Strategies for Solving Potential Problems Associated with Laboratory Diffusion and Batch Experiments—Part 1: An Overview of Conventional Test Methods

M. Zhang, M. Takeda, H. Nakajima
Research Center for Deep Geological Environments
National Institute of Advanced Industrial Science and Technology (AIST)
Higashi 1-1-1, Tsukuba, Ibaraki 305-8567
Japan

ABSTRACT

Laboratory diffusion testing as well as batch experiments are well established and widely adopted techniques for characterizing the diffusive and adsorptive properties of geological, geotechnical, and synthetic materials in both scientific and applied fields, including geological disposal of radioactive waste. Although several types of diffusion test, such as the through-diffusion test, in-diffusion test, out-diffusion test, and column test, are currently available, different methods may have different advantages and disadvantages. In addition, traditional methods may have limitations, such as the need for relatively long test times, cumbersome test procedures, and the possibility of errors due to differences between analytical assumptions and actual test conditions. Furthermore, traditional batch experiments using mineral powders are known to overestimate the sorption coefficient. In part 1 of this report, we present a brief overview of laboratory diffusion and batch experiments. The advantages, disadvantages, limitations, and/or potential problems associated with individual tests were compared and summarized. This comprehensive report will provide practical references for reviewing the results obtained from relevant experiments, especially from the viewpoint of regulation. To solve and/or eliminate the potential problems associated with conventional methods, and to obtain the diffusion coefficient and rock capacity factor from a laboratory test both rapidly and accurately, part 2 of this study discusses possible strategies involving the development of rigorous solutions to some relevant test methods, and sensitivity analyses for the related tests that may be helpful to judge the accuracy of the two parameters to be determined from individual tests.

INTRODUCTION

Safety assessment of facilities involved in geological disposal of hazardous waste, including radioactive nuclear waste, is generally performed through mass transport simulations combined with uncertainty and sensitivity analyses. Transport of contaminants, such as radionuclides, through an engineered and natural barrier system is mainly controlled by advection, dispersion, sorption, and chain decay. When groundwater flow is very slow and advection is not a dominant transport process, the most important mechanisms of transport and retardation are diffusion through and sorption onto engineered and geological or natural barrier materials, and thus evaluation of relevant parameters, particularly the effective diffusion coefficient and sorption coefficient or rock capacity factor, is of fundamental importance for safety assessment [*e.g.*, 1–10].

Laboratory diffusion testing as well as batch experiments are well-established and widely adopted techniques for characterizing the diffusive and adsorptive properties of geological, geotechnical, and synthetic materials in different scientific and applied fields, including geological disposal of radioactive waste. Although several types of diffusion test are currently available, such as the through-diffusion test [*e.g.*, 11–13], the in-diffusion test [*e.g.*, 14–16], the out-diffusion test [*e.g.*, 17, 18], and the column test [*e.g.*, 19–21], the different methods have different advantages and disadvantages. In addition, traditional methods may have limitations, such as the need for relatively long test times, cumbersome test procedures, and the possibility of errors due to differences between analytical assumptions and actual test conditions. Furthermore, traditional batch experiments using mineral powders are known to overestimate the sorption coefficient. Part 1 of this report presents a brief review of the basic theories for diffusion in and sorption onto geological materials, along with an overview of laboratory diffusion and batch experiments. The advantages, disadvantages, limitations, and/or potential problems associated with individual tests are compared and summarized.

BASIC THEORIES FOR THE DIFFUSION AND SORPTION EXPERIMENTS

Governing Equation for Diffusion Tests

The diffusion of a solute into a porous medium under transient conditions can be described by Fick's second law [*e.g.*, 22]:

$$\varepsilon_{tot} \frac{\partial c}{\partial t} = D_e \frac{\partial^2 c}{\partial x^2} - \rho \frac{\partial q}{\partial t} \qquad \text{(Eq. 1)}$$

where ε_{tot}, c, t, D_e, x, ρ, and q denote the total porosity, the solution concentration in pore water, the time, the effective diffusion coefficient, the distance, the bulk density of the porous medium, and the sorbed concentration in the porous medium, respectively. The total porosity of the porous medium is defined as the sum of "transport porosity" and "storage porosity," which correspond to pores that aid in transporting the species from one place to another and those that are connected to transport pores but have a dead end, respectively. The latter contribute to the capacity of the pore system to hold dissolved species, but contribute little to transport [*e.g.*, 11]. The term $\partial q / \partial t$ represents the sink due to sorption of the solute.

