

A Study on the Migration Characteristics of Cs-137 in a Packed Column

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충전층에서의 세슘-137의 이동특성에 관한 연구

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Abstract

In this study the migration experiment using packed column with crushed tuff was conducted as a basic research to develop migration model of radionuclides through geologic media. The main emphasis was put on evaluating the validity of migration models. For this, two models were introduced: one is the model which is based on the assumption of instantaneous equilibrium reaction and the other the model based on kinetic process such as intraparticle diffusion. The coefficient of hydrodynamic dispersion in packed column was determined using iodine as nonsorbing tracer. The hydrodynamic dispersion coefficient, D_L was shown to be $0.11 \times 10^{-2} \text{ cm}^2/\text{min}$ under the condition of the column porosity of 0.483 and the average water velocity of $0.915 \times 10^{-2} \text{ cm}/\text{min}$. The distribution coefficient, K_d of Cs-137 on crushed tuff was 11.3 cc/g at the concentration of $2 \times 10^{-6} \text{ M}$ and the temperature of 20°C . The breakthrough curve of Cs-137 through packed column was shown to have an asymmetric curve in which long trailing tail appears at the end part of the curve. The results obtained from the comparison of introduced models with experimental data indicated that the mass transfer model with intraparticle diffusion as rate-controlling step simulated the behaviors of Cs-137 migration more adequately, when compared with the bulk reaction model in which the assumption of instantaneous equilibrium reaction was made. Consequently, the intraparticle diffusion was found to be an important factor in the migration of Cs-137 through packed column.

요 약

처분 안전성 평가를 위해서는 지하매질을 통한 방사성핵종의 이동특성 규명과 신뢰성 있는 지하 핵종이동 모델의 확보가 무엇보다 중요하다. 본 연구에서는 지하핵종이동 모델 개발을 위한 기초연구로서 충전층 실험을 수행하고, 실험결과를 제안된 핵종이동모델과 비교·검토하였다. 실험에서는 분쇄응회암으로 충전된 칼럼에서의 핵종이동 현상을 규명하고, 모델 시뮬

레이션을 통해서 세공확산을 모델에 고려하여 핵종이동에서 세공확산의 역할을 검토하였다. 충전층 실험에서 수력학적 분산계수는 비흡착성의 iodine을 사용하여 측정하였으며, 이 때 측정한 분산계수는 공극율 $\epsilon=0.483$, 평균유속 $\bar{V}=0.915 \times 10^{-2}$ cm/min에서 $D_L=0.11 \times 10^{-2}$ cm²/min이었다. 그리고 중·저준위 방사성폐기물의 대표 핵종으로 사용한 Cs-137은 응회암에 대해 높은 지연특성을 보였으며, 과과곡선은 비대칭 형태로서 단말현상이 길게 나타났다. 모델 시뮬레이션 결과, 매질 세공내 확산과정은 다공성의 지하매질을 통한 핵종이동에서 중요한 윤회단계 역할을 하였다.

I. Introduction

The objective of radwaste disposal is to isolate radioactive wastes from biosphere for the prevention of a radiological impact of radionuclides on human environment which are released via groundwater from disposed wastes. For this, the capacity of geologic media to the retardation of the transport of radionuclides during the period of institutional regulation should be evaluated before constructing an underground repository for the disposal of radioactive wastes.

The safety assessment of a geologic system should be performed in the way that the migration of radionuclides in geologic media is theoretically predicted and then a radiological impact of the radionuclides released on human environment is assessed, to assure the safety and reliability of the disposal system for radioactive wastes. Thus, the safety assessment requires the migration model to predict the behavior of radionuclides through geologic media from a repository.

