Leaching behavior of Cesium from geopolymer waste form with heterogeneously distributed spent ion exchange resin

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1. Introduction

Ion exchange resins (IERs) used in nuclear facilities should be managed as radioactive waste after use, and are generally expected to be processed and disposed of through solidification [1]. When solidifying spent IERs, homogeneity should be tested if the IERs are distributed uniformly within the waste form. However, not much research has been done on how heterogeneity affects the performance of waste form. In this study, we analyzed the effect of heterogeneity on the leaching characteristics of waste forms containing spent IERs on artificially produced heterogeneous and homogeneous waste forms using leaching tests.

2. Materials and methods

Simulated spent IERs were made by adsorbing cesium (Cs) on Amberlite's IRN-150. A metakaolin-based geopolymer waste form was made, and the geopolymer was synthesized by mixing metakaolin and potassium silicate solution, an alkali activator, at a liquid/solid ratio of 1.2. In the case of the homogeneous waste form, constituents of geopolymer and simulated co-contaminated spent IERs were placed in a mixing bottle and mixed evenly, and then poured into a cylindrical mold for curing. The size of the cylindrical mold was 2.9 cm in diameter and 5.8 cm in height, and curing was carried out for a total of 7 days (1 day at room temperature and 6 days at 60 degrees Celsius) [2]. In the case of heterogeneous waste form, geopolymer paste with different waste loading was made in the same manner as the homogeneous waste form making method above, and then sequentially placed in the mold. For example, the paste with a waste loading of 20 wt% was poured into the lower half of the mold, and then the paste with a waste loading of 10 wt% was poured into the upper half of the mold. A total of 4 waste form samples, one homogeneous and three heterogeneous samples with different degrees of heterogeneity were prepared, and the total waste loading was fixed at the same as 15 wt%. The details of the samples are described in Table I.

A leaching test to confirm the Cs leaching characteristics of the waste form samples was performed according to ANS 16.1-2019 [3]. ANS 16.1-2019 describes short-term tests, but long-term tests with the leaching period extended to 90 days were also performed for some samples to determine long-term leaching characteristics and leaching mechanisms.

TABLE I. Details of samples prepared

Sample name	Waste loading
HOM	15 wt% (homogeneous)
HET-20	10 wt% + 20 wt%
HET-25	5 wt% + 25 wt%
HET-30	0 wt% + 30 wt%
HET-45	0 wt% + 45 wt%

3. Results

In the short-term leaching test, the cumulative fraction leached (CFL) was plotted in Fig. 1. As shown in Fig. 1, the HOM, HET-20, and HET-25 samples all showed almost the same Cs leaching characteristics, and the HET-30 and HET-45 samples showed significantly higher Cs leaching compared to the homogeneous sample. This means that heterogeneity at the level of HET-20 and HET-25 does not cause a significant defect on the Cs leaching from the heterogeneous geopolymer waste form. The leachability indices were calculated according to ANS 16.1-2019 (Table II). The leachability indices also show that the increasing in Cs leaching begins from the heterogeneity level of the HET-30 sample, similar to the previous CFL plot.

Long-term Cs leaching tests were performed on HOM and HET-30 samples, and the results are described in Fig 2. It can be seen that long-term leaching characteristics show the same tendency as short-term leaching characteristics. To investigate the leaching mechanism of Cs from homogeneous and heterogeneous samples and to determine whether there were differences between homogeneous and heterogeneous samples, the CFL was fitted using leaching model equations.

Mechanisms that can explain the phenomenon of Cs leaching from waste form can include diffusion and dissolution with first-order kinetics. In the case of diffusion, leaching occurs when Cs moves from inside the waste form to the external solution due to concentration gradient. In the case of a dissolution, Cs leaching occurs by dissolution of waste form in proportion to the amount of Cs at a first-order rate [4].

In a one-dimensional semi-infinite diffusion system, the solution to Fick's second law (equation (1)), can be expressed as equation (2), and the total amount of diffusion during time t can be written as equation (3) [5].

$$C(x,t) = C_0\left\{1 - erf\left(\frac{x}{2\sqrt{D_e t}}\right)\right\} \quad (1)$$