If sorption is linear, meaning that the concentration of the species adsorbed onto the solid phase is proportional to its concentration in the mobile phase, and the local equilibrium assumption is valid, the distribution or sorption coefficient, K_d, can be used to express Eq. 1 as follows:

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

The term $\varepsilon_{tot} + K_d \rho$ is defined as rock capacity factor α [*e.g.*, 11, 23]. The volume sorption coefficient, $\rho \cdot K_d$, is zero if there is no sorption or retardation, and the rock factor α is then equal to the total porosity. The ratio D_e / α is generally defined as the apparent diffusion coefficient D, which is a function of porosity, tortuosity, and sorption, whereas D_e is not.

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

Where ε^+ and D_p are denoted as the transport porosity and the pore diffusion coefficient, respectively.

The retardation factor for pore diffusion $1 + K_d \cdot \varepsilon_{tot} / \rho$ can be obtained through dividing the rock capacity factor, α, by the total porosity, ε_{tot}.

Comparing Eqs. 2 and 3 gives

$$\frac{\partial c}{\partial t} = \frac{D_e}{\alpha} \frac{\partial^2 c}{\partial x^2}$$ (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 [24]. In the present study, we used Eq. 4 as the governing equation for describing diffusion through specimens in the laboratory. This governing equation has been used by most investigators. Rigorous solutions to relevant diffusion tests can be obtained by solving the governing Eq. 4 together with the initial and boundary conditions for individual types of diffusion test (see part 2 of this study).

If the sorption is non-linear, (Eq. 1) and (Eq. 4) should be modified: for an instantaneous, reversible, non-linear sorption equilibrium, the Freundlich isotherm can be used; for the sorption process during which the forward reaction is either linear or non-linear and the backward reaction is linear, a reversible, first-order non-linear kinetic equation can be used [*e.g.*, 17, 25]. Due to the complexity of the problem, laboratory diffusions involving non-linear sorption must be solved by numerical approaches or semi-analytical methods [*e.g.*, 26, 27].

Formulations for Sorption Experiments

The distribution or sorption coefficient, K_d, is defined as the ratio of the solute concentration in solid material to the solute concentration in liquid solution:

$$K_d = \frac{C_{rock}}{C_{solution}}$$ (Eq. 5)

where C_{rock} is the solute concentration per solid mass (mol K_g^{-1}) and $C_{solution}$ is the solute concentration in the pore water (mol m^{-3}).

In general, the distribution or sorption coefficient, K_d, is determined from batch experiments using grounded mineral powders or crushed materials, and its value can be calculated by the following equation [*e.g.*, 28]:

$$K_d = \frac{C_{init} - C_{eq}}{C_{eq}} \cdot \frac{V}{m}$$ (Eq. 6)

where C_{init} is the total initial liquid or aqueous solute concentration (mol m^{-3}), C_{eq} is the total equilibrium aqueous solute concentration (mol m^{-3}), V is the volume of the liquid phase, and m is the mass of the solid phase. A batch experiment requires a certain period to reach equilibrium—the larger the particle size, the longer the time required for the experiment. Grounded and sieved mineral powders are generally used to reduce the time required for a batch experiment. However, many researchers have reported that batch experiments may overestimate the K_d value [*e.g.*, 29, 30], which is probably due to the creation of new surfaces when crushing the material for batch experiments. The K_d value back-calculated from a diffusion test using a rock specimen of appropriately large size is more representative of the rock mass *in situ*. Therefore, it is important to simultaneously and accurately determine the rock capacity factor, a function of the total porosity, density, and distribution coefficient of a rock specimen, directly from a diffusion test.

LABORATORY DIFFUSION TESTS

Many kinds of diffusion test are available for determining the diffusive transport properties in the laboratory. Different researchers have divided the methods with different standards. Shackelford (1991) [31] divided the laboratory diffusion tests into two categories, *i.e.*, the steady-state and transient methods,

based on the status from which the values of the diffusion coefficient are derived. Lever (1986) [32] divided the laboratory diffusion methods into in-diffusion, out-diffusion, reservoir depletion, and through-diffusion experiments, possibly based on the structure of the systems for individual experiments. Similar to Lever (1986), we prefer dividing the laboratory diffusion tests into through-diffusion, in-diffusion, out-diffusion, and column methods because the reservoir depletion method is generally regarded as a kind of in-diffusion test and the column method should also be included.