To date, some studies on the migration model of radionuclides in geologic media have been carried out with the emphasis on the interaction between radionuclides and geologic media, e.g., the kinetics of sorption by which the movement of radionuclides via groundwater is retarded. The sorption of radionuclides on solid phase during the migration of radionuclides from a repository can in general be described by the following three steps: diffusion from the bulk of liquid solution to the external surface of solid phase, diffusion into the pore within solid, and sorption on the pore surface. It has been reported in the previous papers

that the overall rate of sorption in geologic media such as granite and tuff rocks is mainly controlled by intraparticle diffusion, the second step of the above mechanisms.[1-2] In the point of view for developing migration model suitable for the safety assessment of disposal system, two models (i.e., bulk reaction model and mass transfer model) are introduced in this study to investigate the importance of intraparticle diffusion in the migration of radionuclides through rock. The bulk reaction model which is based on the assumption of instantaneous equilibrium reaction, has been used widely for the safety assessment because of simple assumptions, while the mass transfer model with intraparticle diffusion as a rate-controlling step has been known to be useful in predicting the movement of radionuclides in rock for the improvement of the reliability of the safety assessment.

In this study, the validity of two models introduced is reviewed and the migration characteristics of Cs-137 is investigated by the migration experiment using a packed column with crushed tuff.

II. Theory

Mathematical Models

Migration experiment, using packed column with crushed tuff, is carried out to investigate the migration characteristics of Cs-137 through porous media. A schematic representation of packed column used here is given in Fig. 1.

The migration of Cs-137 through packed column involves a number of mechanisms, e.g., advection, dispersion, intraparticle diffusion, sorption, etc.. This

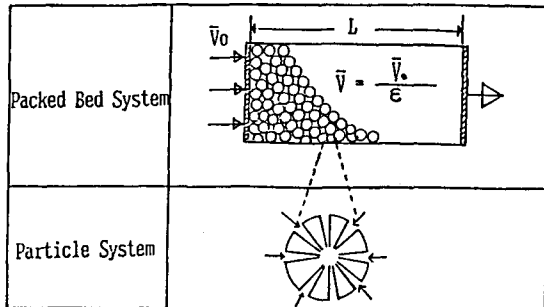


Fig. 1. A Schematic Diagram of the Transport Mechanisms of Cs-137 in Packed Column

study focuses on the effect of advection, dispersion, sorption, and diffusion into pores during the transport of Cs-137.

In order to predict the transport of Cs-137 through packed column two mathematical models are introduced: one is called "the bulk reaction model" with instantaneous equilibrium reaction, and the other "the mass transfer model" with intraparticle diffusion as a rate-controlling step which is followed by sorption. The models introduced are as follows:

The Bulk Reaction Model: This model is made by assuming the following: (1) a saturated homogeneous granular porous medium, (2) an one-dimensional flow system, and (3) the instantaneous equilibrium reaction between solid and liquid, in which adsorption isotherm is represented to be the linear type of $q = K_d C$. As for the migration of Cs-137 through a packed column with crushed tuff, equation (1) is obtained based on the above assumptions.

$$\frac{\partial C}{\partial t} + \frac{\rho_s q}{\epsilon} \frac{\partial q}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - \bar{V} \frac{\partial C}{\partial x} \quad (1)$$

where C is the concentration of Cs-137 in solution (moles/cm³), q the mass of Cs-137 in solid phase per unit mass of porous medium (moles/g), D_L the coefficient of hydrodynamic dispersion (cm²/sec), \bar{V} the average linear pore-water velocity (cm/sec), ρ_s the bulk density of packed column (g/cm³), ϵ the column porosity (-), x the Cartesian coordinate in the direction of flow (cm), and t the time (sec).

The initial and boundary conditions for the solution of eqn. (1) are

$$\left. \begin{aligned} C(x, 0) &= 0 & : x > 0 \\ C(0, t) &= C_0 & : t > 0 \\ \partial C / \partial x \big|_{x=L} &= 0 & : t > 0 \end{aligned} \right\} \quad (2)$$

where $0 < x < L$, and L is the column length used in this study (cm). In deriving the solution, however, the boundary condition $C(\infty, t) = 0$ is used rather than $\partial C / \partial x (L, t) = 0$ when the criteria established by Gershan and Nir exist.[3] Reynolds et al. reported in their paper that the solution to eqn. (1) with the two boundary condition was in excellent agreement under the condition satisfying the Gershan and Nir's criteria[4]. According to these results the boundary condition $C(\infty, t) = 0$, instead of $\partial C / \partial x (L, t) = 0$, is used in this study.

