

Quantitative Evaluation of Possible Errors Induced by Using Simplified Analytical Solutions to the Laboratory In-Diffusion Test

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ABSTRACT

Laboratory diffusion test has been widely used for characterizing the diffusive and adsorptive properties of synthetic, geological and geotechnical materials in many scientific fields and engineering practices. Although many types of laboratory diffusion test are currently available, different methods have different advantages and disadvantages. An overview of conventional test methods has recently been performed by Zhang and Takeda et al. (WM06) and rigorous solutions to the laboratory through-diffusion tests were developed and discussions on how to select an appropriate test method, design optimum test conditions and determine data sampling for the through-diffusion tests were performed by Takeda and Zhang et al. (WM06). In addition, theoretical evaluation of possible errors which may be caused by using simplified boundary conditions for developing solutions to the laboratory through-diffusion tests were quantitatively examined by Zhang and Takeda (WM05). As a new part of the systematic study, rigorous solutions to the laboratory in-diffusion test, with emphasis on the decreasing source concentration in-diffusion test, are further derived and illustrated in this paper. The new solutions are then used to exam possible errors which may be induced by using simplified solution in interpreting the in-diffusion test data, or data analyses. The theoretical examinations in this study found that the errors in determining the transport properties for a test specimen depend on both test condition and test duration. The conditions and/or applicability of using the simplified solutions are then clarified and illustrated through a series of theoretical simulations. The theories and approaches presented in this paper may offer practical considerations for effective implementations of an in-diffusion test and for proper interpretation of the test results. They can also be used to assess the quality of, or analyze the potential errors in existing data when citing them from previous scientific articles.

INTRODUCTION

Laboratory diffusion test has been widely used for characterizing the diffusive and adsorptive properties of synthetic, geological and geotechnical materials in many scientific fields and engineering practices. Although many types of laboratory diffusion test are currently available, different methods have different advantages and disadvantages. An overview of conventional test methods has recently been performed by Zhang and Takeda et al. (WM06)[1] and rigorous solutions to the laboratory through-diffusion tests were developed and discussions on how to select an appropriate test method, design optimum test conditions and determine data sampling for the through-diffusion tests were performed by Takeda and Zhang et al. (WM06)[2]. In addition, theoretical evaluation of possible errors which may be caused by using simplified

boundary conditions for developing solutions to the laboratory through-diffusion tests were quantitatively examined by Zhang and Takeda (WM05)[3]. As a new part of the systematic study, rigorous solutions to the laboratory in-diffusion test, with emphasis on the decreasing source concentration in-diffusion test, are further derived and illustrated in this paper. The new solutions are then used to examine possible errors which may be induced by using simplified solutions in interpreting the in-diffusion test data. The conditions and/or applicability of using the simplified solutions for interpreting the test data are discussed and illustrated through a series of theoretical simulations.

