Polydispersed Colloid Transport in Porous Media : An Experiment and Modeling

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다공성 매질에서의 크기 분포를 갖는 콜로이드 이동 : 실험과 모델

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Abstract

The mechanism of radionuclide colloid transport in porous media was studied through modeling and experiments. A nondestructive column scanning system was developed to improve the traditional destructive core slicing method. With an aid of this system we could get much more results from one experiment. Neutron activated clay soaked with soluble isotopes was used as colloid suspension. Filtration coefficients obtained through the experiments show two families of colloids despite their size distribution. New modeling of polydispersed colloid transport was made with two lumped parameters. This new model simulates well. Among the soluble isotopes ^{137}Cs moved mainly as a form of colloid, but ^{85}Sr did not.

요   약

다공성 매질을 통한 방사성 핵종의 콜로이드에 의한 이동을 실험과 새로운 모델을 도입하여 살펴보았다. 본 실험에서는 기존의 컬럼 슬라이스 방법을 개선하기 위하여 비파괴 스캐닝 시스템을 개발하였다. 이 장치를 이용하여 기존의 방법보다 훨씬 많은 핵종이동에 관한 자료를 측정하였다. 중성자 조사를 시킨 진흙 입자와 여기에 방사성 핵종을 흡착시켜 콜로이드 입자를 만들었다. 실험결과 콜로이드 입자의 크기 분포에도 불구하고 콜로이드 여과계수는 2개의 그룹으로 명백히 구분되었다. 이를 모사하기 위하여 2개의 파라미터를 이용한 새로운 모델식이 개발되었고, 모델식은 실험결과를 잘 모사하였다. 흡착된 핵종중 ^{137}Cs은 주로 콜로이드 형태로 이동하였으나 ^{85}Sr은 그렇지 않았다.

1. Introduction

It is found that radionuclides sometimes move much faster than expected, which is not explained by a solute transport model. Lysimeter experiments with a simulated waste form and neutron activated clay showed colloid transport of radionuclides [1]. The results were evidenced by earlier appearance of radionuclides in the effluent and similar concentration profiles of dissolved radionuclides and neutron activ-

ated clay. The colloid transport was also observed in the experiments done by others [2, 3, 4].

The sources of colloids are precipitates of some metallic ions, bacterias, and clay minerals. The radionuclides leached from waste forms are adsorbed onto clay minerals, which are called pseudo-colloid. The movement of monosize colloid has been modeled using filtration concept. However, these pseudo-colloids have distribution in size, which makes it difficult to obtain an analytical or numerical solution. The polydispersed colloid transport in porous media was modeled by Saltelli et. al. [2] with filtration and adsorption of the colloid onto the packing materials.

In this paper the characteristics of colloid transport are investigated using a column packed with porous media, and a nondestructive scanning system is developed to measure the concentration profile in the column. ^{137}Cs and ^{85}Sr were soaked onto neutron activated clay to examine the migration properties of soluble isotopes on the pseudo-colloid. Clay is activated with neutron to measure the behavior of clay itself. The electrophoretic property of colloids is characterized by the measurement of zeta potential. A column experiment was conducted around 160 hours at a flow rate of 0.8 ml/h.

The results from a column experiment show that colloid transport can be modeled using two filtration coefficients despite their size distribution. Mathematical model with two lumped filtration coefficients has a simple analytical solution.

2. Theory

It is difficult to apply the simple equilibrium solute transport model to the situation that colloid transport is suspected as a dominant mechanism. Saltelli et. al. [2] conducted experiments with Americium colloids and columns packed with soil. They found several phenomena of interest through the experiment. Americium moved as colloids with a special size distribution. The column was saturated rapidly with the adsorption of colloids on the packing material, and it

made the effluent constant and plateau in the column. Their model has a problem of determining parameters, which should be optimised through the simulation.