The Mass Transfer Model: In this model, intraparticle diffusion is considered as a rate-controlling step in place of the term (3) in the assumptions of the bulk reaction model. It is assumed that diffusion mechanism in a particle is described by the Fick's law of diffusion, and the effective diffusion coefficient is constant and independent of solution concentration.

Mass balances for the packed column and particle system with these assumptions give the following equations:

$$\frac{\partial C}{\partial t} + \frac{1-\epsilon}{\epsilon} \frac{3}{R} D_e \frac{\partial C}{\partial r} \bigg|_{r=R} = D_L \frac{\partial^2 C}{\partial x^2} - \bar{V} \frac{\partial C}{\partial x} \quad (3)$$

$$\left(1 + \frac{1-\epsilon_p}{\epsilon_p} \rho_s K_d \right) \frac{\partial C_p}{\partial t} = D_e \left(\frac{\partial^2 C_p}{\partial r^2} + \frac{2}{r} \frac{\partial C_p}{\partial r} \right) \quad (4)$$

where C_p is the concentration of Cs-137 in the pores within particle, D_e the effective diffusion coefficient, ϵ_p the porosity of particle, ρ_s the density of solid particle, R the radius of spherical particle, and r the radial distance in a spherical particle.

These equations include convective transport, axial dispersion, diffusion into the pores within a particle, and the sorption of Cs-137 onto solid phase.

For a step injection the following initial and boundary conditions may be applied

$$\begin{aligned}
 C(x, 0) &= 0 & : x > 0 \\
 C(0, t) &= C_0 & : t > 0 \\
 C_p(r, x, 0) &= 0 & : x > 0, r > 0 \\
 \partial C_p(0, x, t) / \partial r &= 0 & : x > 0, t > 0
 \end{aligned} \quad (5)$$

The equations (3) and (4) are solved by finite difference method using the initial and boundary conditions of equation (5). Central difference and Crank-Nicolson schemes are applied in the finite difference method.

Determination of Hydrodynamic Dispersion and Adsorption Parameters

Hydrodynamic Dispersion Coefficient: Hydrodynamic dispersion describes the influence of radionuclide diffusion and pore-water velocity variation on the transport of radionuclide. Its effect is to impose a sigmoid spreading on the advecting front of radionuclide, and the hydrodynamic coefficient which consists of axial and transverse components, governs the rate of this spreading.

In this study, it is assumed that the hydrodynamic dispersion coefficient in the packed column is constant, and the transverse component of this coefficient is negligible when compared with the axial one.

The hydrodynamic dispersion coefficient may be determined in several methods. Levenspiel and Smith mentioned three methods for calculating the axial hydrodynamic dispersion coefficient[5]: first, by point calculation for the breakthrough curve of a pulse input; second, by finding the variance for the breakthrough curve of a pulse input; and third, by a slope method for the breakthrough curve of a step input. The hydrodynamic dispersion coefficient in this study is calculated using the empirically derived relationship of Rifai et al. which belongs to the third method mentioned above.[6] It is used here in the form:

$$D_L = \bar{V}_s L / (4\pi \bar{V}_0^2 S_0^2) \quad (6)$$

where \bar{V}_s is the average pore velocity of the nonsorbing tracer (cm/sec), V_0 the volume of the effluent solu-

tion at $C/C_0 = 0.5$ (cm^3), and S_0 the slope of the breakthrough curve at $C/C_0 = 0.5$ (cm^{-3}). However, the following assumptions are required for the use of eqn. (6).

