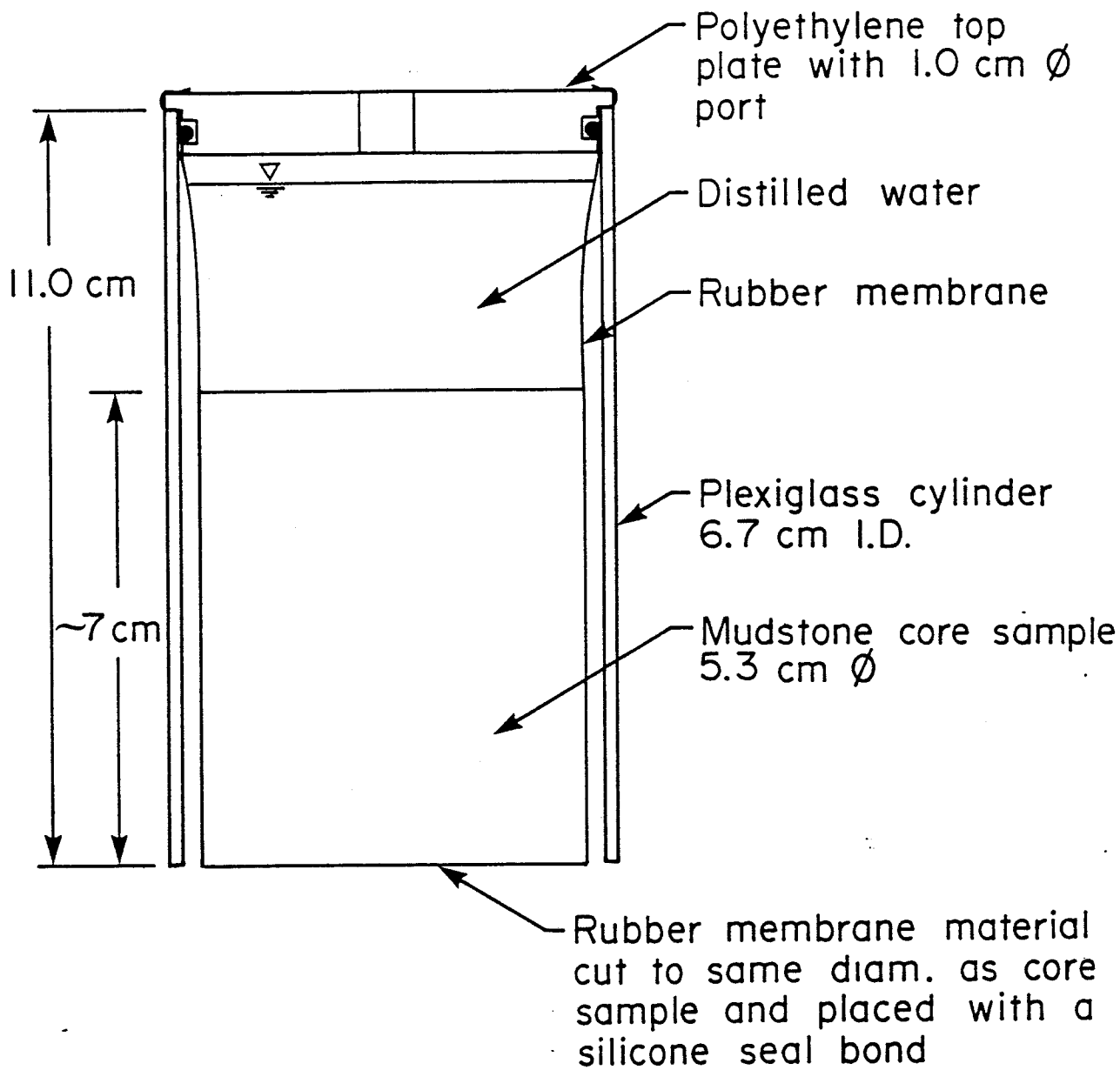
FIGURE 1   SCHEMATIC DIAGRAM OF AN ASSEMBLED DIFFUSION MODEL
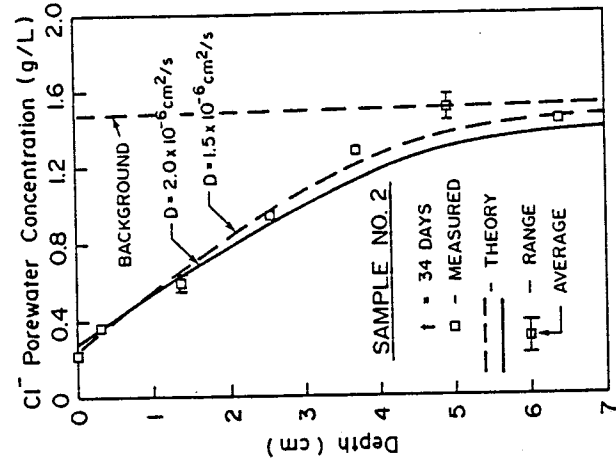
FIGURE 2   MOISTURE CONTENT