CONCEPTS OF LABORATORY IN-DIFFUSION TESTS

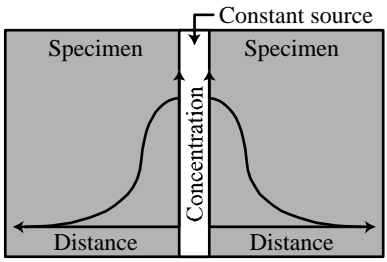
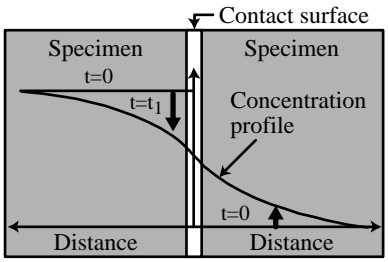
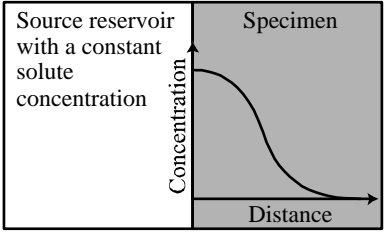
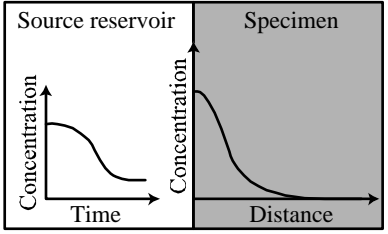
Currently, there are many kinds of diffusion test which are available for determining the diffusive transport properties of test specimens in the laboratory. Based on the structure of the systems for individual experiments, we divided the laboratory diffusion tests into 4 types: 1) through-diffusion, 2) in-diffusion, 3) out-diffusion and 4) column methods. In addition, subdivisions of different types of diffusion test were made according to the boundary conditions being controlled during individual tests, and the basic concepts for individual tests were summarized in the same paper[1]. To facilitate discussions, the concepts and schematic diagrams for the laboratory in-diffusion tests are summarized and illustrated here again as follows.

In general, in-diffusion tests are used to determine the apparent diffusion coefficients of test specimens in the laboratory. The basic concept of in-diffusion tests involves contacting the specimen end(s) with a tracer solution for a certain period. By sectioning or slicing the test specimen and analyzing the concentration distribution along the specimen axis, the apparent diffusion coefficient of the test specimen can then be calculated. According to the boundary conditions, in-diffusion tests can be divided into constant source concentration and decreasing source concentration in-diffusion tests as shown in Table 1.

Constant Source Concentration In-Diffusion Tests

Constant source concentration in-diffusion tests can be further divided into half-cell and single-reservoir methods as shown in Table 1. In most studies using the half-cell method [e.g., 4, 5, 6], an amount of tracer solute is tagged onto the contact surface between two half specimens. After a certain period of diffusion, the concentration profiles along one or two half specimens' axes are measured and the apparent diffusion coefficient of the test specimen is determined by fitting the experimental data with the analytical solution assuming a constant concentration solute diffuses into an infinite medium. An alternative type of half-cell method involves the tagging of the whole of a half specimen with a tracer solute, and use of corresponding solutions compatible with the initial and boundary conditions for the test to determine the apparent diffusion coefficient [e.g., 7]. However, this alternative method may not be efficient because tagging the whole of a half specimen with a constant concentration may take a relatively long time, especially when the diffusion coefficient of the test specimen is low. As for the single reservoir in-diffusion test method, a source reservoir with a constant solute concentration is connected to one end of the test specimen. Other processes for determining the concentration profile along the specimen axis and for calculating the apparent diffusion coefficient of the test specimen are similar to those for the half-cell method.

Table I. Classification of and Concepts for the Laboratory In-Diffusion Tests

	Constant Source Concentration		Decreasing Source Concentration (*also known as Reservoir Depletion Test)	
Concept	Half Cell Method		Single Reservoir Method	
	Constant concentration between half cells	Initial constant concentration in a half cell		
				
Measurement item(s)	Concentration profile along specimen axis	Concentration profile along specimen axis	Concentration profile along specimen axis	Concentration decrease in the source reservoir Concentration profile along specimen axis (concentrations are not to scale)

Constant source concentration in-diffusion tests do not require periodic sampling and thus less care is needed for the test. This feature may be helpful for testing specimens with low diffusive and/or high sorbing capacities. The specimen must be sectioned unless the concentration profile can be scanned directly, e.g., by using radioactive tracers and counting devices. Sectioning rock specimens can be cumbersome and difficult, especially for testing hard rocks. This may be why this method has been used mainly for testing soft specimens, such as compacted bentonite, bentonite mixtures, and clay.

