Migration Rates of Some Cations in Unsaturated Layer around the Near-Surface Disposal Facilities of Radioactive Wastes – 16116

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ABSTRACT

In the porous layer around the near-surface underground, the intermittent recharge process of rainwater forms a layer perfectly not saturated with liquid phase. Here, such a layer is simply called “unsaturated layer”. In this study, the retardation effects of radionuclide migration were examined under an unsaturated condition by using a column packed with silica sand particles. As tracer ions, sodium (Na), europium (Eu) and cesium (Cs) were selected for estimating the retardation effects under both the saturated and unsaturated condition. Particularly, Cs is one of the key elements included in the contaminated soil due to Fukushima Daiichi Nuclear Power Plant Accident. These tracer ions were injected into column with the condition of constant flow rate or constant pressure flow. To quantify the influence of the unsaturated condition on the migration of radionuclides, retardation coefficient (R_d) and Peclet number (P_e) were estimated by applying advection diffusion equation to the experimental results. As a result, the conflicting effects on the retardation effect in the unsaturated layer were suggested; one is the decrease in the retardation effect by interrupting the sorption of ions with gas phase, the other is the increase in the retardation effect by the clogging with gas phase in flow paths. For the assessment of the radionuclide migration in the unsaturated layer, it is important to clarify such complicated behaviors with considering key parameters related to the migration of ions.

INTRODUCTION

Around the near-surface disposal facilities of low-level radioactive wastes, the intermittent recharge of rainwater to subsurface soil brings the saturated and unsaturated conditions repeatedly with the liquid phase. So far, many studies have reported the migration of radionuclides through the porous media under the saturated condition [1, 2]. Other studies have examined transport of ions under unsaturated condition [3, 4], however, little is known about the detailed mechanism of both sorption and transport of radionuclides. The migration of radionuclides under the unsaturated condition would be significantly complicated in comparison with that under the saturated condition. Because, in the unsaturated layer, gas phase such as air does not only obstruct liquid flow but also limits the sorption of radionuclides on solid phase. Furthermore, the dispersion (local mixing-effects) of radionuclides with liquid phase in porous media increases due to the presence of gas phase. The obstruction of flow path will contribute to the retardation effect for the radionuclide migration. On the other hand, the higher dispersion and the lower sorption may accelerate the migration of radionuclide. In order to obtain primary knowledge about the influence of unsaturated condition on the radionuclide migration, this study examined the migration of tracer ions under the saturated and unsaturated conditions by column experiments. The ions used were cesium, sodium and europium ions. Cs is well-known to be one of key elements included in the contaminated soil due to Fukushima Daiichi Nuclear Power Plant Accident [5]. Sodium (monovalent ions) and europium (trivalent ions) were examined for the comparison of cesium ions (monovalent ions) in this study.

METHODS

Column Experiment

Figure 1 shows the illustration of the packed column used in the experiments. The porous layer was simulated by the column (10 cm for length, 1 cm for bore diameter) packed with silica sand (average particle diameter: 350 μm or 850 μm). A rubber sheet was attached on the inner wall of column in order to avoid forming a local flow path at the inner wall [6]. Stainless nets were also attached on inlet and outlet to prevent silica sand particles from leaking.