INCREASES WITH DEPTH AFTER DIFFUSION
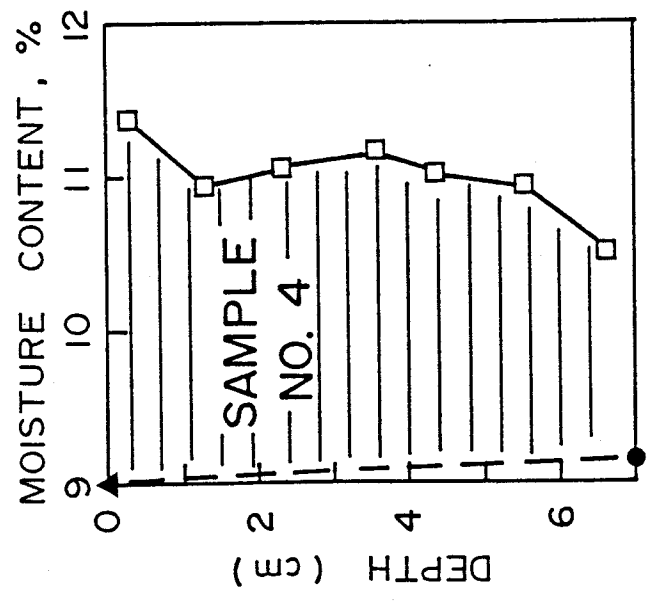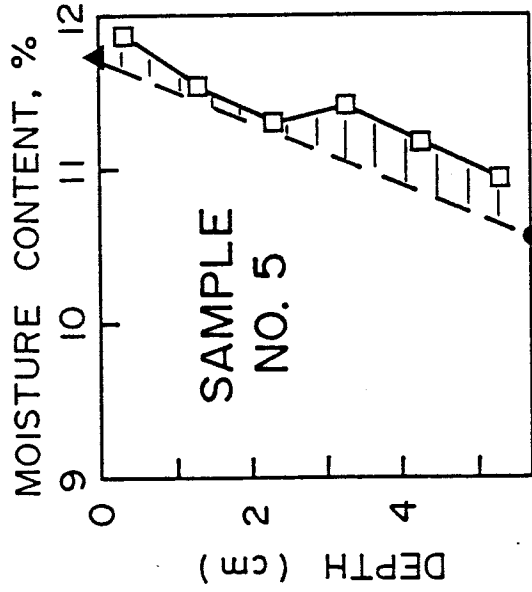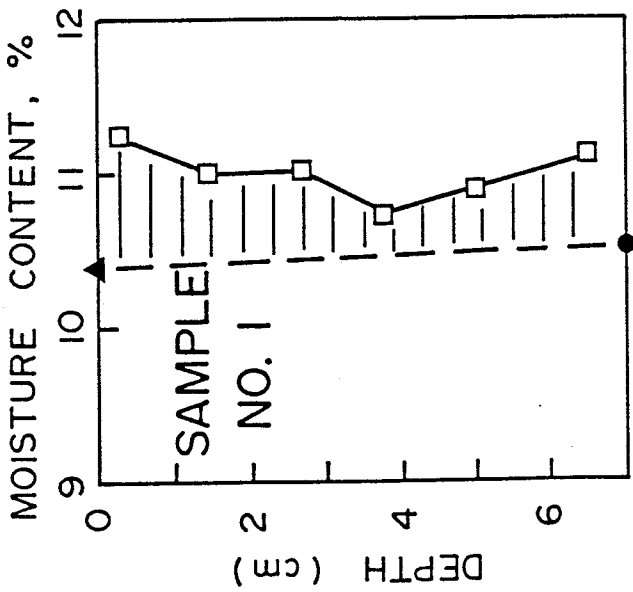