If we look into the data from colloid transport experiments, most of results show trends in their concentration profile which consists of two parts with different slopes. That is, one part seems to be affected by the filtration with greater filtration coefficient, and the other influenced by the adsorption of small particles that can penetrate the bed not filtered or the filtration with smaller filtration coefficient. If a threshold diameter of the particle is assumed to account for two parts, the following transport equations can be used for the polydispersed colloid transport [2] ; for colloids larger than the threshold diameter,

$$\frac{\partial C_L}{\partial t} = D_L \frac{\partial^2 C_L}{\partial x^2} - V \frac{\partial C_L}{\partial x} - \frac{1}{\varepsilon} \frac{\partial \sigma_L}{\partial t} \tag{1}$$

$$\frac{\partial \sigma_L}{\partial t} = \varepsilon K_L V C_L \tag{2}$$

for colloids smaller than the threshold diameter,

$$\frac{\partial C_s}{\partial t} = D_s \frac{\partial^2 C_s}{\partial x^2} - V \frac{\partial C_s}{\partial x} - \frac{1}{\varepsilon} \frac{\partial \sigma_s}{\partial t} \tag{3}$$

$$\frac{\partial \sigma_s}{\partial t} = \varepsilon K_s V C_s \tag{4}$$

where C is the concentration of colloid in mobile water, σ the moles of colloid fixed per litre of column, V groundwater velocity, D the dispersion coefficient, ε porosity of packing material, and K_L and K_s denote the filtration coefficients.

Initial and boundary conditions are given by

$$C(x,0) = 0 \tag{5}$$

$$\sigma(x,0) = 0 \tag{6}$$

$$C(0,t) = C_0 \tag{7}$$

These conditions hold for both smaller and larger colloids.

If the dispersion terms in the equations (1) and (3) are neglected, the solutions can be obtained analyti-

cally with the boundary and initial conditions given in (5) to (7).

$$C(x,t) = C_0 \exp(-Kx)U(t - x/V) \tag{8}$$

$$\sigma(x,t) = \varepsilon K C_0 \exp(-Kx)S(t - x/V) \tag{9}$$

where functions U(y) and S(y) are defined as follows ;

$$\begin{array}{lll} & & \tag{10} \\ U(y) = 1 & y \geq 0 & \\ U(y) = 0 & y < 0 & \\ S(y) = y & y \geq 0 & \\ S(y) = 0 & y < 0 & \end{array}$$

The solutions (8) and (9) hold for both larger and smaller colloids. The main advantage of these solutions is that it is not necessary to get information on particle size distribution. If the filtration coefficient for large particles is great enough to neglect the appearance of them in effluent, the initial concentration for small particles can be estimated with the equation (8) and the concentration in the effluent. Another advantage is that two filtration coefficients can be directly obtained from the experiment.

3. Experimental

The experimental apparatus shown in figure 1 consists of a soil column, a peristaltic pump, a fraction collector, and a gamma scanning system. The gamma scanning system consisting of a motor controller, a Germanium crystal detector for gamma ray, and an IBM AT computer for the automatic control was de-
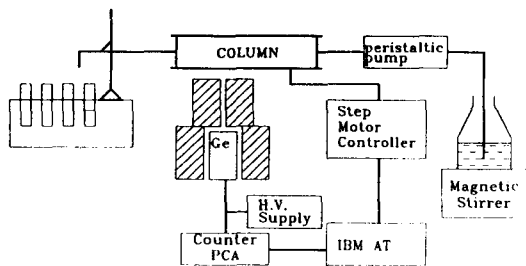
veloped for the nondestructive scanning. Gamma scanning was conducted through a collimator made of 0.4 cm slit between two 6 inch thick lead blocks that were optimised to reduce the effects of the high energy gamma rays from the other parts of the column and to increase the efficiency of the gamma detector. The dimensions of the columan are 5 cm in diameter and 15 cm in length, and the column was packed with 90 weight percents of sand and 10 percents of clay. The packing procedure is outlined in ref. 5. The packed column shows the bulk density of 1.71 g/ml and the porosity of 0.36.

The colloid suspension is prepared through the following procedure. About 1 gram of neutron activated clay was put into distilled water and agitated with an ultrasonic probe inserted 2.5 cm into the solution to get more fine particles. The top 5 cm of the suspension was taken off after 50 hours because the particle size given by a settling time of 0.1 cm/h was needed. The radionuclide tracers, ^{85}Sr and ^{137}Cs, were added to this suspension and neutralized with NaOH solution to prevent the particles from agglomerating in acid. The electrophoretic property of the suspension was characterized by measuring the zeta potential(see figure 2). Since the suspension starts to agglomerate at the zeta potential of around -15.0 mV in general [6], it is necessary to keep the suspension at neutral or basic state. During the experiment the suspension