Through-Diffusion Tests

Among the many types of laboratory diffusion test, through-diffusion has been used extensively for testing compacted bentonite, bentonite-sand mixtures, and rock and rock-like materials, such as concrete, in the field of geological disposal of radioactive nuclear waste [*e.g.*, 11–13, 18]. The basic concept of the through-diffusion test involves sandwiching the test specimen between two reservoirs or cells as shown in Table I. One of the reservoirs serves as the source reservoir spiked with the trace solute of interest and the other serves as the measurement reservoir. Changes of solution concentrations in the measurement and/or source reservoirs are monitored, and the effective diffusion coefficient and the rock capacity factor are then calculated from the measured data. Through-diffusion tests can be further divided into four types according to the boundary conditions being controlled during individual tests (Table I): the constant inlet concentration-constant outlet concentration, constant inlet concentration-increasing outlet concentration, decreasing inlet concentration-increasing outlet concentration, and decreasing inlet concentration-constant outlet concentration through-diffusion tests.

Constant Inlet Concentration-Constant Outlet Concentration Through-Diffusion Test
As defined by its name, the constant inlet concentration-constant outlet concentration through-diffusion test 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 as well as the rock capacity factor of the test specimen are estimated from the data (concentration variations) of steady-state measurements. To allow 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 the measurement reservoir at the outlet side is replaced continuously with fresh solution throughout the test [*e.g.*, 17, 11]. To prevent the laborious procedure of replenishing the reservoirs with fresh solution, many researchers simply ignore the effects of the concentration increase in the measurement reservoir during analysis. This conventional type of through-diffusion test has the following advantages and disadvantages.

The conventional through-diffusion test has been used by many researchers and thus many actual results can be cited. The values of the effective diffusion coefficient and the rock capacity factor can be determined simply using the well-known time-lag method [*e.g.*, 11–13, 18]. However, the time required to establish steady-state conditions can be very long, especially when testing a long specimen with a low effective diffusion coefficient and/or a large rock capacity factor. The procedures for replacing solution in the measurement reservoir can be laborious, cumbersome, and may introduce the effects of hydraulic gradients into the diffusion test. As the flux through the test specimen is measured *via* very small concentration variations in the measurement reservoir, relative errors for the analysis can be significant. A recent theoretical evaluation illustrated that both the effective diffusion coefficient and the rock capacity factor can be underestimated if the solution in the measurement reservoir is not replaced—the higher the concentration increase in the measurement reservoir, the larger the error in estimating the two parameters [33].

Constant Inlet Concentration-Increasing Outlet Concentration Through-Diffusion Test
With the exception of the report by Rebour *et al*. (1997) [12], there have been no previous studies using the constant inlet concentration-increasing outlet concentration through-diffusion tests. A through-diffusion test can be performed by maintaining a constant solute concentration in the source reservoir and allowing the solute concentration in the measurement reservoir to increase (*i.e.*, the solution in the

measurement reservoir is not replaced with fresh solution). This method is shown schematically in Table I. Test results can be analyzed by a numerical approach combined with a curve fitting method [12], or using the recently derived rigorous solution to this method, which takes into account the increase in concentration in the measurement reservoir combined with the

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

	Constant Inlet Concentration-Constant Outlet Concentration	Constant Inlet Concentration-Increasing Outlet Concentration	Decreasing Inlet Concentration-Increasing Outlet Concentration	Decreasing Inlet Concentration-Constant Outlet Concentration
Concept				
Measurement item(s)	Time-dependent flux at the downstream boundary Total or accumulated quantity diffused into the downstream reservoir	Time-dependent variations in concentration in the measurement reservoir	Concentration decrease in the source reservoir Concentration increase in the measurement reservoir	Concentration decrease in the source reservoir

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

	Constant Source Concentration			Decreasing Source Concentration
	Half Cell Method		Single Reservoir Method	
	Constant Concentration between half cells	In half cell		
Concept				
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

parameter identification technique [33]. The advantages and disadvantages of this method can be summarized as follows.