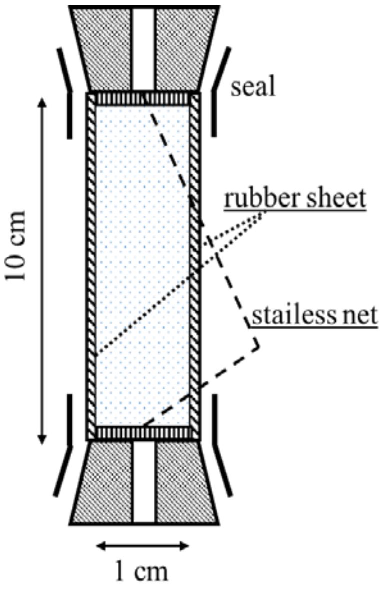

Fig.1 Illustration of packed bed

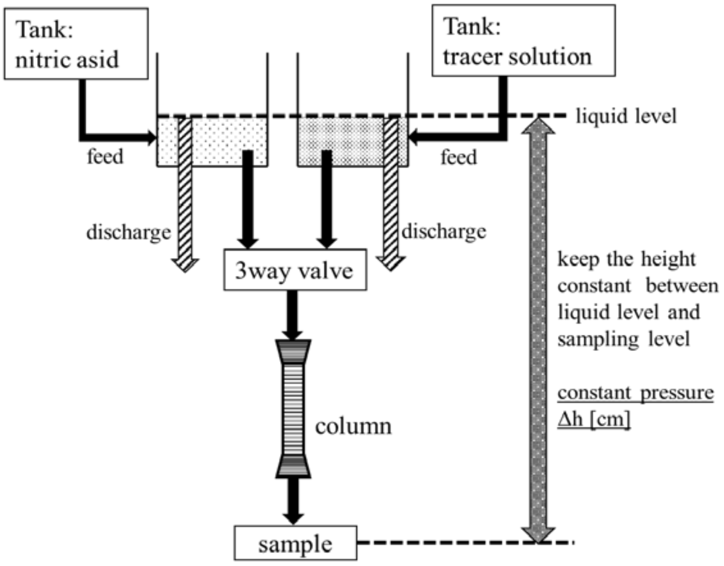

Fig.2 Schematic view of the flow system with over-flow system

First of all, the saturated condition was prepared by pouring silica sand into the column filled with pure water. The porosity (ε) was determined by the volume of water filled sufficiently in the column. Then, once air was injected into the column, pure water was injected again to simulate the process formed the unsaturated condition. (That is, a part of air is left under a wetted condition of the solid phase.) After prepared the saturated or unsaturated condition, the top and bottom parts of column were sealed with water proof tape to forbid water leakage and gas penetration, as shown in Fig.1. The water saturation, S_w, was determined by the difference of the column weights of the saturated condition and the unsaturated condition, and those values were estimated in the range of 0.7 to 0.9. For the continuous injection of the solution to the column, two kinds of flow conditions were selected; one is constant flow rate used by a syringe pomp and the other is constant pressure flow adjusted by over-flow system (Fig. 2). The constant flow rate was set to 80 ml/h, and the constant pressure was set to 1.47 kPa. Besides, the rate of constant pressure flow estimated by the elution rate at outlet were 63.7 ml/h under a saturated condition and 63.3 ml/h under an unsaturated condition, as the results of the experiment in this study.

Sodium (Na), europium (Eu) and cesium (Cs) were selected as tracer ions for estimating the retardation effects under saturated and unsaturated conditions. Those concentrations were set to 10 mM for Na, and 1 mM for Eu and Cs. In addition, multiple tracer (Na 10 mM, Eu 1 mM, Cs 1 mM) was prepared. The pH of all solutions including Eu was set to 4 in order to avoid the formation of precipitates with hydrolysis. Under the condition of constant flow rate, tracer solutions were continuously injected into the column during 30 minutes, meanwhile the sample solutions were collected every 1.0 ml. On the other hand, under the condition of constant pressure flow, tracer solutions were injected into the column for 30 seconds only, then nitric acid (pH 4) were continuously injected and the elution concentration of tracer ions was monitored with time by Inductively Coupled Plasma-Atomic Emission spectrometry (SPS7800, Seiko Instruments Inc.) for Na and Eu ions, and Atomic Adsorption Spectrometry (iCE330, Thermo Fisher Scientific Inc.) for Cs ions.

Analysis

In this study, the theoretical analysis for the solute migration in unsaturated layer followed the basic procedures reported by the previous study [7]. The advection dispersion equation (ADE) for the unsaturated condition was defined as follows:

$$-u\frac{\partial c}{\partial x}+D_\mathrm{e}\frac{\partial^2 c}{\partial x^2}=\varepsilon S_\mathrm{w} R_\mathrm{d}\frac{\partial c}{\partial t} \quad , \tag{1}$$

where u is the flow velocity [m/s], D_e is the dispersion coefficient [m^2/s], S_w is the water saturation [-],ε is the porosity [-], c is the concentration of the solute in liquid phase [mol/m^3], t is the time (s), and x is the distance (m). Besides, the retardation coefficient [-], R_d, is defined as

$$R_\mathrm{d}=\left(1+\frac{1-\varepsilon}{S_\mathrm{w}\varepsilon}\rho K_\mathrm{d}\right) \quad , \tag{2}$$

where K_d is the distribution coefficient [-], and ρ is the density of solid phase [kg/m^3]. From Eq. (2), R_d for the unsaturated condition (S_w <1) exceeds that for the saturated condition (S_w=1). However, considering that the sorption sites of solid phase are generally limited by gas phase, the retardation effect might become smaller with the decrease in S_w.

