

THEORETICAL EVALUATION OF THE THROUGH-DIFFUSION TEST FOR DETERMINING THE TRANSPORT PROPERTIES OF GEOLOGICAL MATERIALS

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ABSTRACT

The laboratory diffusion test is a well-established and widely adopted approach for characterizing the transport properties of geological materials. Although there are several types of diffusion tests currently available, through-diffusion has been extensively used for testing rock samples and the data are interpreted with the time-lag method. The time-lag method is based on an approximate analytical solution assuming constant inlet and outlet concentrations at the ends of a test specimen. To meet these conditions, a large-sized cell, or reservoir, is generally used at the inlet side as a container for the source solution, and the solution in the measurement cell at the outlet side is continuously replaced with fresh solution throughout the duration of the test. This procedure may be time-consuming, cumbersome, and may introduce errors due to differences between analysis assumptions and actual test conditions. In this paper, we present two rigorous solutions to the through-diffusion test. Boundary conditions are improved to illustrate the following two cases: 1) constant inlet concentration, increasing outlet concentration; and 2) decreasing inlet concentration, increasing outlet concentration. A companion approach for back-calculating the effective diffusion coefficient and rock capacity factor from a diffusion test is also proposed. Possibilities of using the improved techniques in engineering practices are verified through a series of theoretical evaluations.

INTRODUCTION

The safe disposal or isolation of hazardous contaminants, including radioactive nuclear wastes, by using natural and/or engineering barriers requires a good understanding of their fate and transport properties in geological materials. Diffusion through and sorption onto geological materials can be the most important mechanisms of transport and retardation (1, 2), and a thorough evaluation of pertinent parameters is of crucial significance for the safety assessment.

Laboratory diffusion test is a well-established and widely adopted approach for characterizing the transport properties of geological materials. Although there are several types of diffusion tests currently available (3), through-diffusion has been extensively used for testing rock or rock-like samples in the field of geological disposal of radioactive nuclear wastes (1, 4). This method is based on an approximate analytical solution assuming constant inlet and outlet concentrations at the ends of a test specimen, and the effective diffusion coefficient of the specimen is estimated from the data (concentration variations) of steady-state measurements. To be able to perform an analysis satisfying these assumptions, a large-sized cell, or reservoir, containing the source solution is generally placed at the inlet side to dampen concentration variations, and the solution in measurement cell at the outlet side is continuously replaced with fresh solution throughout the

duration of the test (e.g. 4, 5). This procedure may be laborious and cause errors due to differences between analysis assumptions and actual test conditions. In addition, the procedure may be time-consuming, especially when the effective diffusion coefficient of a test specimen is relatively low and/or the rock capacity factor is relatively high.

In this paper, we present two rigorous solutions to the through-diffusion test. Boundary conditions are improved by taking into account concentration variations in the measurement cell alone or in both measuring and source cells. We also propose a companion approach for back-calculating the effective diffusion coefficient and rock capacity from a diffusion test. Using these rigorous solutions, we perform a theoretical evaluation of the conventional through-diffusion test and illustrate the possibilities of using these improved techniques.