The solute concentration in the measurement reservoir is allowed to increase naturally, and it is not necessary to replace the solution in the measurement reservoir with fresh solution during the test. Therefore, there is no need for the laborious and cumbersome procedure of replacing reservoir solution. Consequently, possible errors that may be induced by the effects of hydraulic gradients during the solution replacement procedure can be eliminated. Compared to the conventional constant inlet concentration-constant outlet concentration method, it is not necessary to collect data under the steady-state condition and thus the time required for a test can be reduced. However, the time required for testing a specimen can still be relatively long because it is also necessary to wait for the tracer solution to diffuse through the whole length of the test specimen. In addition, detection of low concentration variations may involve relatively large errors in analysis.

Decreasing Inlet Concentration-Increasing Outlet Concentration Through-Diffusion Test
A through-diffusion test can be performed by using reservoirs of limited size for both the source and measurement reservoirs and detecting both the concentration decrease in the source reservoir and the concentration increase in the measurement reservoir (Table I). Garcia-Gutierrez *et al.* (2004) [34] used a numerical method to solve the governing equation together with the related initial and boundary conditions for this method. To further improve this method, we derived a rigorous analytical solution to this method by considering the concentration decrease in the source reservoir and concentration increase in the measurement reservoir [33]. We have also used this improved method recently to investigate the diffusive transport properties of a rock sample taken from the Kanamaru Research Site in Japan [35]. The advantages of this improved through-diffusion test have been illustrated through practical application and can be summarized as follows.

Testing management is relatively easy because it is not necessary to control the constant inlet concentration in the source reservoir or to replenish the solution in the measurement reservoir. Thus, potential errors due to the induced hydraulic gradients during the solution replacement procedure can be avoided. The effective diffusion coefficient and the rock capacity factor can be estimated from the concentration decrease in the source reservoir, concentration increase in the measurement reservoir, and also the concentration difference between the two reservoirs. Cross-checking of the results obtained from the three types of analyses can increase the reliability of the parameter being estimated. In the case of testing a long specimen with a relatively low effective diffusion coefficient and/or large rock capacity factor, transient concentration variations detected in the source reservoir can be used to determine the necessary diffusive parameters (assuming sorption is linear). This feature benefits the design and testing of large-sized rock specimens, which are more representative of the rock mass *in situ*.

Decreasing Inlet Concentration-Constant Outlet Concentration Through-Diffusion Test
The accuracy of detecting high concentrations is generally higher than detecting low concentrations for chemical analysis with a given resolution. That is, the relative error of analysis can be significant when analyzing low concentrations using a device with a given resolution. A possible modification of the through-diffusion test is to detect only the concentration decrease in a properly designed small-sized source reservoir, and to maintain a constant outlet concentration (practically zero) simply by continuously flushing the outlet side of the test specimen with fresh solution or using a sufficiently large reservoir to dampen concentration variations within it (Table I). Although there are still no examples of such experiments in the literature, we believe that this method, in principle, would have the following advantages over the traditional constant inlet concentration-constant outlet concentration through-diffusion test.

Detecting the concentration decrease in the source reservoir is faster than detecting the concentration variation in and/or solute flux in the measurement reservoir, because it is not necessary to wait for the tracer solution to diffuse through the whole length of the test specimen. The accuracy of detecting large concentration variations is higher and thus the error of analysis is relatively small. Zero concentration at

the outlet side can be accomplished easily by continuously flushing the outlet end of the test specimen with fresh solution or by using a sufficiently large-sized reservoir, and thus testing management can be simplified.

In-Diffusion Tests

In-diffusion tests are generally 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 II.

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 II. In most studies using the half-cell method [*e.g.*, 7, 9, 15], an amount of tracer solute is tagged to 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.*, 36]. 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.