Decreasing Source Concentration In-Diffusion Test

The decreasing source concentration in-diffusion, known as the reservoir depletion test, is also shown schematically in Table 1. The test setup for the decreasing source concentration in-diffusion test is similar to that for the single-reservoir constant source concentration in-diffusion test except for the use of a small-sized source reservoir in which the solute concentration is not controlled but allowed to decrease naturally. During the diffusion test, time-dependent variations in the source reservoir are monitored and the data can be used to determine the effective diffusion coefficient and rock capacity factor of the test specimen. After the diffusion test, the concentration profile along the specimen axis direction can be determined and the data can be used to determine the apparent diffusion coefficient of the specimen. This method was used by Rowe et al. [8], who used numerical approaches for the analyses.

The decreasing source concentration in-diffusion test has the advantage that both the effective and apparent diffusion coefficients can be determined simultaneously from one test, and test management is relatively easy because it is not necessary to maintain a constant concentration in the source reservoir. In addition, detecting the concentration decrease in the source reservoir can be performed with a relatively high degree of accuracy. However, a generalized form of the solution to this method has not been established.

With emphasis on the decreasing source concentration in-diffusion test, solutions to the constant and decreasing source concentration in diffusion tests are derived, and then used to discuss the possible errors induced by using simplified analytical solutions in the following sections.

SOLUTIONS TO CONSTANT AND DECREASING SOURCE CONCENTRATION IN-DIFFUSION TESTS

One-dimensional diffusion of a solute in a porous medium under transient conditions can be described by the following equation (1).

$$\frac{\partial C}{\partial t} = \frac{D_e}{\alpha} \cdot \frac{\partial^2 C}{\partial x^2} \quad (\text{Eq. 1})$$

Where C is concentration, t is the time, x is the distance from the specimen end, D_e is the effective diffusion coefficient, α is the rock capacity factor which can be defined as: $\alpha = \varepsilon_{tot} + K_d \rho$, in which ε_{tot} is the total porosity, K_d is the sorption coefficient, and ρ is the density of the test material.

Semi-Infinite Specimen Model

The initial condition for the semi-infinite specimen model can be expressed as:

$$C = 0 \quad 0 < x \leq \infty, \quad t = 0 \quad (\text{Eq. 2})$$

The downstream boundary condition can be expressed as:

$$C = 0 \quad x = \infty, \quad t > 0 \quad (\text{Eq. 3})$$

Constant source concentration in diffusion test

The upstream boundary condition for the constant source concentration in diffusion test can be expressed as shown in Eq. 4 and the solution can then be obtained from solving Eq. 1 together with Eqs. 2, 3 and 4, and expressed in Eq. 5[9].

$$C(0, t) = C_0 \quad (\text{Eq. 4})$$

$$c(\xi, \tau) = \text{erfc}\left(\frac{\xi}{2 \cdot \sqrt{\tau}}\right) \quad (\text{Eq. 5})$$

In which, $c = \frac{C}{C_0}$, $\xi = \frac{x}{L}$, $\tau = \frac{D_e \cdot t}{\alpha \cdot L^2}$, and called dimensionless concentration, dimensionless distance and dimensionless time, respectively. C_0 is the constant concentration in the source reservoir, and L is the length of test specimen.

Decreasing source concentration in diffusion test

The upstream boundary condition for the decreasing source concentration in diffusion test can be expressed as shown in Eq. 6 and the corresponding solution can be obtained as expressed in Eq. 7[9].

$$V_{in} \cdot \frac{\partial C}{\partial t} = D_e \cdot A \cdot \frac{\partial C}{\partial x} \quad t > 0, \quad C(0, 0) = C_0 \quad (\text{Eq. 6})$$

$$c(\xi, \tau) = \exp\left(\frac{\tau}{\beta_{in}^2} + \frac{\xi}{\beta_{in}}\right) \cdot \text{erfc}\left(\frac{\sqrt{\tau}}{\beta_{in}} + \frac{\xi}{2 \cdot \sqrt{\tau}}\right) \quad (\text{Eq. 7})$$

In which, $\beta_{in} = \frac{V_{in}}{\alpha \cdot A \cdot L}$, V_{in} is the volume of the source reservoir for in diffusion test, exactly the volume of solution in the source reservoir, A is the cross-sectional area of test specimen, and C_0 is the initial concentration in the source reservoir. $\alpha \cdot A \cdot L$ is generally defined as the total sorption capacity of test specimen.