Furthermore, the dimensionless form of Eq. (1) for the practical calculation is

$$-\frac{\partial C}{\partial X}+\frac{1}{P_e}\frac{\partial^2 C}{\partial X^2}=\frac{\partial C}{\partial T} \quad . \tag{3}$$

Here, Pecret number [-],P_e, which means the ratio of dispersion to advection, is defined as

$$P_e=\frac{uL}{D_e} \quad , \tag{4}$$

where L is the length between the inlet and the outlet of column [m]. For discussing the effect of the unsaturated condition on radionuclide migration, this study estimated the parameters, P_e and R_d, by applying the theoretical curve calculated with ADE to the results of column experiments.

RESULTS and DISCUSSION

The results of columns experiments for the condition of constant flow rate (average particle diameter: 350 μm) are shown in Fig. 3, and Table 1 shows the experimental conditions of the concentration of tracer ions and the water saturation. In Fig.3, the responses of tracer ions for the unsaturated condition became slightly faster than those for the saturated condition. Furthermore, in comparison with these tracer ions in Fig. 3, the migration of tracer ions became slower in the order of Na^+, Eu^{3+}, Cs^+. These differences of the migration of tracer ions are due to the hydrated ionic radius. In general, the sorption of ions on solid phase significantly depends on hydrated ionic radius, and as the hydrated ionic radius of ions is larger, the more tracer ions sorb on solid phase. Such differences of the sorption effect strongly affected the migration of tracer ions, also in these column experiments.

Table 1. Concentration of tracer ions and saturation factor.

Ions	Na	Eu	Cs
Conc. of tracer ions [mM]	10	1	1
S_w	0.693	0.783	0.666

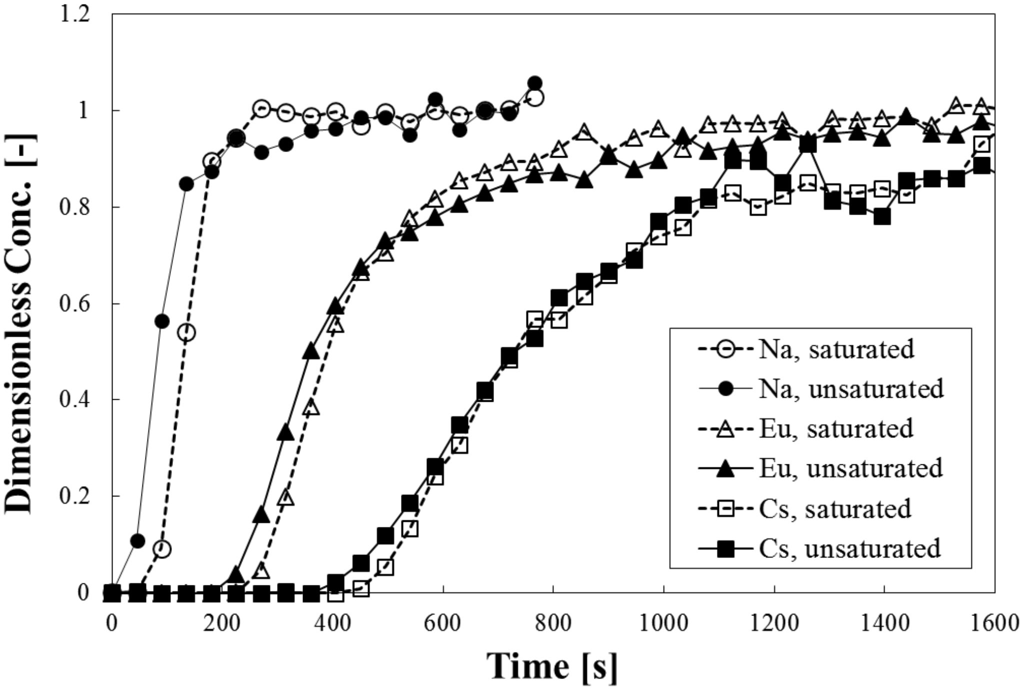

Fig. 3. Response curves of column experiments for the condition of constant flow rate. (grain diameter: 350 µm)