Constant source concentration in-diffusion tests do not require periodical 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. In addition, 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 or reservoir depletion test is also shown schematically in Table II. 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*. [20], 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, practical application of this method is rare with only a few examples

in the literature, such as the report by Van *et al.* [4]. In addition, a generalized form of the solution to this method has not been established and this work will be described in paper 2 of this study.
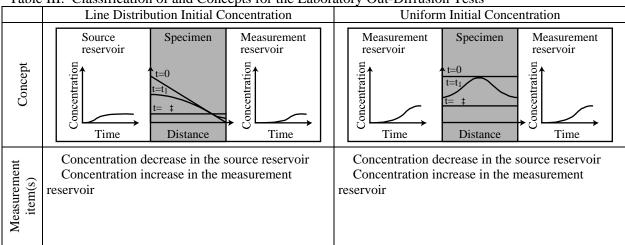
Table III. Classification of and Concepts for the Laboratory Out-Diffusion Tests

	Line Distribution Initial Concentration	Uniform Initial Concentration
Concept		
Measurement item(s)	Concentration decrease in the source reservoir Concentration increase in the measurement reservoir	Concentration decrease in the source reservoir Concentration increase in the measurement reservoir

Out-Diffusion Tests

An out-diffusion test can be performed after a traditional through-diffusion test by replacing the solution in both source and measurement reservoirs with fresh solution. The relevant diffusive properties of the test specimen can be determined by measuring the time-dependent variations in solute concentration in both reservoirs and appropriate solutions to the method (Table III). The results obtained from the out-diffusion test can be used to cross-check the results obtained from the through-diffusion test, and can thus increase the reliability of and/or confidence in the tests [*e.g.*, 17, 18].

In principle, an out-diffusion test can also be performed by first tagging a uniform solute concentration within a test specimen, and then dipping it into a reservoir (Table III). The relevant diffusive properties of test specimen can be determined by measuring the concentration variation in the reservoir [32]. This method may not be efficient, because tagging a specimen with a uniform solute concentration may take a long time and it may be very difficult to check the concentration distribution within the specimen.

Similar to many other methods that require detection of variations in low concentrations, the accuracy of chemical analyses may be limited.

Column Tests

Column tests are methods for determining transport properties of test specimens under advection-dispersion conditions. Diffusion tests are incorporated into a flow field with a constant advective component of transportation. Column tests can be separated into three types according to the boundary conditions, as shown in Table IV: *i.e.*, the constant source concentration [19], decreasing source concentration [20], and pulse injection methods [21].

Constant Source Concentration Column Test
The constant source concentration column test, referred to as the traditional column test, has been used extensively in studies of mass transport through porous materials. The concept underlying this method is illustrated in Table IV. A steady-state fluid flow is first established through the test specimen and then the fluid in the source reservoir is changed to a solution with a constant concentration. The hydrodynamic dispersion coefficient, rather than the effective diffusion coefficient, can be back-calculated from the so-called break-through curve that illustrates the relative concentration defined as the ratio of the

concentration measured in the outlet reservoir divided by the constant source concentration *vs.* the time or pore volume of flow.
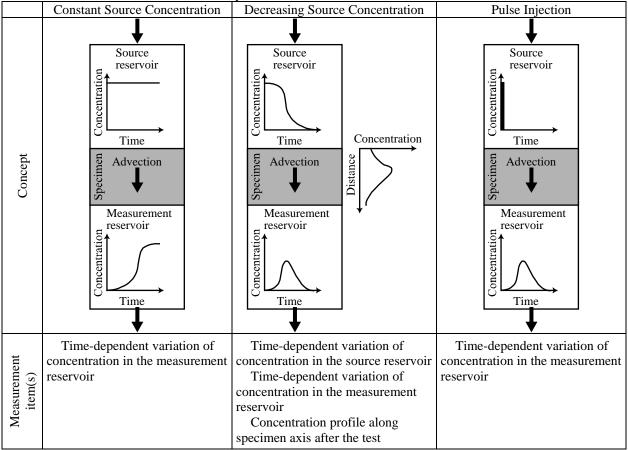
Table IV. Classification of and Concepts for the Column Tests

	Constant Source Concentration	Decreasing Source Concentration	Pulse Injection
Concept			
Measurement item(s)	Time-dependent variation of concentration in the measurement reservoir	Time-dependent variation of concentration in the source reservoir Time-dependent variation of concentration in the measurement reservoir Concentration profile along specimen axis after the test	Time-dependent variation of concentration in the measurement reservoir

This traditional constant source concentration column test has been used for a relatively long time, and thus most investigators should be quite familiar with it. However, this method cannot be used to determine the effective diffusion coefficient, and cannot be used to test specimens with low permeability. In cases in which the velocity of seepage is very small, the hydrodynamic dispersion coefficient can be regarded as the same as the effective diffusion coefficient.