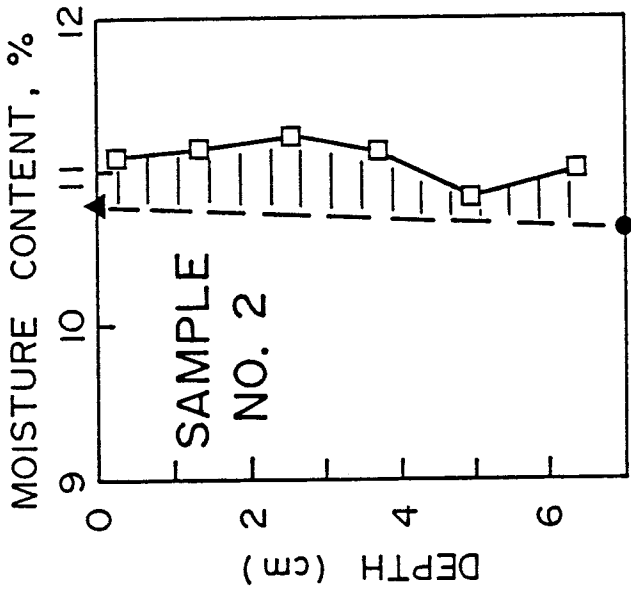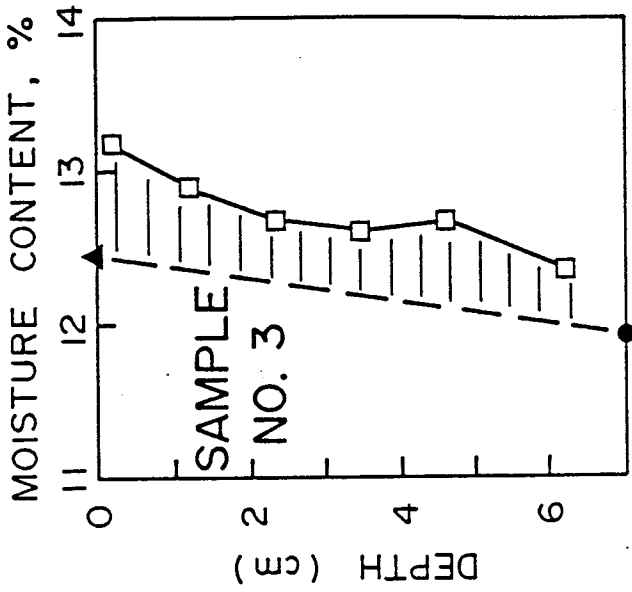
LEGEND

□ - Slice average moisture content after diffusion experiment

▲, ● - Background moisture content