Fig. 1. Schematic Diagram of Experimental Apparatus for Colloid Transport.
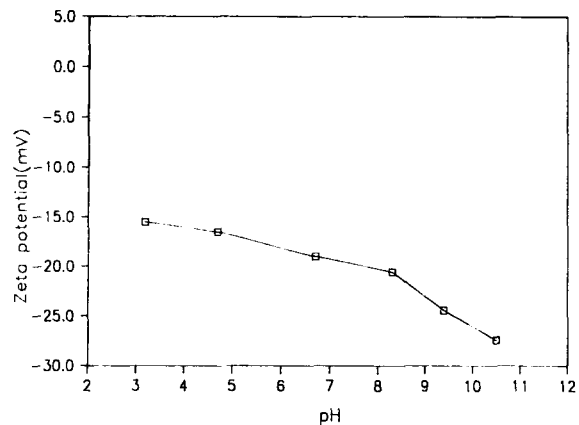

Fig. 2. Zeta Potential of Clay Colloids.

was stirred with a magnetic stirrer to avoid the sedimentation of fine particles.

The hydrodynamic property of a column was measured using tritiated water. Water was injected into the column at a flow of 0.8 ml/h. For a period of 17 hours the water was labeled with HTO. The effluent from the column was collected every 60 minutes and analyzed using a liquid scintillation counter.

After the column was saturated with water, the suspension was injected into the column for 160 hours at a flow rate of 0.8 ml/h. During the injection the column was scanned with a gamma scanning system. The column was scanned every 0.3 cm with a time interval of 10 minutes. Radionuclides, ^{60}Co and ^{40}K, were counted for the movement of neutron activated clay, and ^{85}Sr and ^{137}Cs were for solutes adsorbed on the clay. However, it was not possible to measure the gammas from ^{60}Co and ^{40}K due to low radioactivities. After injecting the suspension for 160 hours, the column was eluted with distilled water for 160 hours again. The column was scanned in the same way. Then, the coumn was sliced by 0.159 cm from 0 to 3.975 cm and by 0.625 cm from 3.975 to 13.975 cm. Gammas from individual slices were counted with a Germanium detector.

At the end of experiment the colloid sample was analyzed to get information on adsorption properties of soluble isotopes onto neutron activated clay by centrifuging clays in a 0.2 μm microfilter unit.

4. Results and Discussion

The effluent curve for the tritiated water is given in figure 3. The dispersion coefficient, D, was determined to 0.06 cm^2/h by adjusting the parameter with an analytical solution [7]. As shown in figure 3, effluent tritium concentration is lower than predicted, which is regarded due to isotopic exchange between the water in the column and the moisture in the air. The dynamic longitudinal Peclet number for the column is obtained as follows [8] ;

$$Pe = \frac{VL}{D} = 27.5$$

where L denotes the length of a colume. This great Peclet number means that the effect of dispersion is negligible compared with advection. The use of solutions (8) and (9) are justified in this way.

The scanning result during the injection of colloid is presented for ^{137}Cs in figure 4. Cesium moved further than expected. It is difficult to explain the phenomenon with a solute transport model because of the high sorption property of Cesium on the geo-
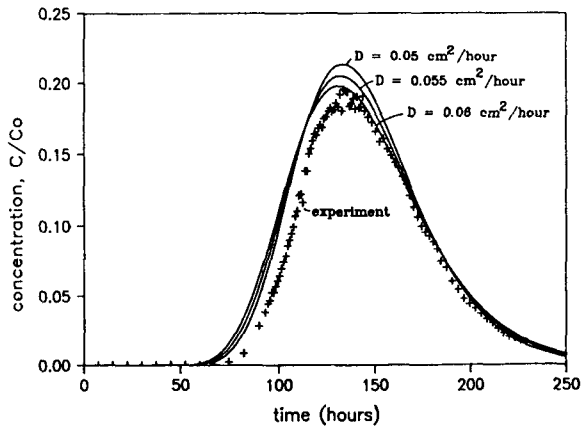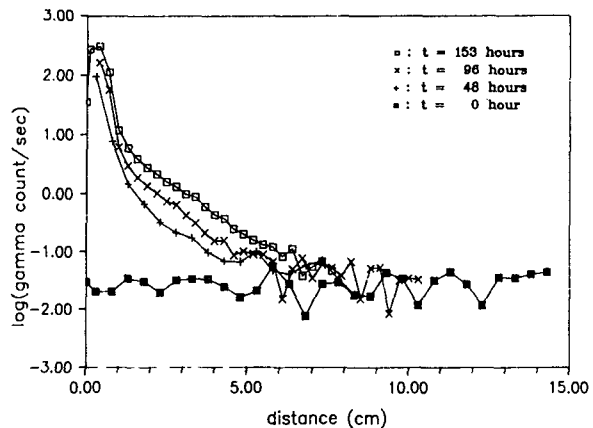

Fig. 3. Determination of Dispersion Coefficient.