1. The tracer used has no retardation.
2. The tracer solution is fed into a column as constant flux and step input.

Sorption Distribution Coefficient: The distribution coefficient, K_d of sorption indicates the extent to which the reaction takes place for a particular nuclide. The K_d is the ratio of the mass of nuclide sorbed per unit mass of solid phase to the mass of nuclide remaining in solution per unit volume of liquid:

$$K_d = \frac{(\text{g of sorbed nuclide}) / (\text{g of solid})}{[(\text{g of nuclide remaining in solution}) / (\text{cm}^3 \text{ of solution})]} \quad [\text{cm}^3/\text{g}] \quad (7)$$

Measurement of the K_d is based on the assumptions that the sorption is reversible and linear, other reactions such as precipitation do not occur, and near-equilibrium conditions exist. Currently, no standard methodology exists for experimentally determining distribution coefficients for rock samples. The K_d being determined by batch or column experiments is in most common use.

$$\frac{\bar{V}}{\bar{V}_N} = 1 + (\rho_b / \epsilon) K_d \quad (8)$$

where \bar{V} and \bar{V}_N are the velocities of water and radionuclide, respectively.

The first complete derivation of the linear retardation equation appears in Mayer and Tompkins,[8] but it was not presented in the form of eqn. (8) until Vermeulen and Hiester.[9] Equation (8) allows the direct determination of K_d from a breakthrough curve, where the \bar{V}/\bar{V}_N ratio is determined at $C/C_0 = 0.5$. That is, rearranging eqn. (8) gives

$$K_d = \frac{\epsilon}{\rho_b} \left(\frac{\bar{V}}{\bar{V}_N} - 1 \right) \quad (9)$$

When the results are plotted using dimensionless variables, as in Fig. (4) of the latter section IV, \bar{V}_N can

be determined from the measured breakthrough curve by

$$\bar{V}_N = L / [(NPV_{0.5}) (V_v/Q)] \quad (10)$$

where $NPV_{0.5}$ is the number of pore volume of column effluent at $C/C_0 = 0.5$ (—), V_v the volume of void space in a packed bed, and Q is the volumetric solution flow rate (cm^3/sec). [4]

III. Experiments

Packed column experiment was conducted to investigate the migration characteristics of Cs-137 via groundwater through porous media.

Tuff samples in the experiment were from a candidate disposal site in Korea. The samples were crushed and screened, and the particle size fraction of 0.0279 to 0.0535 cm was used in the packed column (mean radius of particle = 0.0407 cm). The specific surface area of the tuff was measured by BET method with nitrogen as a sorbing gas. The surface area of the samples was $1.299 \text{ m}^2/\text{g}$. The density ρ_s and porosity ϵ_p of the crushed particles are 2.408 g/cm^3 and 0.04, respectively.

NaI solution of 10^{-1} M as nonsorbing tracer was used to investigate the characteristics of hydrodynamic dispersion within packed column. Cesium tracer solution in the migration experiment was prepared by adding radioactive isotope of Cs-137 to the cesium chloride solution of $2 \times 10^{-6} \text{ M}$, and the prepared tracer solution of cesium had the activity of $10^{-1} \mu\text{Ci/cm}^3$.

The experimental setup used in this study, which is represented in Fig. 2, mainly consists of a reservoir for spiked solution, a peristaltic pump to deliver solution from the reservoir to the column, an apparatus to physically contain crushed particles of tuff, and a sample collector for column effluent. The column section, the main part of an experimental setup was made of a glass tube of 1.78 cm in inner diameter and 16.25 cm in height.

Experimental procedure consists of several steps. The glass column is first packed with crushed particles