obtained from a core section directly above and below the test sample
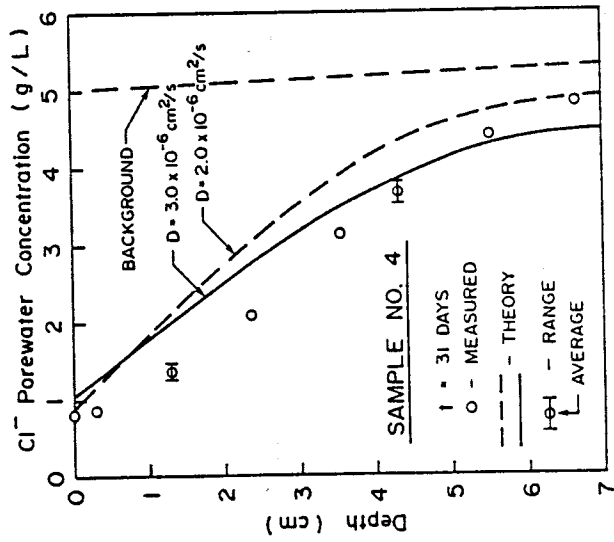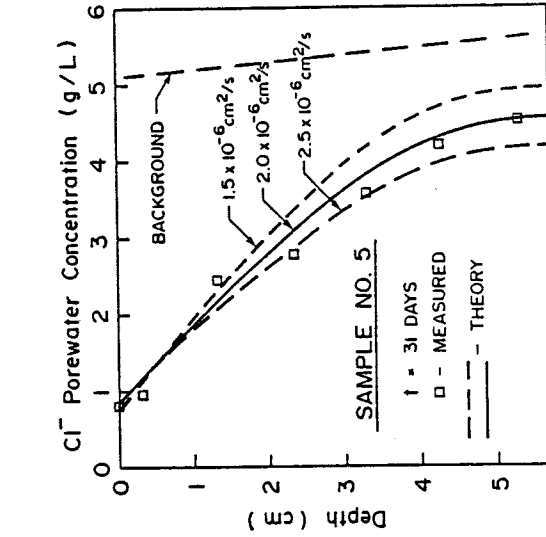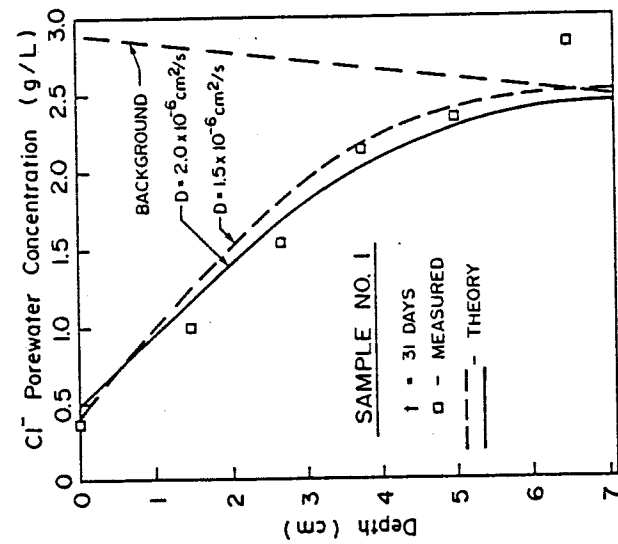