Fig. 4. Scanning Results for Cs-137 at
t=48,96,153 hours.

logic medium [1]. The most reasonable explanation is to introduce the adsorption of ^{137}Cs onto the clay particles and movement of clay particles. Also, this result shows the colloids seem to be filtered by packing materials. After 50 hours the concentration profile in the column shows that it consists of two straight lines in semi-log scale. This means that even though clay colloids have the size distribution, the mechanism for colloid movement is the filtration of two monodispersed families of colloid.

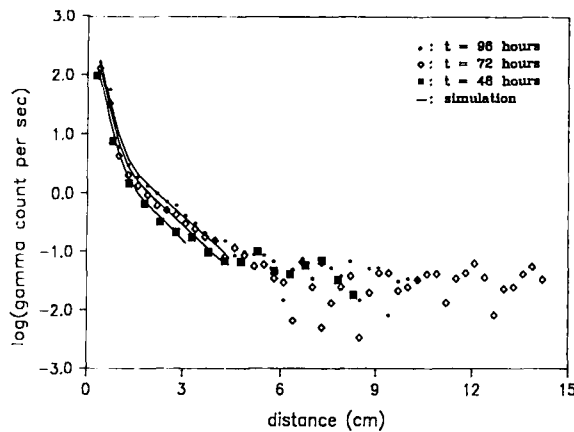From these curves two filtration coefficients, K_L and K_s, are calculated in the same manner given in

Fig. 5. Simulation of Colloid Transport for Cs-137 at
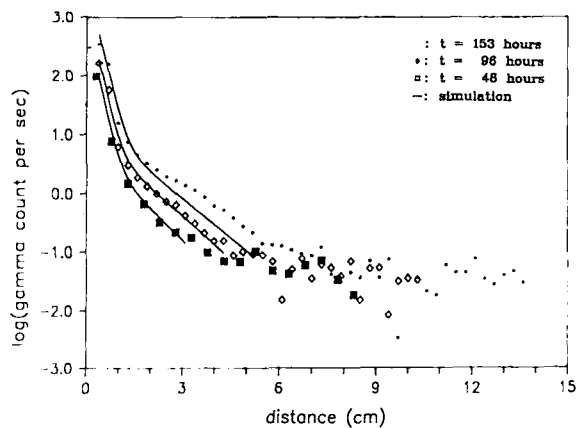t =48,72,96 hours.

ref.1. The values obtained from figure 4 are 4.29 cm^{-1} for large particles and 0.95 cm^{-1} for small particles, respectively. The filtration coefficient, K_L, 4.29 cm^{-1}, was obatined by substracting K_s of 0.95 cm^{-1} from the apparent K_L of 5.24 cm^{-1} since the apparent value of K_L consisted of the summation of K_L and K_s. The simulation with these filtration coefficients and equations (8) and (9) is shown in figure 5 and figure 6. The calculations show good agreements with the experimental data upto 100 hours(figure 5). Then, the amount of colloid filtered moved further (figure 6), which is considered due to the resuspension of the filtered colloid. As shown in figure 7, most of [85]Sr are transported as solutes rather than colloids due to a low distribution coefficient of Strontium.

Figure 8 and 9 represent the comparisons of scanning and column slicing results. The scanning results for [85]Sr are better than those for ^{137}Cs because of a less sharp decrease in concentration. Even though the scanning result for [137]Cs(figure 9) shows a curvature, it is not easy to conclude that this lumped parameter model does not simulate the experiment well since the slicing results are affected by both resuspension and filtration. Results from the analysis of colloid sample show K_d values of 540 $\langle$ [85]Sr $\langle$ 1,140 and 6,080 $\langle$ [137]Cs $\langle$ 12,800.

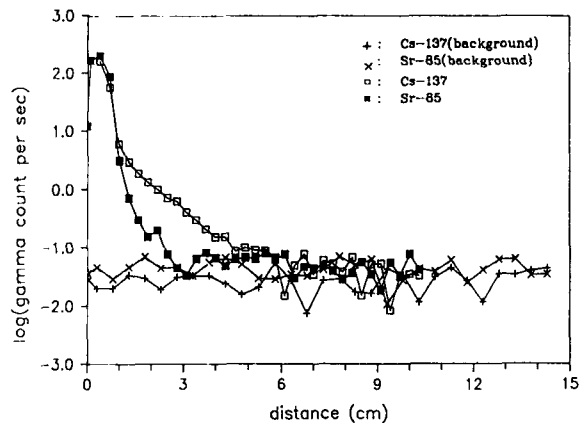Fig. 6. Simulation of Colloid Transport for Cs-137 at
t=48.96.153 hours.