Mathematical Formulations and Solutions

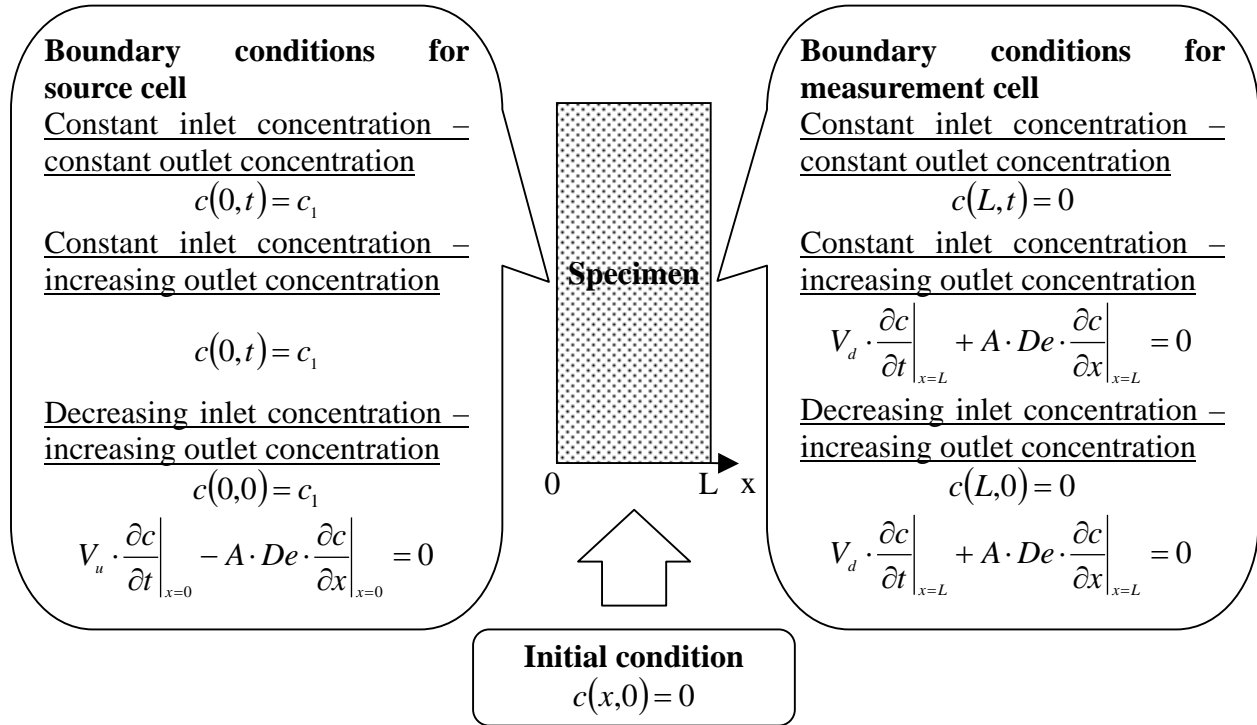
Mathematical Formulations

Schematic diagrams illustrating the concepts, and initial and boundary conditions for the through-diffusion tests are given in Table I. The rate of change of concentration at a point in a one dimensional system is given by Fick's second law (5, 6):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (\text{Eq. 1})$$

In Table I and Eq. 1, A is cross-sectional area of specimen, L is the specimen length, c_1 is the constant or initial concentration in the source cell, V_u and V_d are the volumes of source and measurement cells, respectively, c is concentration; t is the time from the onset of the experiment; x is the distance along the specimen axis referenced from the inlet end; D is the

Table I. Schematic Diagrams and Initial and Boundary Conditions for Through-Diffusion Tests



apparent diffusion coefficient, which reflects the effects of porosity, tortuosity and sorption. The total porosity of the test material is defined as the sum of “transport porosity” and “storage porosity”, which correspond, respectively, to pores aiding in transporting the species from one side of the specimen to the other and pores that are connected to transport pores but have a dead end. The latter contributes to the capacity of the pore system to hold dissolved species, but contributes nothing or little to the transport. Eq. 1 can then be written as follows (5):

$$(\varepsilon_{tot} + K_d \rho) \frac{\partial c}{\partial t} = D_p \varepsilon^+ \frac{\partial^2 c}{\partial x^2} \quad (\text{Eq. 2})$$

Where ε_{tot} is the total porosity; ε^+ is the transport porosity; K_d is the sorption coefficient; ρ is the density of the test material; D_p is the pore diffusion coefficient.

Comparing Eqs. 1 and 2 gives

$$D = \frac{D_p \varepsilon^+}{\varepsilon_{tot} + K_d \rho} = \frac{D_e}{\alpha} \quad (\text{Eq. 3})$$

Where $D_e = D_p \varepsilon^+$ is defined as the effective diffusion coefficient and $\alpha = \varepsilon_{tot} + K_d \rho$ is defined as the rock capacity factor (5).

By the above definitions, Eq. 1 can then be rewritten as follows:

$$\frac{\partial c}{\partial t} = \frac{D_e}{\alpha} \frac{\partial^2 c}{\partial x^2} \quad (\text{Eq. 4})$$

Eq. 4 is similar to the equation describing one-dimensional transient flow of a compressible fluid through a saturated, porous, and compressible medium which combines the principle of

conservation of fluid mass in a deformable matrix and Darcy's law for laminar flow through a hydraulically isotropic matrix (7). In this paper, we use Eq. 4 as the governing equation for describing diffusion through rock materials. Rigorous solutions to through-diffusion tests can be obtained by solving Eq. 4 together with the initial and boundary conditions illustrated in Table I for the individual types of diffusion tests.

Constant Inlet Concentration - Constant Outlet Concentration

The solution for the conventional type of diffusion test, i.e., constant inlet concentration ($c(0,t) = c_1$) and constant outlet concentration ($c(L,t) = 0$), can be obtained as follows (5, 6):

$$c(x,t) = c_1 \left[1 - \frac{x}{L} - \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \cdot \sin\left(n \cdot \pi \cdot \frac{x}{L}\right) \cdot \exp\left(-\frac{n^2 \cdot \pi^2 \cdot D_e}{\alpha \cdot L^2} \cdot t\right) \right] \quad (\text{Eq. 5})$$