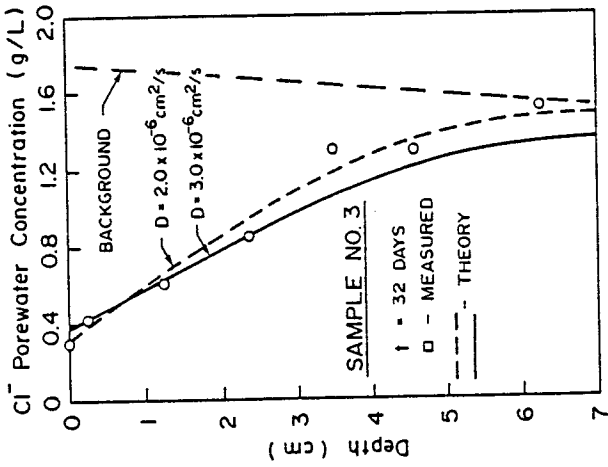
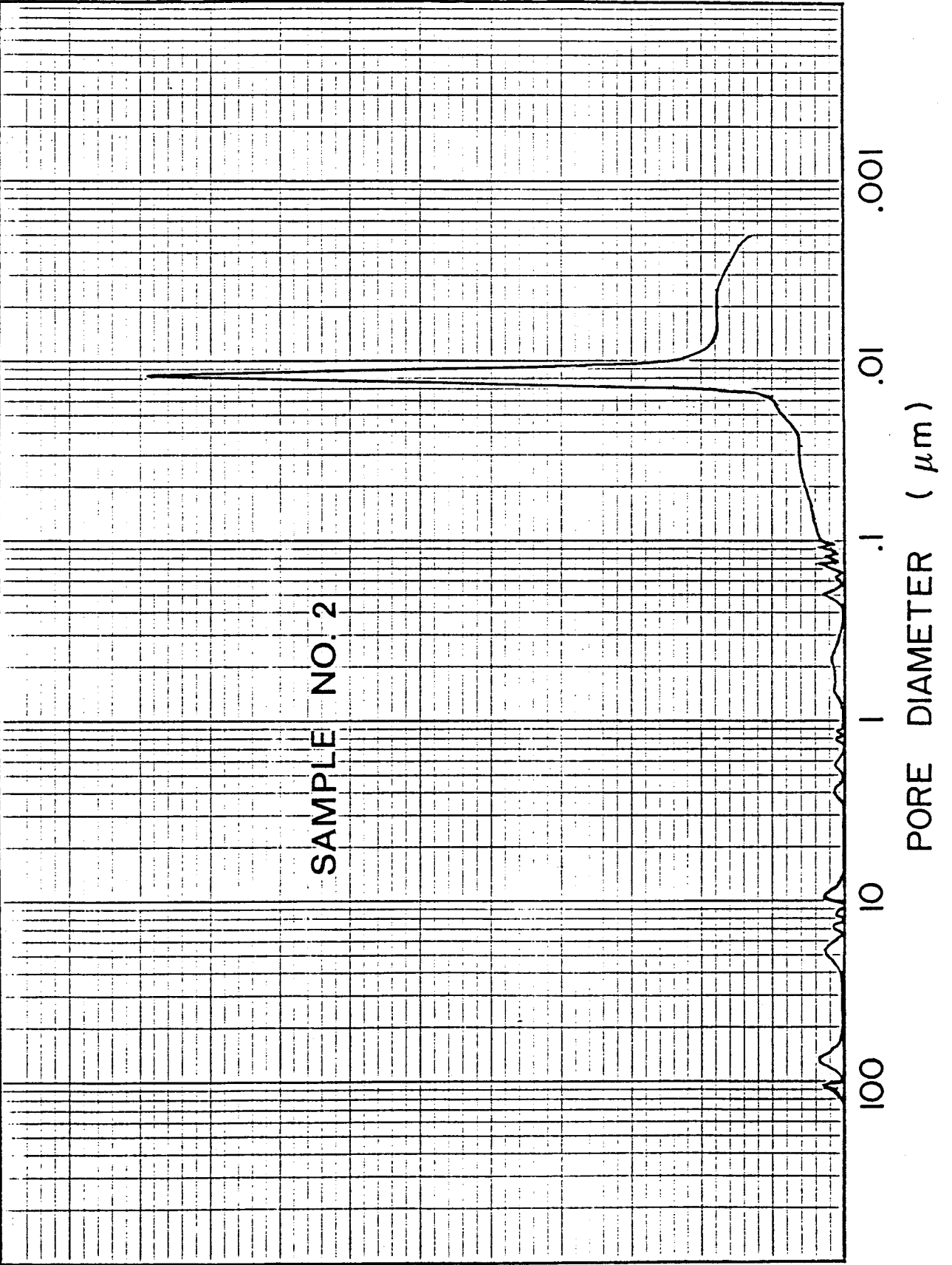FIGURE 3   CHLORIDE PORE WATER CONCENTRATION VARIATION WITH DEPTH FOR SAMPLES #1-5