Finite Specimen Model

The initial condition for the finite specimen model can be expressed as:

$$C = 0 \quad 0 < x \leq L, \quad t = 0 \quad (\text{Eq. 8})$$

Constant source concentration in diffusion test

The upstream boundary condition for the constant source concentration in diffusion test can be expressed using the same Eq. 4, and the downstream boundary condition for this type of diffusion test can be expressed as:

$$\frac{\partial C}{\partial x} = 0 \quad x = L, \quad t > 0 \quad (\text{Eq. 9})$$

That means the downstream specimen end is completely sealed and there is no diffusive flux through this boundary. And the solution can be obtained as follows[9]:

$$c(\xi, \tau) = 1 - 4 \cdot \sum_{n=1}^{\infty} \frac{\exp\left(-\frac{(2 \cdot n - 1)^2 \cdot \pi^2 \cdot \tau}{4}\right) \cdot \sin\left(\frac{(2 \cdot n - 1) \cdot \pi \cdot \xi}{2}\right)}{(2 \cdot n - 1) \cdot \pi} \quad (\text{Eq. 10})$$

Decreasing source concentration in diffusion test

The upstream boundary condition for the decreasing source concentration in-diffusion test can be expressed as follows:

$$\begin{aligned} C &= C_0 & x = 0, \quad t = 0 \\ \frac{V_{in}}{D_e \cdot A} \cdot \frac{\partial C}{\partial t} - \frac{\partial C}{\partial x} &= 0 & x = 0, \quad t > 0 \end{aligned} \quad (\text{Eq. 11})$$

The downstream boundary condition can be expressed with the same Eq. 9.

Rigorous solution to the decreasing source concentration in-diffusion test can be obtained by solving the Eq. 1 together with the initial and boundary conditions represented by Eqs. 8, 9, 11 using the Laplace Transform Method and expressed in dimensionless variables as follows:

$$c(\xi, \tau) = \frac{\beta_{in}}{\beta_{in} + 1} + 2 \cdot \sum_{n=1}^{\infty} \frac{\exp(-\phi_n^2 \cdot \tau) \cdot \beta_{in} \cdot \{\cos(\phi_n \cdot \xi) - \beta_{in} \cdot \phi_n \cdot \sin(\phi_n \cdot \xi)\}}{\beta_{in}^2 \cdot \phi_n^2 + \beta_{in} + 1} \quad (\text{Eq. 12})$$

In which ϕ_n are the roots of $\tan(\phi_n) = -\beta_{in} \cdot \phi_n$.

SIMULATION AND DISCUSSIONS

Constant Source Concentration In-Diffusion Test

Transient variations of normalized concentrations at the downstream end of test specimen and concentration profiles within the test specimen calculated by the finite and semi-infinite models for the constant source concentration in-diffusion tests are illustrated in Fig. 1. At early times, when the dimensionless time is typically less than 0.1, both the finite and semi-infinite models produce almost the same concentration distributions across the specimen. When dimensionless time is larger than 0.1, the concentrations derived from the semi-infinite model (simplified solution) diverge from those derived from finite model (rigorous solution) in the downstream side. The larger the time, the bigger is the difference between the concentration distributions. In other words, if one wants to use the solution of semi-infinite model, i.e., the simplified solution, to interpret the test data, only the data obtained from the start of an experiment to about 0.1 dimensionless time can be used. If the analyses contain the data obtained later than 0.1 dimensionless time, potential errors will be induced in the analytical results. The dimensionless time depends on both the effective diffusion coefficient and the rock capacity factor (see definition), it is an unknown parameter before an analysis. To ensure less errors of data analyses, a "back-check" of

experimental time period used for the data analysis is necessary (make sure the dimensionless time is less than 0.1). However, the use of the solution derived from finite specimen model, i.e., the rigorous solution, does not have such a restriction.