The total or accumulated quantity $Q(t)$ diffused into the outlet side reservoir, or measurement cell, after time t can be calculated as the time integral of the flux through the boundary $x = L$, and can be derived as follows (5):

$$\begin{aligned} Q(t) &= -D_e \cdot A \int_0^t \left. \frac{\partial c(x,\tau)}{\partial x} \right|_{x=L} d\tau \\ &= A \cdot L \cdot c_1 \left\{ \frac{D_e}{L^2} \cdot t - \frac{\alpha}{6} - \frac{2\alpha}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \exp\left(-\frac{n^2 \cdot \pi^2 \cdot D_e}{\alpha \cdot L^2} \cdot t\right) \right\} \end{aligned} \quad (\text{Eq. 6})$$

At long times, the exponential function in Eq. 6 approaches zero. Consequently, $Q(t)$ at $t \rightarrow \infty$ or at the steady state approaches the linear relation

$$Q(t) \Big|_{t \rightarrow \infty} = A \cdot L \cdot c_1 \left[\frac{D_e}{L^2} \cdot t - \frac{\alpha}{6} \right] \quad (\text{Eq. 7})$$

with a slope of $(A \cdot c_1 \cdot D_e)/L$ and an intercept on the time axis $(\alpha \cdot L^2)/(6D_e)$. By plotting the $Q(t)$ versus t curve and obtaining the slope at steady state measurement and the corresponding intercept on the time axis, both the effective diffusion coefficient, D_e , and rock capacity factor, α , can be determined.

If the species diffused into the outlet reservoir, i.e., the measurement cell, are not removed and the increase in concentration in the measurement cell is extremely low compared with the concentration c_1 in the source reservoir, the concentration in the measurement cell can be approximated using Eq. 6, by dividing $Q(t)$ with the measurement cell volume, V_d . The effective diffusion coefficient and rock capacity factor can be similarly determined by plotting the concentration in the measurement cell versus time. This latter method has been used by most researchers (4, 5, 8).

Constant Inlet Concentration – Increasing Outlet Concentration

A theoretical expression for the constant inlet concentration – increasing outlet concentration through-diffusion test can be obtained from the solution of Eq. 4, together with the initial and boundary conditions illustrated in Table I by means of the Laplace transform method:

$$c(x,t) = c_1 \left\{ 1 - 2 \sum_{m=0}^{\infty} \frac{(\lambda_m^2 + \beta^2) \cdot \exp\left(-\frac{D_e \cdot \lambda_m^2 \cdot t}{\alpha \cdot L^2}\right) \cdot \sin\left(\lambda_m \cdot \frac{x}{L}\right)}{\lambda_m \cdot [\lambda_m^2 + \beta(\beta + 1)]} \right\} \quad (\text{Eq. 8})$$

in which $\beta = (\alpha \cdot A \cdot L)/V_d$ and λ_m are the roots of the following equation:

$$\tan(\lambda) = \frac{\beta}{\lambda} \quad (\text{Eq. 9})$$

At long times, the exponential functions, or the second term on the right side of Eq. 8, approach zero. Consequently, $c(x,t)$ eventually reaches the value c_1 , i.e., the concentration in the source cell.

Similar to Eq. 6, the total quantity $Q(t)$ diffused into the measurement cell after time t can be calculated as the time integral of the flux through the boundary $x = L$, and can be derived as follows:

$$\begin{aligned} Q(t) &= -D_e \cdot A \int_0^t \frac{\partial c(x,\tau)}{\partial x} \Big|_{x=L} d\tau \\ &= 2\alpha \cdot A \cdot L \cdot c_1 \left\{ \sum_{m=0}^{\infty} \frac{(\lambda_m^2 + \beta^2) \cdot \cos(\lambda_m)}{\lambda_m^2 [\lambda_m^2 + \beta(\beta + 1)]} \cdot \left[1 - \exp\left(-\frac{D_e \cdot \lambda_m^2 \cdot t}{\alpha \cdot L^2}\right) \right] \right\} \end{aligned} \quad (\text{Eq. 10})$$

At long times, i.e., when the concentration in the outlet cell reaches the value of c_1 and there is no more diffusion, the total quantity diffused into the measurement cell reaches a constant value.

Decreasing Inlet Concentration – Increasing Outlet Concentration

The solution to the decreasing inlet concentration – increasing outlet concentration diffusion test can be derived from Eq. 4 together with the associated initial and boundary conditions illustrated in Table I using an approach similar to that used by Hsieh et al.(7) for deriving the exact solution for the transient pulse permeability test. Note that x in this paper is referenced from the inlet end (upstream end), rather than the outlet side (downstream end), and the symbols used here for the associated parameters are different from those used in (7). Thus, we obtain the exact solution for the decreasing inlet concentration – increasing outlet concentration diffusion test as follows:

$$\begin{aligned} c(x,t) &= \frac{c_1}{\delta + \gamma + 1} - \\ & 2c_1 \sum_{m=0}^{\infty} \frac{\exp\left(-\frac{D_e \cdot \phi_m^2 \cdot t}{\alpha \cdot L^2}\right) \cdot \left[\delta \cdot \cos\left(\phi_m \cdot \frac{L-x}{L}\right) - \gamma \cdot \phi_m \cdot \sin\left(\phi_m \cdot \frac{L-x}{L}\right) \right]}{[\gamma \cdot \phi_m^2 - \delta(\delta + \gamma + 1)] \cos(\phi_m) + [\delta \cdot \gamma + \delta + 2\gamma] \phi_m \cdot \sin(\phi_m)} \end{aligned} \quad (\text{Eq. 11})$$

where $\delta = (\alpha \cdot A \cdot L)/V_u$, $\gamma = V_d/V_u$ and ϕ_m are the roots of the following equation:

$$\tan(\phi) = \frac{\delta \cdot (\gamma + 1) \cdot \phi}{\gamma \cdot \phi^2 - \delta^2} \quad (\text{Eq. 12})$$

Variations in source and measurement cells, i.e., $c(0,t)$ and $c(L,t)$, can be calculated by

substituting $x = 0$ and $x = L$ into Eq. 11.

At long times, the exponential functions, or the second term on the right side of Eq. 11, approach zero. Consequently, concentrations at any point along the length of the specimen, $c(x,t)$, reach a certain constant value determined by the cross-sectional area and the length of the test specimen, the rock capacity factor, and the volumes of the source and measurement cells.

Theoretical Simulations and Comparisons

To illustrate the features of individual diffusion tests and compare the three types of diffusion tests, first, theoretical simulations were performed using the associated equations derived in the above section and the conditions tabulated in Table II. These hypothetical test conditions are determined with reference to the test conditions and results reported in a number of articles, such as references (1) to (5). Figures 1 to 3 illustrate the results of these theoretical simulations. Each test requires a relatively long time, up to several tens of days in the simulated case, to approach steady-state or equilibrium conditions. Examination of Eqs. 5, 8 and 11 shows that the lower the effective diffusion coefficient and/or the larger the rock capacity factor of the specimen, the longer will be the time required to establish steady state or equilibrium for each test. Unsteady or non-equilibrium conditions will also persist for a longer time if the specimen length, L , is increased. Examination of Eqs. 6 and 10 shows that the use of a specimen with a larger cross-section will facilitate the measurement of concentration variations because changes in concentration are proportional to the cross-sectional area of test specimen, A . Although an expression for the diffused quantity is not shown for the decreasing inlet concentration – increasing outlet concentration diffusion test, the same conclusion can be drawn for this test method.

Table II. Hypothetical Test Conditions for the Theoretical Simulations of Through-Diffusion Tests

Specimen	Cross-sectional area, A (m^2)	3.85E-3
	Length, L (m)	1.00E-2
	Effective diffusion coefficient, D_e (m^2/s)	2.50E-13
	Rock capacity factor, α	3.50E-2
Source cell	Volume, V_u (m^3)	4.00E-6
	Concentration, c (ppm)	127000
Measurement cell	Volume, V_d (m^3)	4.00E-5
	Concentration, c (ppm)	0

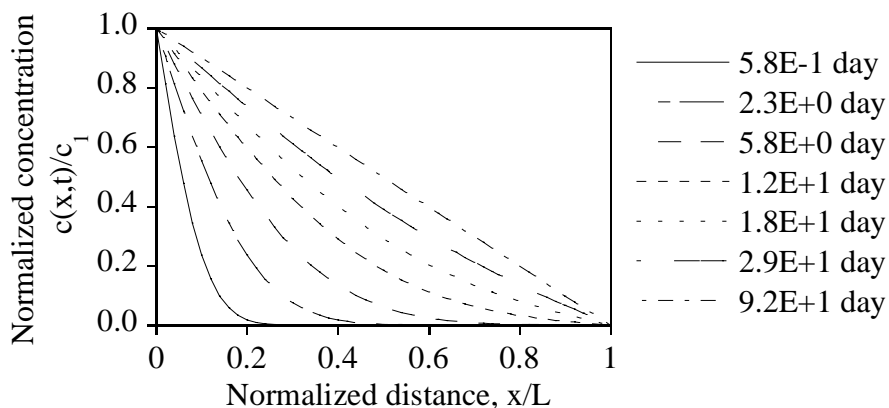
Figure 1 shows the simulated results for the constant inlet concentration – constant outlet concentration diffusion test in which a) and b) illustrate the time-dependent variations of concentration distribution across the specimen axis and the total diffused quantity through the cross-section of the outlet end of the specimen, respectively. At the onset of the experiment, the concentration at the inlet end of the specimen is suddenly increased. Concentrations at points along the specimen axis gradually increase, finally reaching a linear distribution, which means the diffusion through the specimen reached a steady-state condition (Figure 1a). This steady-state condition corresponds to the linear portion in the curve of total diffused quantity versus time (Figure 1b).