Decreasing Source Concentration Column Test
The concept of the decreasing source concentration column test is similar to that of the traditional test (Table IV), with the only difference being that the tracer concentration in the source reservoir is allowed to decrease over time. Due to the complexity of the problem, test data are generally interpreted by a semi-analytical solution combined with numerical approaches [*e.g.*, 37].

Both the effective diffusion coefficient and the rock capacity factor of the test specimen can be determined using the concentration variations detected in the source and measurement reservoirs during the test, and the concentration profile along the direction of the specimen axis measured after the test. In addition, test management is relatively easy because the concentration in the source reservoir is allowed to decrease with time and it is not necessary to maintain a constant source concentration.

Pulse Injection Column Test

The experimental setup for the pulse injection test is similar to those for the above two column tests (Table IV). The experiment consists of injecting a quantity of a (tracer) solute into the source reservoir at zero time, and then letting water pass through the test specimen. The concentration variation of injected solute in the measurement reservoir is measured until the tracer has flowed out of the system. The apparent diffusion coefficient and the diffusion accessible porosity can be determined from the test results by a recently derived analytical solution to this method [21]. The major advantages of the pulse injection column test are similar to those of the decreasing concentration column test. As this method requires detection of the tracer that has flowed into and dispersed within the measurement reservoir, it may be difficult for testing low-permeability specimens.

CONCLUDING REMARKS

Laboratory diffusion and batch experiments are very important test methods in both scientific and applied fields, including geological disposal of radioactive nuclear waste. Although many test methods are currently available, different methods may have different advantages and disadvantages. A systematic overview of the methods may help us to better understand the technology and may provide information necessary to allow the appropriate design and interpretation of laboratory diffusion tests. Limited by time and space, we performed a brief overview of laboratory diffusion and batch experiments based on conceptual principles of individual test methods without detailing the solutions to the problems associated with each test method. Major conclusions drawn from the present overview can be summarized as follows.

1) Batch experiments using mineral powders or crushed rock materials have a tendency to overestimate the sorption coefficient. To obtain more reliable values of sorption coefficient for test material, it is preferable to use an appropriately large specimen that may be representative of the rock mass *in situ*. In addition, simultaneous determination of the effective diffusion coefficient and the rock capacity factor directly from a diffusion test may be more effective and meaningful.

2) Laboratory through-diffusion tests have the advantage of allowing the simultaneous determination of the effective diffusion coefficient and rock capacity factor of a test specimen. However, traditional constant inlet concentration-constant outlet concentration through-diffusion tests have a number of disadvantages, including long test times, low chemical analysis accuracy for detecting small variations of solute concentration, and large error caused by differences between the analytical assumptions and actual test conditions. Improved laboratory through-diffusion tests consider the concentration variations in the source reservoir as well as in the measurement reservoir and further studies on these test methods are needed.

3) Laboratory in-diffusion tests have the advantage of easy test management as there is no need for periodic sampling. However, traditional constant source concentration in-diffusion tests can only be used to determine the apparent diffusion coefficient and not the effective diffusion coefficient. In addition, sectioning of the test specimen can be cumbersome and may be difficult for hard rocks. The improved in-diffusion test using a single reservoir may improve these issues, and therefore further studies of this test method are needed.

4) Laboratory column tests can be used to determine the relevant transport properties of a test specimen under advection and dispersion conditions, but they may not be efficient when used to test specimens with low permeabilities. When the seepage flow is very low, the hydrodynamic dispersion coefficient derived from the column test is reduced to the same value for the effective diffusion coefficient.

1. To provide a theoretical basis for effective organization of a laboratory diffusion test and to facilitate appropriate interpretation of the test results, part 2 of this study involves a systematic theoretical study on major improved through- and in-diffusion tests—specifically the decreasing inlet concentration-increasing outlet concentration through-diffusion test, decreasing inlet concentration-constant outlet concentration through-diffusion test, and decreasing source concentration in-diffusion

test, *i.e.*, single-reservoir in-diffusities of Geological Materials, Proceedings of Waste Management 2005, CD-ROM

2. Garcia-Gutierrez, M., Cormenzana, J. L., Missana, T., and Mingrarro, M. (2004). Diffusion Coefficients and Accessible Property for HTO and 36Cl in Compacted FEBEX Bentonite. *Applied Clay Science* 26: 65-73.