FIGURE 4   PORE SIZE DISTRIBUTION FOR SAMPLE #2 (BY MERCURY POROSIMETER)
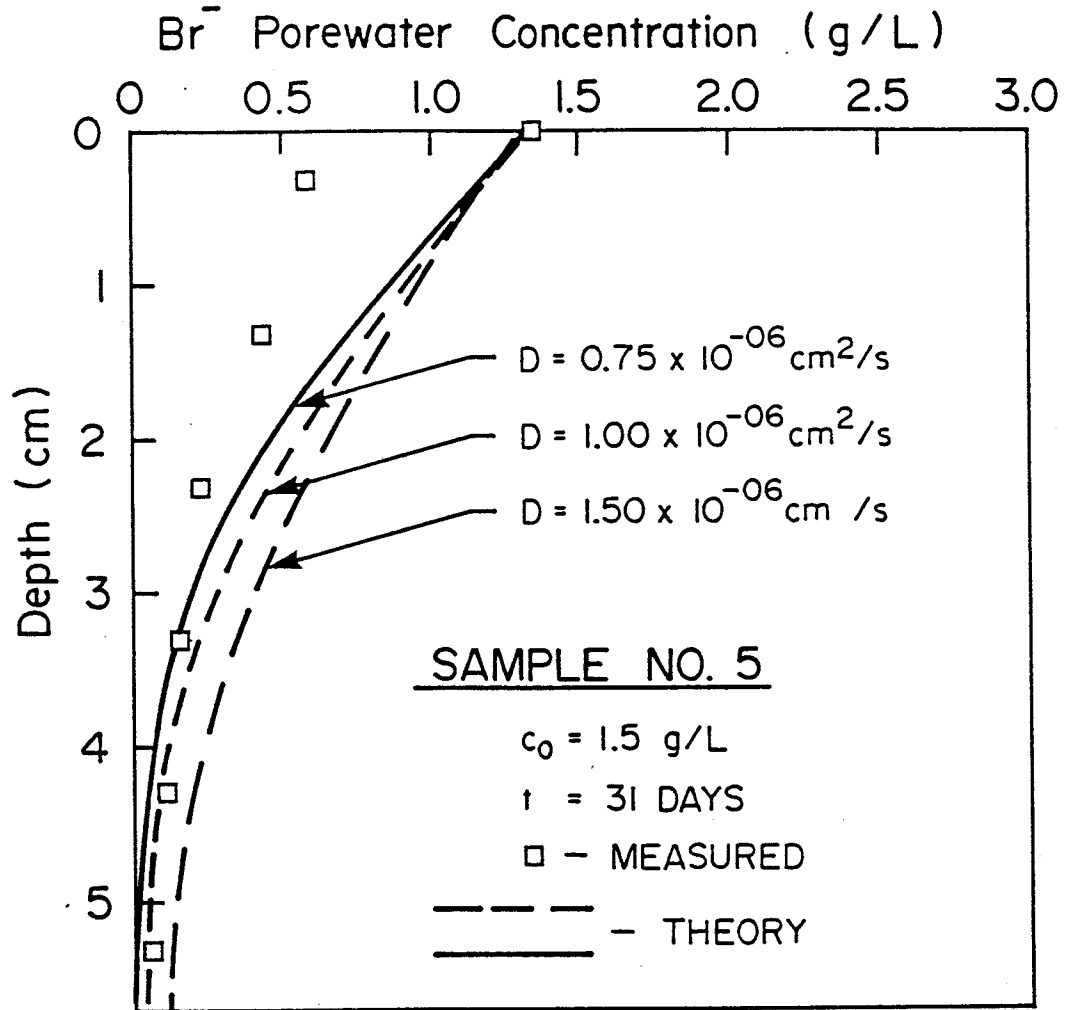
FIGURE 5   BROMIDE PORE WATER CONCENTRATION VARIATION WITH DEPTH