Figure 2 shows the simulated results for the constant inlet concentration – increasing outlet concentration diffusion test in which a), b) and c) illustrate the time-dependent variations of concentration across the specimen axis, time-dependent variations of concentration in the measurement cell and the total diffused quantity through the cross-section of the outlet end of the specimen, respectively. At the onset of the experiment, the concentration at the inlet end of the specimen is suddenly increased. Concentrations at points along the specimen axis gradually increase, finally reaching the concentration of the source solution (Figure 2a). The concentration in the measurement cell and the total diffused quantity through the cross-section of the outlet end of the specimen increase slowly at an early stage of the experiment, then increase nearly linearly, and finally converge to a certain value (Figure 2b and c). At this equilibrium state, there will be no more diffusion through the specimen. In quantifying the errors associated with using Eq. 6, i.e., the conventional time-lag method, to estimate the effective diffusion coefficient and rock capacity factor from the constant inlet concentration – increasing outlet concentration diffusion test, the values of the two parameters are determined from the curves shown in Figure 2b and c using the data up to different concentration levels, viz., $1\%c_1$, $3\%c_1$, $5\%c_1$ and $9\%c_1$. These results are tabulated in Table III, in which the relative errors are defined as follows:

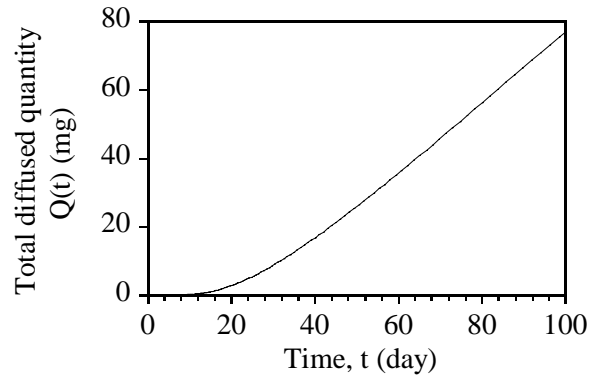
$$D_{e-err} = \frac{D_{e-determined}}{D_{e-input}} \cdot 100\% \quad \alpha_{err} = \frac{\alpha_{determined}}{\alpha_{input}} \cdot 100\% \quad (\text{Eq. 13})$$

The subscripts determined and input refer, respectively, to the data determined from the curve in Figure 2c using Eq. 6 and input for simulating the curve in Figure 2c.

If the solution in the measurement cell is not replaced with fresh solution to maintain the 0 concentration condition at the outlet end of specimen, and the data are interpreted using the conventional time-lag method, there will be a tendency to underestimate both the effective diffusion coefficient and rock capacity factor. The higher the concentration increase in the measurement cell, the larger will be the error in estimating the two parameters. To avoid the



a) Time-dependent variations of concentration distribution across the specimen

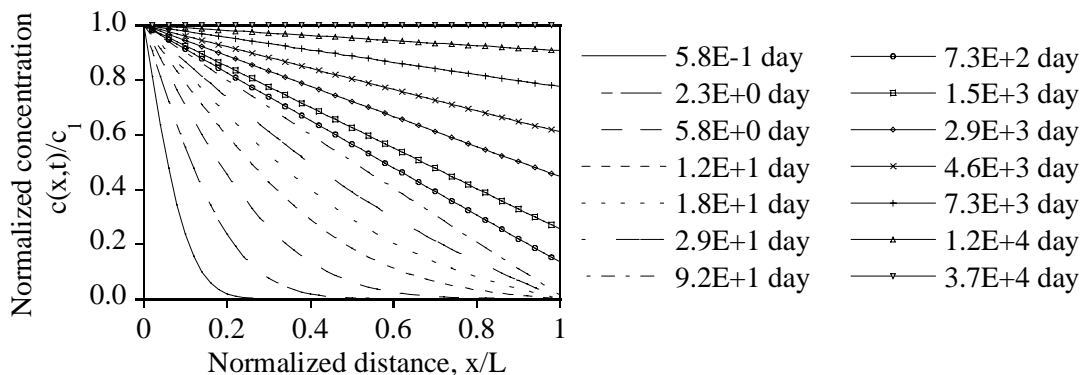


b) Total diffused quantity through a cross-section of the outlet end of the specimen