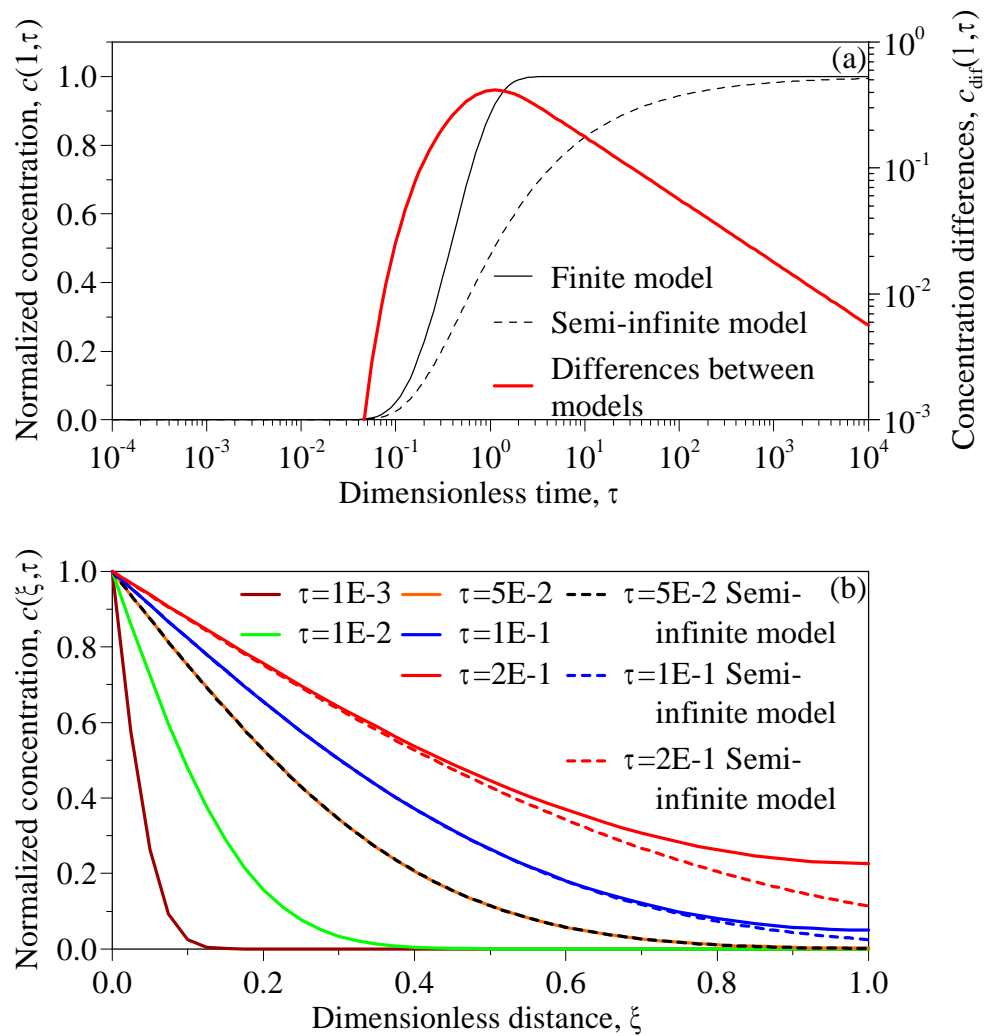


Fig. 1. (a) Transient variations of normalized concentrations at the downstream end of the specimen and (b) concentration profiles within the specimen calculated by the finite and semi-infinite models for the constant source concentration in-diffusion test.