3. Zhang, M., Takeda, M., and Nakajima, H. (2006). Determining the Transport Properties of Rock Specimens using an Improved Laboratory Through Diffusion Technique. *Proceedings of the 29th International Symposium on the Scientific Basis for Nuclear Waste Management* (In press).

4. Gillham, R. W., Robin, M. L. J., Dytynyshyn, D. J., and Johnston, H. M. (1984). Diffusion of Nonreactive and Reactive Solutes through Fine-Grained Barrier Materials. *Canadian Geotechnical Journal* 21: 541-550.

Rowe, R. K. and Bookon test methods, also referred to as decreasing inlet concentration-no flux downstream boundary in-diffusion tests.

REFERENCES

5. Neretnieks, I. (1980). Diffusion in the Rock Matrix: An Important Factor in Radionuclide Retardation? *Journal of Geophysical Research* 85(B8): 4379-4397.

6. Wadden, M. M. and Katsube, T. J. (1982). Radionuclide Diffusion Rates in Igneous Crystalline Rocks. *Chemical Geology* 36: 191-214.

7. Lever, D. A., Bradbury, M. H., and Hemingway, S. J. (1983). Modelling the Effect of Diffusion into the Rock Matrix on Radionuclide Migration. *Progress in Nuclear Energy* 12(1): 85-117.

8. Van Loon, L. R. and Eikenberg, J. (2005). A High-Resolution Abrasive Method for Determining Diffusion Profiles of Sorbing Radionuclides in Dense Argillaceous Rocks. *Applied Radiation and Isotopes* 63: 11-21.

9. Muurinen, A. (1990). Diffusion of Uranium in Compacted Sodium Bentonite. *Engineering Geology* 28: 359-367.

10. Kim, H. T., Suk, T. W., and Park, S. H. (1993). Diffusion for Ions through Compacted Na-Bentonite with Varying Dry Bulk Density. *Waste Management* 13: 303-308.

11. Cho, W. J., Oscarson, D. W., and Hahn, P. S. (1993). The Measurement of Apparent Diffusion Coefficients in Compacted Clays: An Assessment of Methods. *Applied Clay Science* 8: 283-294.

12. Eriksen, T. E., Jansson, M., and Molera, M. (1999). Sorption Effects on Cation Diffusion in Compacted Bentonite. *Engineering Geology* 54: 231-236.

13. Kozaki, T., Sato, Y., Nakajima, M., Kato, H., Sato, S., and Ohashi, H. (1999). Effect of Particle Size on the Diffusion Behavior of Some Radionuclides in Compacted Bentonite. *Journal of Nuclear Materials* 270: 265-272.

14. Sato, H., and Suzuki, S. (2003). Fundamental Study on the Effect of An Orientation of Clay Particles on Diffusion Pathway in Compacted Bentonite. *Applied Clay Science* 23: 51-60.

15. Skagius, K. and Neretnieks, I. (1986). Porosities and Diffusivities of Some Nonsorbing Species in Crystalline Rocks. *Water Resources Research* 22(3): 389-398.

16. Rebour, V., Billiotte, J., Deveughele, M., Jambon, A., and Guen, C. L. (1997). Molecular Diffusion in Water-Saturated Rocks: A New Experimental Method. *Journal of Contaminant Hydrology* 28: 71-93.

17. Sato, H., Shibutani, T., and Yui, M. (1997). Experimental and Modeling Studies on Diffusion of Cs, Ni and Sm in Granodiorite, Basalt and Mudstone. *Journal of Contaminant Hydrology* 26: 119-133.

18. Skagius, K. and Neretnieks, I. (1988). Measurements of Cesium and Strontium Diffusion in Biotite Gneiss. *Water Resources Research* 24(1): 75-84.

19. Idemitsu, K., Ishiguro, K., Yusa, Y., Sasaki, N., and Tsunoda, N. (1990). Plutonium Diffusion in

Compacted Bentonite. *Engineering Geology* 28: 455-462.