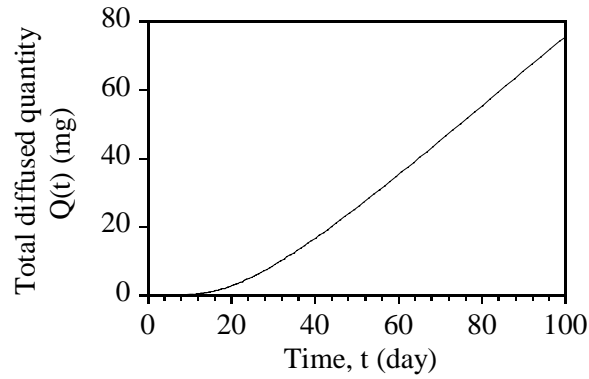
Fig. 1. Simulated results of constant inlet concentration – constant outlet concentration diffusion test

complicated procedure of replacing the solution in the measurement cell during the test and to avoid errors from using the conventional time-lag method, the possibility of adopting the parameter identification technique to back-calculating the effective diffusion coefficient and rock capacity factor by using Eqs. 8 and 9 is illustrated in the next section.

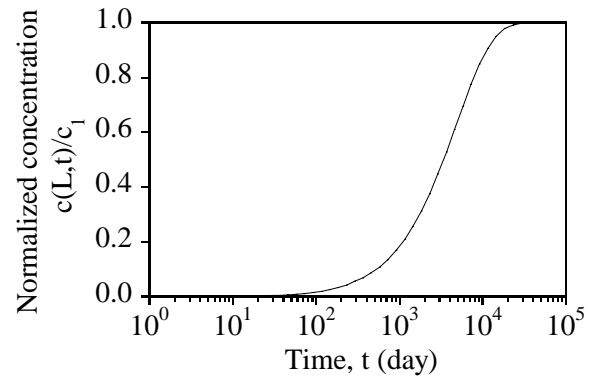
Figure 3 shows the simulated results for the decreasing inlet concentration – increasing outlet concentration diffusion test in which a), b) and c) illustrate the time-dependent variations of concentrations within the specimen, in the source cell and in the measurement cell, respectively. At the onset of a test, the concentration at the inlet end rapidly increases and then gradually decreases. Concentrations at other points along the specimen axis change systematically and eventually approach an equilibrium state (Figure 3b). Detecting the concentration decrease in the source cell is thought to be easier and faster (Figure 3 a) than measuring the concentration increase in a measurement cell (Figures 1b, 2b and 3c). In the next section, we also discuss the possibility of back-calculating the effective diffusion coefficient and rock capacity factor from the time-dependent variations of concentration in the source cell or in both source and measurement cells by using Eqs. 11 and 12.



a) Time-dependent variations of concentration distribution across the specimen



b) Variations of concentration in measuring cell

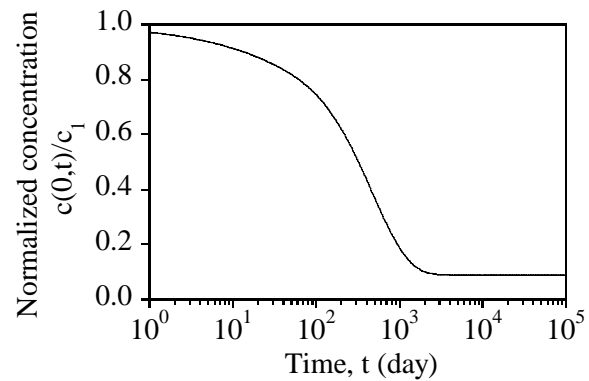


c) Total diffused quantity through a cross-section of the outlet end of the specimen

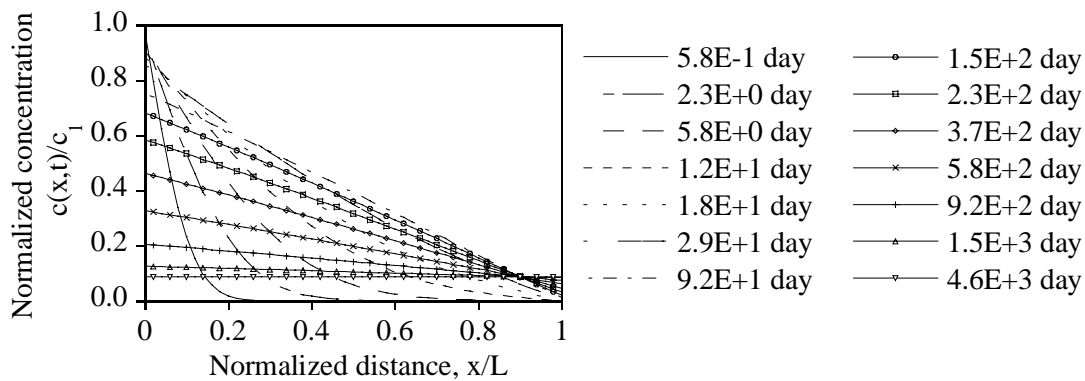
Fig. 2. Simulated results of constant inlet concentration – increasing outlet concentration diffusion test