Decreasing Source Concentration In-Diffusion Test

Transient variations of solute concentrations at the upstream and downstream ends of test specimen calculated by the finite and semi-finite models for the decreasing source concentration in-diffusion test are depicted in Fig. 2 a) and b), respectively. For a comparison, concentration differences between the results obtained from the two models at upstream and downstream specimen ends are also illustrated in the same Fig. 2 as shown in c). Concentration distributions, i.e., the concentration profiles within the specimen calculated by the two models are depicted in Fig. 3.

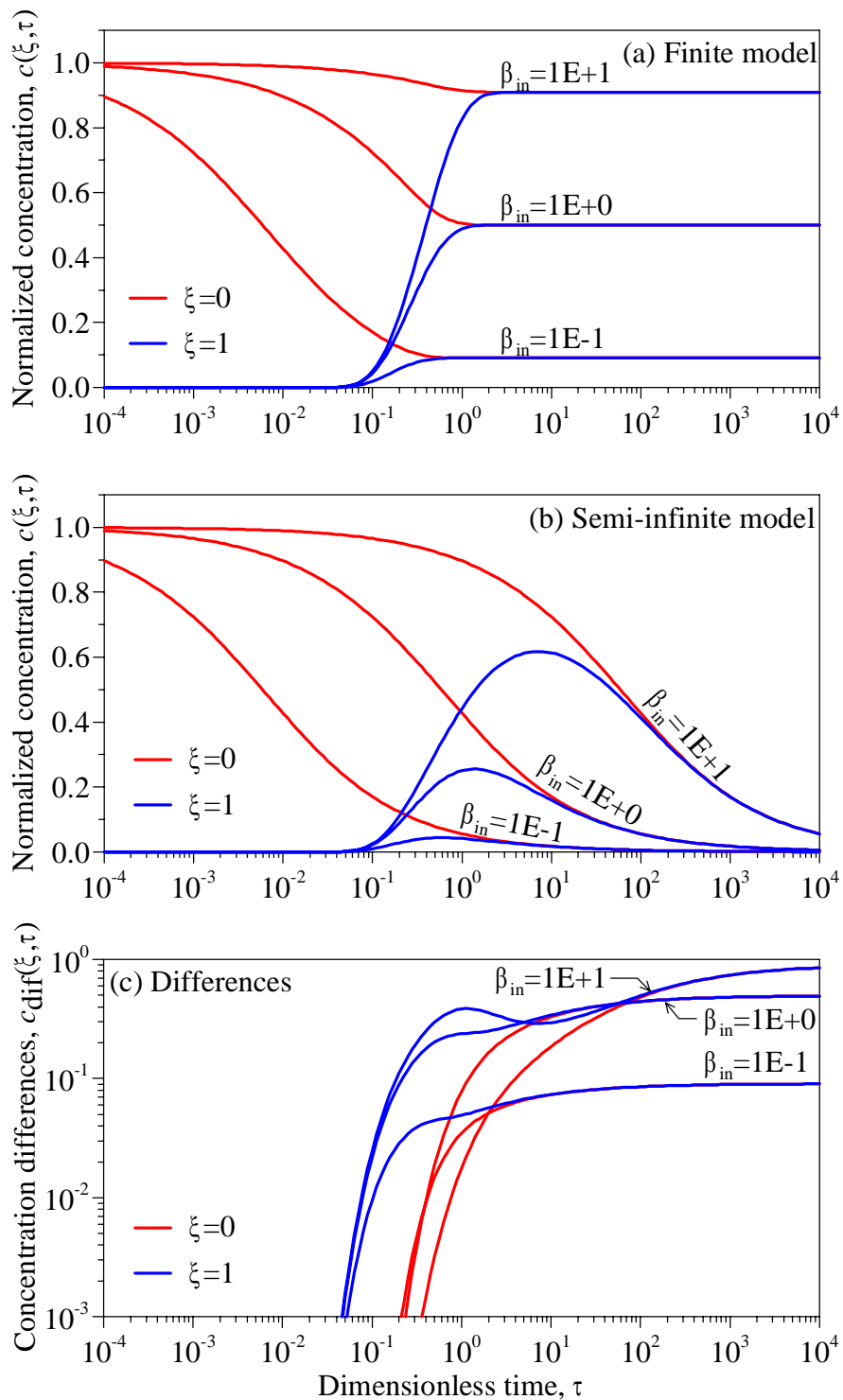


Fig. 2. Transient variations of solute concentrations at the upstream ($\xi=0$) and downstream ($\xi=1$) ends of the specimen calculated by (a) the finite and (b) semi-infinite models and (c) their differences for the decreasing source concentration in-diffusion test.