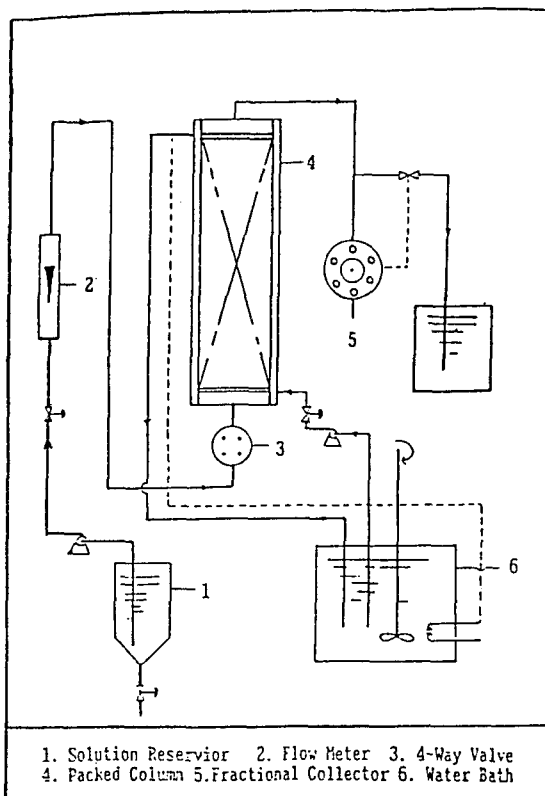


Fig. 2. Experimental Setup used in the Migration Experiment of Radionuclide

of rock. The packed column is saturated with distilled water, and then the solution containing the radionuclide is pumped through the column. Flow rate is adjusted to the value of $0.011 \text{ cm}^3/\text{min}$ to simulate in-situ flow near a possible underground repository. The flow is slow enough to allow equilibrium to be established between the Cs-137 in solution and the ion exchange sites on mineral surfaces. The solution effluent from the packed column is collected periodically and analyzed by NaI detector to determine the concentration of Cs-137 as the function of the column pore volume that pass through the column. The ratio of effluent concentration to influent concentration is plotted against the column pore volume to produce breakthrough curve. The experiment is performed at the temperature of 20°C .

The models proposed for the prediction of Cs-137

movement through packed column required basic model parameters such as bulk density, column porosity and intraparticle diffusivity, which are determined ahead apart from the main column experiment. The bulk density ρ_b and column porosity ϵ are calculated using the following relationships.

$$\rho_b = \frac{M}{V} \quad (11)$$

where M is the mass of solid particles packed into the column which is determined by weighing them before and after packing (g) and V is the bulk volume of packed bed obtained by measuring the internal dimension of the column (cm^3).

$$\epsilon = 1 - \frac{\rho_b}{\rho_s} \quad (12)$$

where ρ_s is the average density of packed particle which is measured by pycnometry. The bulk density and column porosity determined from eqns. (11) and (12) were 1.11 g/cm^3 and 0.483 , respectively. The determination of intraparticle diffusion coefficient made use of the results from Han's diffusion experiment, in which the diffusion coefficient was measured using the same sample as in the packed column experiment. Han et al. showed in their paper that the intraparticle diffusion coefficient, D_e of the crushed tuff was $1.09 \times 10^{-10} \text{ m}^2/\text{sec}$. [10]

IV. Results and Discussion

1. Hydrodynamic Dispersion

The breakthrough curve for the iodine used as non-sorbing tracer is shown in Fig. 3. The curve is plotted as dimensionless concentration (C/C_0) versus dimensionless time represented as the number of pore volume. C_0 is the initial tracer concentration, and the number of pore volume is the volume of solution that has passed through a column at a particular time divided by the total volume of void space in the column. The breakthrough curve was sigmoid in shape and approached a symmetry. The hydrodynamic dispersion coefficient was determined from the

breakthrough curve of the iodine using the Rifai's relationship of eqn. (6). The calculated value of D_L was found $0.11 \times 10^{-2} \text{ cm}^2/\text{min}$ under the conditions of $\epsilon = 0.483$ and $\bar{V} = 0.915 \times 10^{-2} \text{ cm/min}$.

In general, the hydrodynamic dispersion of a fluid through porous media depends on Reynolds number. Farakas & Byleveld showed in their report that it was reasonable to consider the hydrodynamic dispersion term in the migration model, if the Peclet number, Pe , was larger than 0.002 under the condition of Reynolds number, $Re < 10$. [11] According to the above fact this study took into account the term of hydrodynamic dispersion in the migration, because the Reynolds number and Peclet number in the experiment were 8.4×10^{-4} and 0.34 , respectively.