Table III. Relative Errors in Determining Effective Diffusion Coefficient and Rock Capacity Factor by using the Time-Lag Method

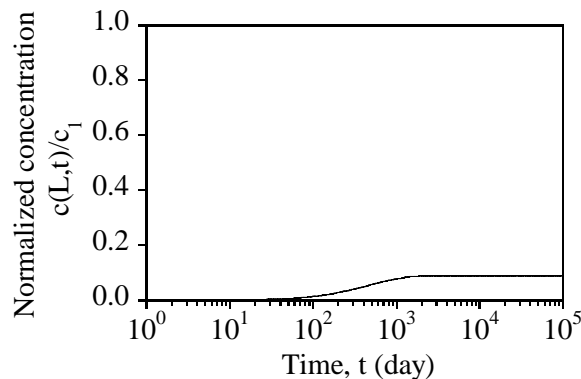
	$1\%c_1$	$3\%c_1$	$5\%c_1$	$9\%c_1$
D_{e-err} (%)	96	96	94	88
α_{err} (%)	93	90	73	26



a) Variations of concentration in source cell



b) Time-dependent variations of concentration distribution across the specimen



c) Variations of concentration in measuring cell

Fig. 3. Simulated results of decreasing inlet concentration – increasing outlet concentration diffusion test

Parameter Identification Technique

The theoretical solutions to the latter two laboratory through-diffusion tests, i.e., the constant inlet concentration-increasing outlet concentration and decreasing inlet concentration-increasing outlet concentration diffusion test, are rigorous (Eqs. 8, 9; Eqs. 11, 12), and it is difficult to determine analytically the effective diffusion coefficient and rock capacity factor of a specimen from experimental measurements. Although graphical methods may be used to quantify these parameters from each kind of test, the attendant procedures may be cumbersome and their accuracy may be quite limited. In this paper, we propose a numerical inverse method to back-calculate the transport properties of a test specimen. This method is based on a parameter identification theory developed in the general context of systems engineering (9) and has been applied to various field problems, structural problems, and model tests. In our previous studies, we have also successfully applied this method to both laboratory and in-situ permeability tests (10, 11). The basic premise of the method is to back-calculate the values of associated parameters by minimizing a properly defined error function that represents a least-squares reduction of the discrepancy between the measured and theoretically calculated results. For the case of diffusion

tests, an error function can be defined as

$$\varepsilon = \sum_{i=1}^n \{Q(t_i) - Q(t_i)^*\}^2 \quad \text{Eq. 14}$$

for the constant inlet concentration – increasing outlet concentration diffusion test. Here N is the number of measured data points, $Q(t_i)$ and $Q(t_i)^*$ are the total quantity diffused into the measurement cell measured up to time t_i and the corresponding data obtained theoretically from Eq. 10, respectively. Since the analytical concentration data depend on the values of the effective diffusion coefficient D_e and the rock capacity factor α , the error function is, in turn, also dependent on these two parameters. Consequently, Eq. 14 can be rewritten as follows:

$$\varepsilon = \sum_{i=1}^n \{Q(t_i)_{(D_e, \alpha)} - Q(t_i)_{(D_e, \alpha)}^*\}^2 \quad \text{Eq. 15}$$

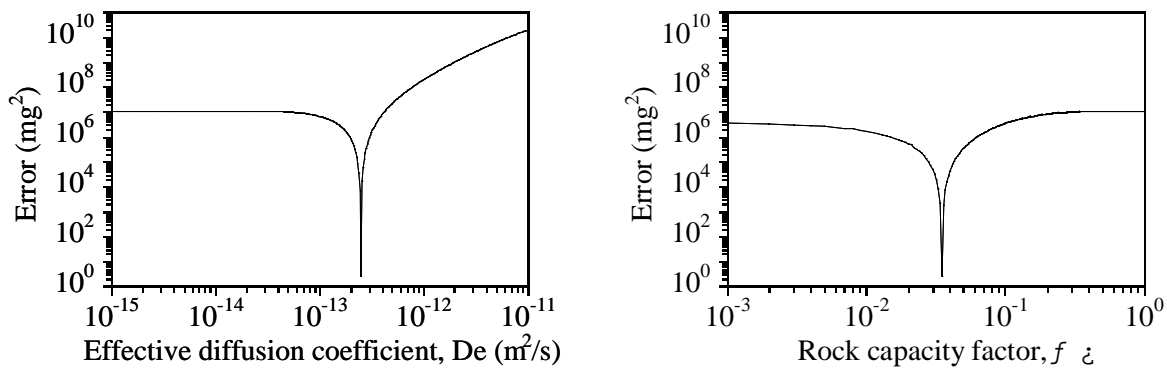
For the decreasing inlet concentration – increasing outlet concentration diffusion test, the error function can be similarly defined as

$$\varepsilon = \sum_{i=1}^n \{c(t_i)_{(D_e, \alpha)} - c(t_i)_{(D_e, \alpha)}^*\}^2 \quad \text{Eq. 16}$$