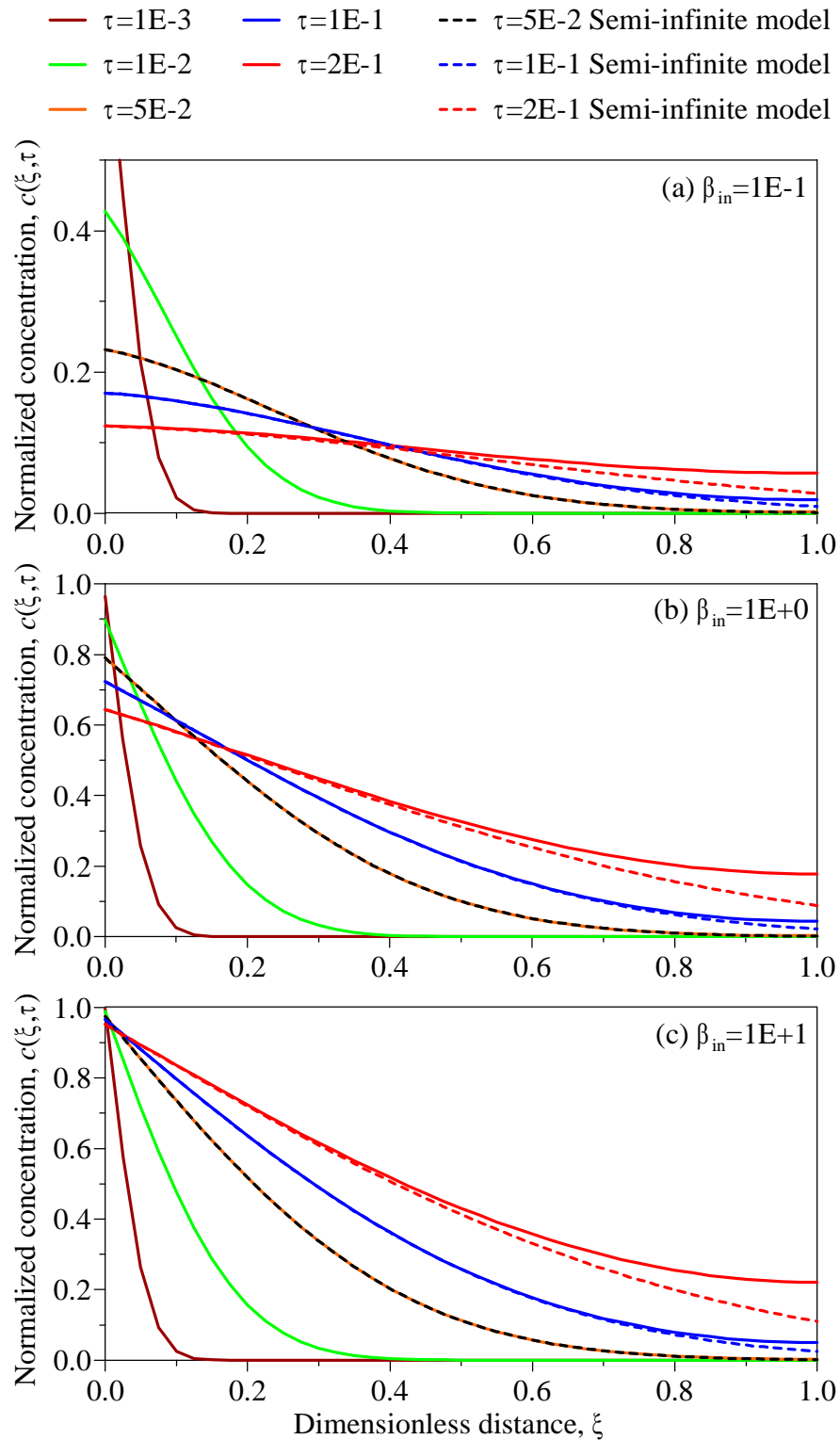


Fig. 3. Concentration profiles within the specimen calculated by the finite (solid lines in figures) and semi-infinite models for the decreasing source concentration in-diffusion test.

Examinations of both Fig. 2 and Fig.3 find that the smaller the reservoir volume(see curves for $\beta_{in} = 0.1$), the bigger the concentration changes in both source reservoir and within test specimen. Since the decreasing source concentration in-diffusion test mainly uses the time-dependent concentration variations in source reservoir for data analyses, it is advisable to use a properly small sized reservoir for a test.

At early test times, when dimensionless time is again typically less than 0.1, there is no significant difference between the results simulated from the finite and semi-infinite specimen models. The solution of the semi-infinite model, i.e., simplified solution, is therefore applicable to analyzing the data obtained from the start of an experiment up to the period of 0.1 dimensionless time. If the simplified solution is used to interpret the test data obtained later than 0.1 dimensionless time, it may induce potential errors in data analyses. This finding is similar to that obtained from the discussion on constant source in-diffusion test.

CONCLUSIONS

Laboratory diffusion test has been widely used for characterizing the transport properties of geo-materials in many practical implications. Although simplified solutions are easier to be derived and used, they may cause possible errors in data analyses. To evaluate the possible errors induced by using simplified solutions to the laboratory in-diffusion test, solutions to the constant and decreasing source concentration in-diffusion tests using finite and semi-infinite models are derived and illustrated. The conditions and/or applicability of using the simplified solutions (i.e., the solutions derived from semi-infinite models) for interpreting the test data are examined and clarified through a series of theoretical simulations. Major conclusions drawn from this theoretical study can be summarized as follows:

- 1) Simplified solutions assuming test specimen as semi-infinite model are applicable only to early experimental time period, typically for the dimensionless time less than 0.1 for both constant and decreasing source concentration in-diffusion tests..
- 2) The application of simplified solutions to interpret data obtained later than 0.1 dimensionless time may cause possible errors in data analyses. The error depends on both test condition, specifically the value of β_{in} defined as the ratio of the volume of source solute to the total sorption capacity of test specimen, and test duration. The smaller the reservoir volume, and/or the longer the test time, the bigger would be the errors in data analyses.
- 3) The dimensionless time is an unknown parameter before data analyses. To ensure the accuracy or applicability of simplified solutions, it is necessary to “back-check” the value of dimensionless time, i.e., to check whether the data used for the analyses were obtained within the time period less than 0.1 dimensionless time.
- 4) Rigorous solutions derived from finite specimen models reflect the actual boundary conditions in both constant and decreasing source concentration in-diffusion tests and thus can be used to analyze the data obtained from the whole test period and to increase the credibility of data analyses.

The theories and approaches presented in this paper may offer practical considerations for effective implementations of an in-diffusion test and for proper interpretation of the test results. They can also be used to assess the quality of, or analyze the potential errors in existing data when citing them from previous scientific articles. To systematize the studies on laboratory diffusion test, studies on other kinds of in-diffusion test and other types of laboratory diffusion test are being continued.

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