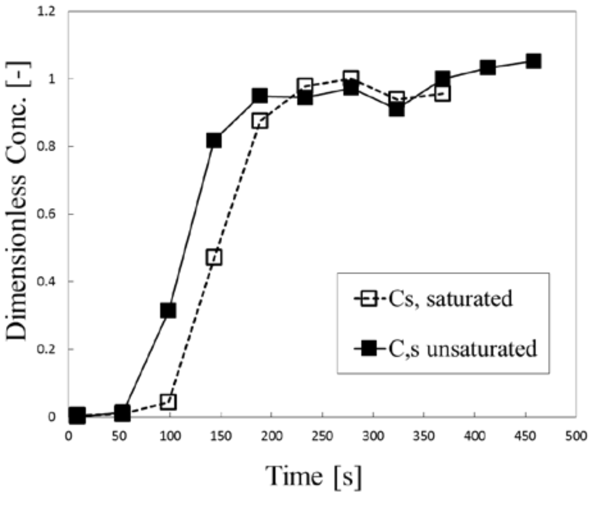

Fig.4 Cs response curve in constant flow rate condition

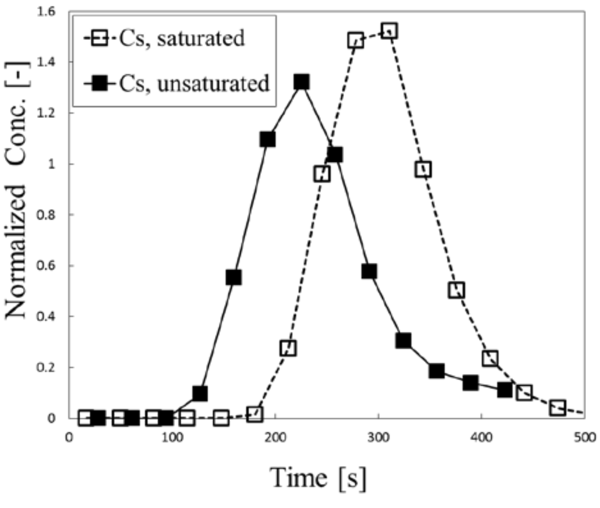

Fig.5 Cs response curve in constant pressure condition

Fig. 4 is the response curves of Cs ions for the condition of constant flow rate (average particle diameter: 850 µm) with applying multiple tracer (Na 10 mM, Eu 1 mM, Cs 1 mM), where the vertical axis “Dimensionless conc.” is the fraction of Cs concentration in the sampling solution to the concentration of Cs ions injected for the experiments. Also, for Na and Eu ions, the similar response curves were obtained without the competition of multiple ions. In Fig. 4, the responses of Cs ions under both the saturated and unsaturated condition became faster than those in Fig. 3 because of the increase of the hydraulic conductivity with using the larger size of silica sand.

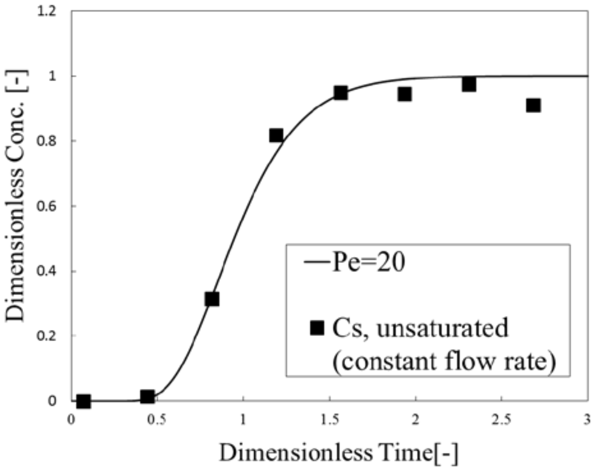

Fig.6 Fitting result of constant flow rate condition

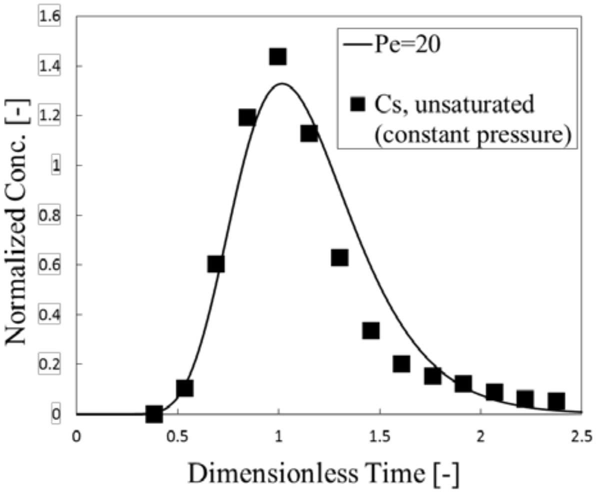

Fig.7 Fitting result of constant pressure condition

Fig. 5 shows the experimental results of Cs ions for the condition of constant pressure flow with multiple tracer (average particle diameter: 850 μm), where the vertical axis “Normalized conc.” is the Cs concentration normalized by molar mass of Cs injected instantaneously to the column. The results in Fig. 5 showed remarkable differences between the saturated and unsaturated conditions, which the elution of Cs ions for the unsaturated condition also was faster than that for the saturated condition, as the results in Fig. 3 and Fig. 4.