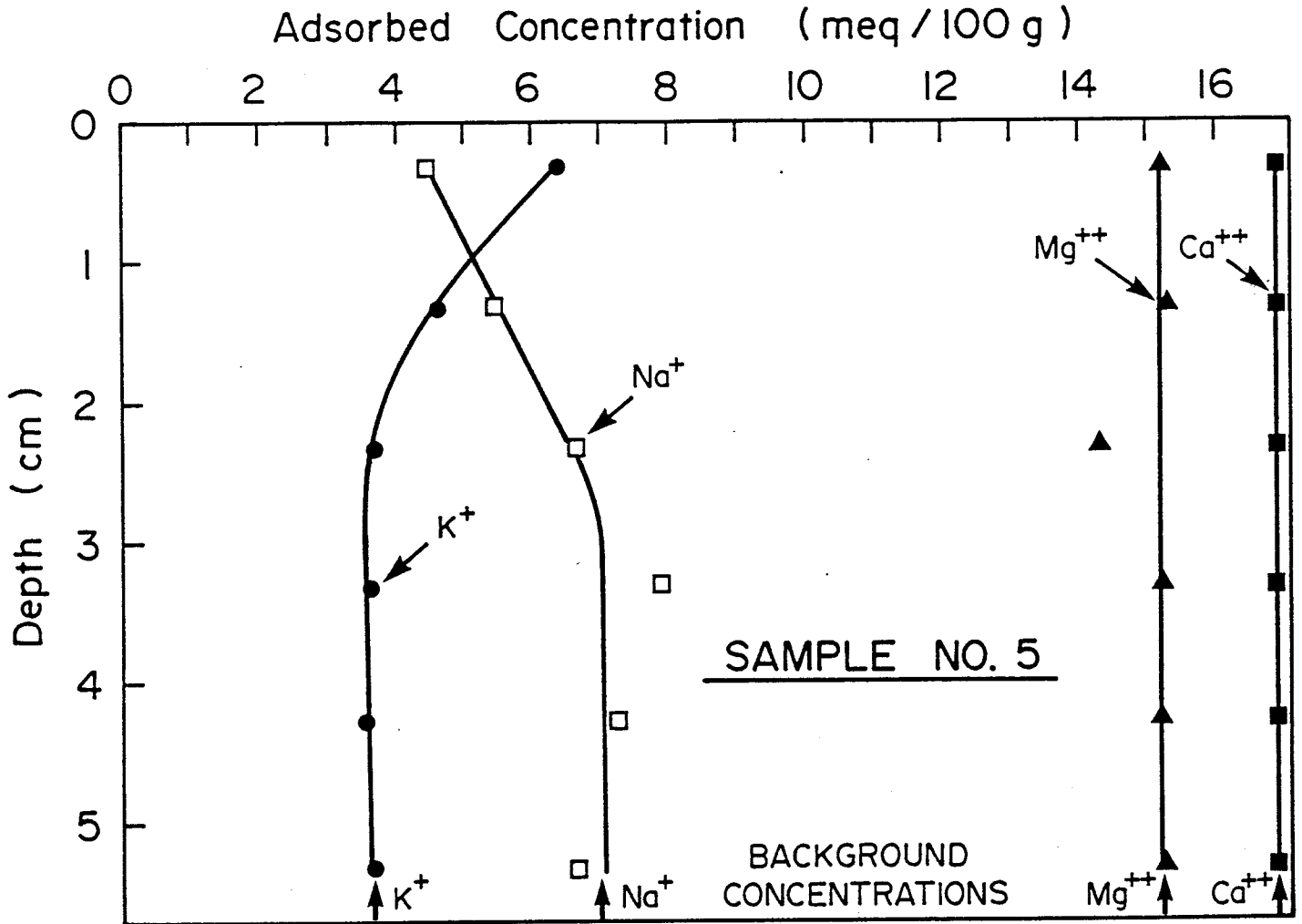   FOR SAMPLE #5

FIGURE 6   ADSORBED CONCENTRATION VARIATION WITH DEPTH FOR SAMPLE #5
            (t = 31 Days)