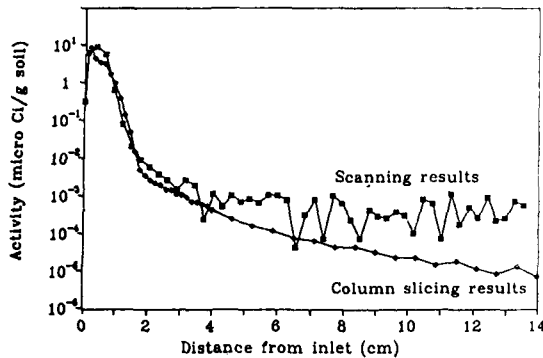Fig. 7. Scanning Results for Sr-85 and Cs-137 at
t=96 hours.

Fig. 8. Comparison of Scanning and Column Slicing
Results for Sr-85.

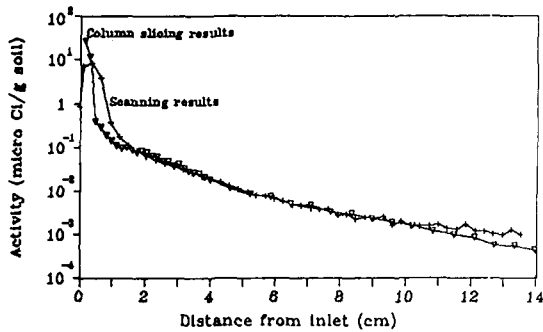Fig. 9. Comparison of Scanning and Column Slicing
Results for Cs-137.

Table 1. Results from Colloid Sample Analysis

	^{85}Sr	^{137}Cs	^{60}Co
Total activities of colloid sample (mCi/5ml) from direct analysis of sample	3.79	14.87	0.0396
Total activities of colloid solid (mCi/A g)	1.14	10.08	0.0166
Total activities of colloid liquid (mCi/ml) from separation analysis	2.44	1.90	none
Recovery percentage of direct and separation analysis	94.6	80.6	47.4

5. Conclusions

The column experiment was conducted to investigate the colloid transport mechanism with neutron activated clay soaked with ^{85}Sr and ^{137}Cs. Using a gamma scanning system, more sets of data could be collected from an experiment compared with a traditional column slicing method. ^{137}Cs moved mainly with colloids, but ^{85}Sr did not. The mechanisms controlling the colloid transport under high Pe number are convection and the filtration of colloid. Even though colloids have the size distribution, the concentration profile in the column is affected by only two families of colloids. This observation is modeled using two lumped filtration coefficients, and the results show good agreements upto 100 hours. However, after 100 hours colloids seem to start to resuspense. This resuspension should be considered for the further modeling of colloid transport. The model developed in this study shows advantage in determining the parameters involved over the model developed by Saltelli et. al. which needed many parameters to be optimized through a fitting.

References

1. Torok, J., L.P. Buckley, B.L. Woods, and Choi, H. J., The mechanism of radionuclide release from waste form and migration through buffer layers in laboratory lysimeters, AECL/TR-466 (1988)
2. Saltelli, A, A Avogadro, and Bidoglio, G., Americium filtration in glauconitic sand column, Nucl. Technol., 67, pp. 245 (1984)
3. Ohtsuka, Y., S. Takebe, T. Yamamoto, and Wadachi, Y., Migration behaviour of radionuclides (Co-60, Sr-85, Cs-137) in aquifer, Journal of nu-

clear science and technology, 25(2), pp. 165 (1988)

4. Ogawa, H., Migration of ^{137}Cs adsorbed on fine soil particles through soil layer, (II), Journal of nuclear science and technology, 25, pp. 38 (1988)

5. Woods, B. L., Physical properties of backfill materials selected for use in low-level waste repository, AECL/TR-259 (1986)

6. Riddick, T. M., Control of colloid stability through zeta potential, pp. 2, Zeta-Meter, Creative Press (1968)

7. Genuchten, M.T.V. and Wierenga, P.J., Methods of soil analysis, part 1. Physical and mineralogical methods, pp. 1025, American society of agronomy (1986)

8. Dullien, F.A.L., Porous media-fluid transport and pore structure, pp. 354-355, Academic Press, New York (1979)