As shown in Fig. 3, Fig. 4 and Fig. 5, the unsaturated condition caused the decrease in the retardation effect for the migration of tracer ions. For the quantitative comparison of the saturated and unsaturated conditions, P_e and R_d, were estimated by fitting the theoretical curves to the experimental results shown in Fig. 4 and Fig. 5. (Fig. 6 and Fig. 7 show the fitting result to the experimental data under the unsaturated conditions of Fig.4 and Fig.5, respectively.) The estimated P_e, R_d and K_d values are summarized in Table 2. The K_d values were calculated by Eq. (2). In the calculating of K_d, ε was set to 0.4, and ρ was set to 2.0 g/cm^3. Moreover, for K_d and R_d, the ratio of the values of the unsaturated condition to those of the saturated condition are shown in Table 2. The R_d and K_d values for the unsaturated condition decreased a little in comparison with those for the saturated condition under the condition of any tracer ions and any flow method. These suggest that the retardation effect for the unsaturated condition becomes smaller than that for the saturated condition because the sorption of tracer ions on solid phase is decreased by the presence of gas phase limiting the sorption sites of the solid. These results are inconsistent with the definition of the retardation coefficient as shown in Eq. (2). For more realistic assessment of the radionuclide migration, it will be necessary to apply the effect of the unsaturated condition to the retardation effect adequately. In addition, as shown in Table 2, the P_e values for the unsaturated condition were less than those for the saturated condition. Considering the definition of P_e, Eq. (4), these changes are due to the increase in the dispersion effect by clogging flow-path with air phase. In the unsaturated layer, the migration of tracer ions is forced to circumvent the clogged flow-paths. As a result, the dispersion of tracer ions is apparently accelerated, and the retardation effect becomes larger. The results for the experiments suggest that such an effect was smaller than the migration acceleration with the decrease in the sorption effect, even though the estimation of P_e showed the increase.

From the estimation of P_e, R_d and K_d values, the conflicting effect for the migration of radionuclides under the unsaturated condition were confirmed. The results in this study showed that the unsaturated condition mainly affected as the decrease in the retardation effect with reducing the sorption of tracer ions. However, the retardation effect does not always decrease under the unsaturated condition. For example, under the condition of lower constant pressure flow expected around the repository, the retardation effect may become larger by the increase in the dispersion effect, considering the ratios of R_d for the condition of constant pressure flow in Table 2 are close to 1. Therefore, the relation of the unsaturated condition and the key factors focused in this study should be more carefully discussed in the future work.

Table 2. Estimated P_e, R_d and K_d values.

Flow condition	constant flow rate			constant pressure flow		
ion	Na	Eu	Cs	Na	Eu	Cs
S_w for unsaturated condition	0.93			0.91		
R_d, saturated	2.10	2.10	2.30	1.20	1.60	1.40
R_d, unsaturated	1.40	1.45	1.60	1.05	1.40	1.20
P_e, saturated	30			30		
P_e, unsaturated	20			20		
K_d, saturated	0.29	0.29	0.35	0.05	0.16	0.11
K_d, unsaturated	0.10	0.11	0.15	0.01	0.10	0.05
R_d ratio (unsaturated/saturated)	**0.67**	**0.69**	**0.70**	**0.88**	**0.88**	**0.86**
K_d ratio (unsaturated/saturated)	**0.34**	**0.38**	**0.43**	**0.20**	**0.63**	**0.46**

CONCLUSIONS

This study discussed the migration of cations under the unsaturated condition with the column experiments and the theoretical analyses. As a result, the retardation coefficients for the unsaturated condition were slightly lower than those for the saturated condition regardless of the flow conditions and tracer ions. This suggests that the surface area of solid phase used for the sorption of tracer ions is decreased by the presence of gas phase. At the same time, Peclet numbers for the unsaturated condition also became lower. This decrease in Peclet numbers means that the tracer ions were apparently dispersed and mixed due to the partial clogging with gas phase in flow paths. Besides, such clogging effect in flow path might also contribute the increase in the retardation effect, because the tracer ions must detour using longer flow-paths. As mentioned above, the unsaturated condition around the repository causes the conflicting influence on the migration of radionuclides through the porous layer. For the assessment of the radionuclide migration under such a complicated condition, it is necessary to discuss the migration rates based on the more systematic experiments considering various parameters such as the surface area of solid phase, the pressure or the flow rate of solution injection and the concentrations of tracer ions.

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