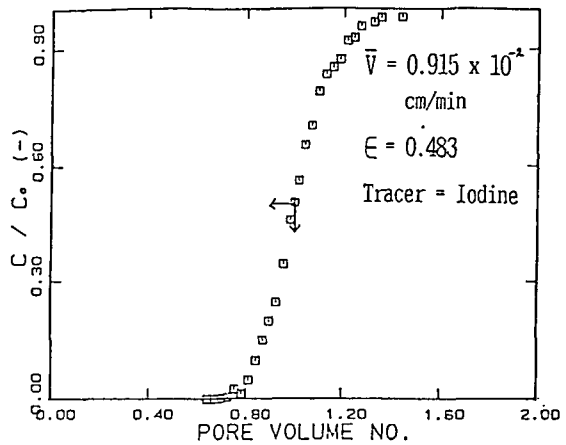


Fig. 3. The Breakthrough Curve of Iodine as Non-sorbing Tracer

2. Sorption of Cs-137 on crushed tuff

One column experiment was conducted to investigate the transport phenomena of Cs-137 under flow condition. The flow velocity of $0.915 \times 10^{-2} \text{ cm/min}$ was used and the column porosity was the same as that of the non-sorbing tracer experiment. Figure 4 represents the breakthrough curve obtained in the column experiment. The breakthrough curve of Cs-137 was highly asymmetrically sigmoid with a tail extension, and the tail asymptotically approached the end

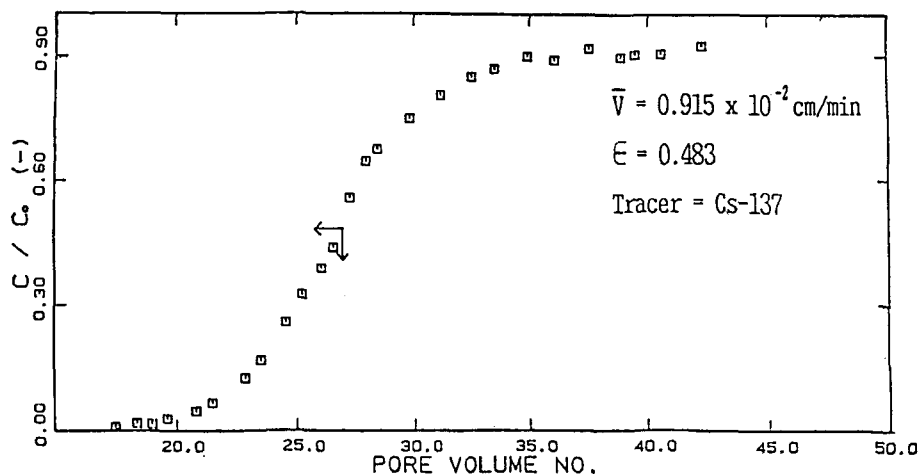


Fig. 4. The Breakthrough Curve of CS-137 through Packed Column with Crushed Tuff

value of C/C_0 .

In this experiment the K_d was determined, using eqn. (8), from \bar{V}_N such that the concentration of measured breakthrough curve matched that of $C/C_0 = 0.5$. The distribution coefficient of Cs-137 on crushed tuff was $11.3 \text{ cm}^3/\text{g}$ at the concentration of $2 \times 10^{-6} \text{ M}$ and the room temperature of 20°C .

3. Comparison between proposed models and experimental data

In order to simulate the behavior of such a breakthrough curve of Cs-137, two models (i.e., the bulk reaction model with instantaneous equilibrium reaction and the mass transfer model which is based on the assumption of intraparticle diffusion as a rate-controlling step followed by sorption) were introduced in this study.

The comparison of the proposed models with experimental data appears in Fig. 5. It is obvious from this figure that the curve of the bulk reaction model deviates considerably from the experimental data in the shape and spread of breakthrough curve. That is, the model showed a little deviation in the estimation of the leading tail of the curve, and it showed a large failure in simulating the end part of the experimental data curve. This suggests that one or more of the

assumptions made concerning the chemical reaction of Cs-137 with geologic media are not correct.