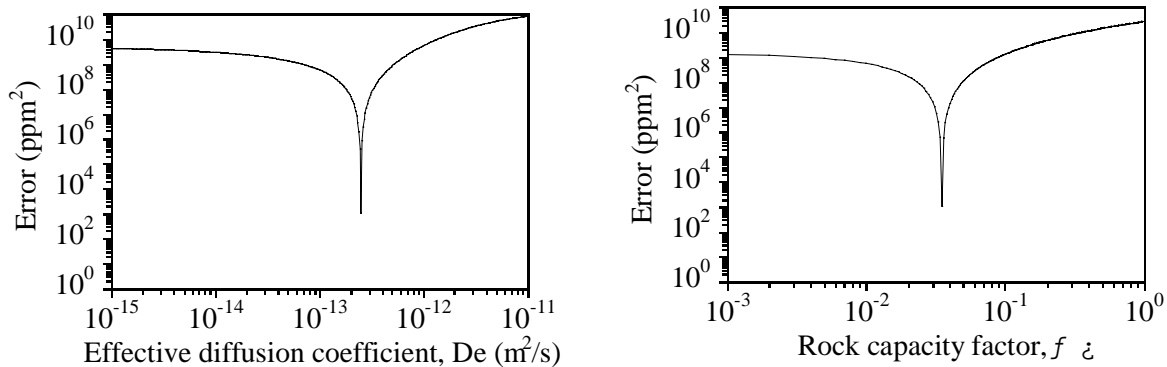
where $Q(t_i)$ and $Q(t_i)^*$ are the concentrations measured at time t_i and the corresponding data obtained theoretically from Eqs. 11 and 12. In principle, the concentrations measured in the source cell and/or the measurement cell can be used as measured data for the back-calculation.

The error functions in Eqs. 15 and 16 are highly nonlinear functions of the parameters D_e and α , and their characteristics cannot be analyzed theoretically. Here we use a numerical approach to investigate the particular behavior of these error functions. It will be helpful for us to evaluate whether the parameters D_e and α can be accurately back-calculated from the measurements through minimizing the error functions defined by Eqs. 15 and 16.

The data numerically generated in the previous section are used as “experimental data” and the values of D_e and α are thought to be “real values”. The relationships between the error functions and each of the parameters can be graphically represented (Figure 4) by varying one parameter across a certain span of magnitude and maintaining the other parameter constant and equal to its “real value”. The error curves are convex in the neighboring domains of the “real values” of the parameters. Therefore, it is possible to uniquely quantify the magnitudes of the parameters from real measurements by minimizing the error functions defined.



a) Constant inlet concentration – increasing outlet concentration diffusion test



b) Decreasing inlet concentration – increasing outlet concentration diffusion test

Fig. 4. Characteristics of error functions

CONCLUDING REMARKS

Although the laboratory diffusion test is a well-established and widely adopted approach for characterizing the transport properties of geological materials, conventional through-diffusion tests may be time-consuming, cumbersome and may cause errors in quantifying the effective diffusion coefficient and rock capacity factor due to the difference between actual test conditions and analytical assumptions. To address these issues, we derived rigorous solutions that consider the concentration variations either in measuring or in both measuring and source cells. Using these rigorous solutions, a theoretical evaluation of the conventional through-diffusion test is performed and a companion approach for back-calculating the effective diffusion coefficient and rock capacity from a diffusion test is proposed. Conclusions drawn from this study can be summarized as follows:

- 1) If the solution in the measurement cell is not replaced with fresh solution to maintain the zero concentration condition at the outlet end of the specimen, and the data are interpreted using the conventional time-lag method, there will be a tendency to underestimate both the effective diffusion coefficient and rock capacity factor. The higher the concentration increase in the measurement cell, the larger will be the error in estimating the two parameters.
- 2) The effective diffusion coefficient and rock capacity factor can be uniquely back-calculated from the measurements of the constant inlet concentration – increasing outlet concentration diffusion test and decreasing inlet concentration – increasing outlet concentration diffusion test by using the rigorous theoretical solutions derived in this paper as well as the parameter identification technique.
- 3) The improved technique proposed in this paper enables the use of the data continuously measured in the measurement cell or both source and measurement cells. This, in turn, may allow automation of laboratory diffusion tests if the concentrations can be automatically detected by appropriate sensors. Thus, test management may become easier and test efficiency may be highly increased.

The findings obtained in this study offer practical considerations in effective implementation of a

diffusion test and in proper interpretation of the test results. To further verify the conclusions obtained in this theoretical study, a series of laboratory through-diffusion tests is currently in progress.

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