20. Van Loon, L. R. and Eikenberg, J. (2005). A High-Resolution Abrasive Method for Determining Diffusion Profiles of Sorbing Radionuclides in Dense Argillaceous Rocks. *Applied Radiation and Isotopes* 63: 11-21.

21. Jakob, A., Sarott, F. A., and Spieler, P. (1999). Diffusion and Sorption on Hardened Cement Pastes – Experiments and Modelling Results. Waste Management Laboratory, PSI-Bericht Nr. 95-05.

22. Tits, J., Jakob, A., Wieland, E., and Spieler, P. (2003). Diffusion of Tritiated Water and 22Na+ through Non-Degraded Hardened Cement Pastes. *Journal of Contaminant Hydrology* 61: 45-62.

23. Bear, J. (1972). *Dynamics of Fluids in Porous Media*. American Elsevier, New York (1972) 569 p.

24. Rowe, R. K., Caers, C. J., and Barone, F. (1988). Laboratory Determination of Diffusion and Distribution Coefficient of Contaminants using Undisturbed Clayey Soils. *Canadian Geotechnical Journal* 25: 108-118.

25. Aertsens, M., Put, M., and Dierckx, A. (2003). An Analytical Model for the Interpretation of Pulse Injection Experiments Performed for Testing the Spatial Variability of Clay Formations. *Journal of Contaminant Hydrology* 61: 423-436.

26. Grathwohl. (1998). *Diffusion in Natural Porous Media: Contaminant Transport. Sorption/Desorption and Dissolution Kinetics.* Kluwer Academic Publishing, Boston (1998), 224 p.

27. Lever, D. A., Bradbury, M. H., and Hemmingway, S. J. (1985). The effect of dead-end porosity on rock matrix diffusion. *Journal of Hydrology* 80: 45-76.

28. Hsieh, P. A., Tracy, J. V., Neuzil, C. E., Bredehoeft, J. D., and Silliman, S. E. (1981). A Transient Laboratory Method for Determining the Hydraulic Properties of "Tight" Rocks – I. Theory. *International Journal of Rock Mechanics and Mining Sciences & Geomechanics Abstracts* 18(3): 245-252.

29. Marczewski, A. W. (2004). A Practical Guide to Isotherms of Adsorption on Heterogeneous Surfaces, An Overview. http://adsorption.org/awm/ads/Ads.thm

30. Baik, M. H. and Lee, K. J. (1991). Analysis of Nonlinear Diffusion Phenomena in the Compacted Bentonite Backfill. *Chemical Engineering Science* 46(12): 3296-3299.

31. Fesch, C., Simon, W., Haderlein, S. B., Reichert, P., and Schwarzenbach, R. P. (1998). Nonlinear Sorption and Nonequilibrium Solute Transport in Aggregated Porous Media: Experiments, Process Identification and Modeling. *Journal of Contaminant Hydrology* 31: 373-407.

32. Van Loon, L. R., Baeyens, B., and Bradbury, M. H. (2005). Diffusion and Retention of Sodium and Strontium in Opalinus Clay: Comparison of Sorption Data from Diffusion and Batch Sorption Measurements, and Geochemical Calculations. *Applied Geochemistry* (In press).

33. Johansson, H. et al. (1998). Diffusion Pathways in Crystalline Rock-Examples for Aspo-Diorite and Fine-Grained Granite. *Journal of Contaminant Hydrology* 35: 41-53.

34. Holtta, P., Siitari-Kauppi, M., Hakanen, M., and Tukiainen, V. (2001). Attempt to Model Laboratory-Scale Diffusion and Retardation Data. *Journal of Contaminant Hydrology* 47: 139-148.

35. Shackelford, C. D. (1991). Laboratory Diffusion Testing for Waste Disposal – A Review. *Journal of Contaminant Hydrology* 7: 177-217.

36. Lever, D. A. (1986). Some Notes on Experiments Measuring Diffusion of Sorbed Nuclides through Porous Media. Harwell Report, AERE R12321, 24 p.

37. Zhang, M. and Takeda, M. (2005). Theoretical Evaluation of the Through Diffusion Test for Determining the Transport Properer, J. R. (1984). The Analysis of Pollutant Migration in a Non-Homogeneous Soil. *Geotechnique* 34(4): 601-612.