In the literature of Van Genuchten and Cameron and Klute it was reported as a cause of the deviation that the asymmetry was attributed to kinetic processes.[12-13] According to this fact, Han et al. conducted separately batch experiment to investigate the kinetic processes in the chemical reaction of Cs-137 with crushed tuff, using the same samples as in the packed column experiment of this study. The results from Han et al.'s experiment showed the sorption of Cs-137 onto crushed tuff was controlled by intraparticle diffusion.[8] In this study, the mechanism of the intraparticle diffusion was incorporated into the predictive model of the transport of Cs-137 through the packed column, which was conveniently called the mass transfer model. The comparison of the mass transfer model with experimental data can be seen in Fig. 5. This comparison indicates that the mass transfer model adequately simulated experimental data at the leading tail of the breakthrough curve, and it satisfied experimental data better than the bulk reaction model. This suggests that the intraparticle diffusion was an important factor in the migration of Cs-137 through the packed column with crushed tuff.

However, the mass transfer model with intraparticle diffusion also did not completely describe the extreme

tail and asymmetry of the experimental data. In order to improve our predictive capability to the migration of Cs-137 through porous media it is necessary that the processes causing the highly dispersed and asymmetrical breakthrough curve should be identified and incorporated into the predictive model.

V. Conclusions

The migration behavior of Cs-137 through the packed column with crushed tuff was investigated, and the validity of the theoretical models introduced was reviewed by the comparison with experimental data.

1. The hydrodynamic dispersion coefficient in the packed column was determined using iodine as non-sorbing tracer. The hydrodynamic dispersion coefficient, D_L was shown to be $0.11 \times 10^{-2} \text{ cm}^2/\text{min}$ which corresponded to $Pe=0.34$, under the condition of $\epsilon=0.483$ and $\bar{V}=0.915 \times 10^{-2} \text{ cm}/\text{min}$. It was revealed in this study that the term of hydrodynamic dispersion should be considered in modelling the migration of Cs-137 in a packed column.

2. The distribution coefficient, K_d of Cs-137 on crushed tuff was 11.3 cc/g at the concentration of $2 \times 10^{-6} \text{ M}$ and the temperature of 20°C . The breakthrough curve of Cs-137 through the packed column was shown to be asymmetric and have long tail

at the end part of the curve.

3. Two models were introduced and reviewed to simulated the migration of Cs-137 in the packed column. The results obtained from the comparison of two models introduced with experimental data indicated that the mass transfer model with the assumption of intraparticle diffusion simulated the migration behavior of Cs-137 more adequately, compared with the bulk reaction model in which the instantaneous equilibrium reaction was assumed. This suggested that the intraparticle diffusion played an important step in the migration of Cs-137 in a packed column with crushed tuff.

4. The mass transfer model with intraparticle diffusion, however, did not completely describe the extreme and asymmetry of the experimental data. This leads to the conclusion that the interaction of Cs-137 with crushed tuff involves other mechanisms besides kinetic process such as intraparticle diffusion.

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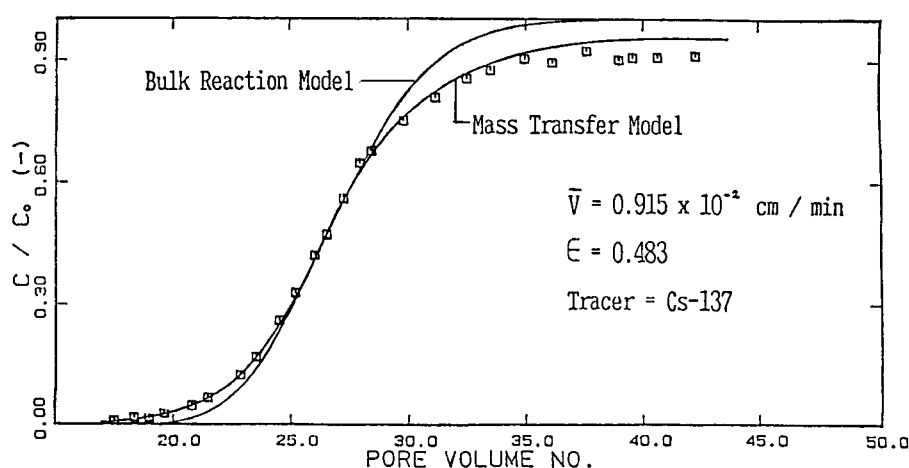


Fig. 5. The Comparison of Experimental Results with the Theoretical Values of Two Models Introduced

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