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \quad (2)$$

$$Q_t = 2AC_0\sqrt{\frac{D_e t}{\pi}} \quad (3)$$

In the case of Cs leaching form waste form, C is concentration of Cs (mg/cm^3), C_0 is initial concentration of Cs in waste form, x is one dimensional diffusion distance (cm), t is cumulative leaching time (sec), D_e is diffusion coefficient (cm^2/s), Q_t is the total amount of Cs that have leached out (mg), and A is the surface area of the waste form sample (cm^2). The distance x is 0 at the surface of waste form sample. When the initial total amount of Cs of the waste form sample is Q_0, CFL can be written as Q_t/Q_0, and when the volume of the waste form sample is V, C_0 can be written as Q_0/V, so CFL can be expressed as the formula below,

$$CFL = 2\left(\frac{A}{V}\right)\sqrt{\frac{D_e t}{\pi}} \quad (4)$$

In the case of a dissolution, because the reaction rate would be proportional to the amount of Cs in the waste form, the following differential equation can be established [4],

$$\frac{dQ}{dt} = -kQ \quad (5)$$

where, Q is the amount of Cs in the waste form (mg), and k is the reaction rate (sec^{-1}). The solution to the above differential equation can be derived as equation (6), and accordingly, CFL can be expressed as equation (7).

$$Q(t) = Q_0 e^{-kt} \quad (6)$$

$$CFL = \frac{Q_0 - Q(t)}{Q_0} = 1 - e^{-kt} \quad (7)$$

A total of six leaching models can be established using diffusion, first-order reaction model equations, and the initial wash-off related term. A model applying only diffusion (DM), a model applying only first-order reaction (FRM), a model applying both diffusion and first-order reaction (DMFRM), and models applying an initial wash-off term (W, mg/mg) to DM, FRM, DMFRM models can be considered. The six formulas below are the formulas for each model, and models that consider initial wash-off are expressed by adding W to the model name that does not consider initial wash-off.

$$\text{DM}: CFL = 2\left(\frac{A}{V}\right)\sqrt{\frac{D_e t}{\pi}} \quad (8)$$

$$\text{FRM}: CFL = 1 - e^{-kt} \quad (9)$$

$$\text{DMFRM}: CFL = 2\left(\frac{A}{V}\right)\sqrt{\frac{D_e t}{\pi}} + 1 - e^{-kt} \quad (10)$$

$$\text{WDM}: CFL = W + 2\left(\frac{A}{V}\right)\sqrt{\frac{D_e t}{\pi}} \quad (11)$$

$$\text{WFRM}: CFL = W + 1 - e^{-kt} \quad (12)$$

$$\text{WDMFRM}: CFL = W + 2\left(\frac{A}{V}\right)\sqrt{\frac{D_e t}{\pi}} + 1 - e^{-kt} \quad (13)$$

The results of fitting the CFL derived from the long-term leaching test using each model are shown in Fig. 3 and Table III ~ VIII. Comparing the R-square values in Table III ~ VIII, it can be determined that Cs leaching from the waste form samples in this study is controlled by diffusion including the initial wash-off. In addition, it can be seen that the model fitting results for CFL show no difference between the HOM and HET-30 samples, and thus, it can be concluded that the heterogeneity of the waste form cannot have a serious effect on leaching property like changing the leaching mechanism.

TABLE II. Leachability indices

Sample name	Leachability index
HOM	10.13
HET-20	10.12
HET-25	10.14
HET-30	9.79
HET-45	9.23

TABLE III. Results of DM model

Parameters	HOM	HET-30
R-square	0.8638	0.7938
D_e (cm^2/s)	4.558×10^{-11}	9.178×10^{-11}

TABLE IV. Results of FRM model

Parameters	HOM	HET-30
R-square	0.6234	0.6403
k (s^{-1})	5.186×10^{-9}	7.317×10^{-9}

TABLE V. Results of DMFRM model

Parameters	HOM	HET-30
R-square	0.8444	0.7644
D_e (cm^2/s)	4.558×10^{-11}	9.178×10^{-11}
k (sec^{-1})	1.000×10^{-23}	1.000×10^{-11}

TABLE VI. Results of DM model with wash-off

Parameters	HOM	HET-30
R-square	0.9425	0.9227
D_e (cm^2/s)	3.042×10^{-11}	5.539×10^{-11}
W (mg/mg)	4.130×10^{-3}	7.150×10^{-3}

TABLE VII. Results of FRM model with wash-off

Parameters	HOM	HET-30
R-square	0.6234	0.6403
k (sec^{-1})	5.185×10^{-9}	7.316×10^{-9}
W (mg/mg)	1.296×10^{-4}	1.732×10^{-4}

TABLE VIII. Results of DMFRM model with wash-off

Parameters	HOM	HET-30
R-square	0.9313	0.9087
D_e (cm^2/s)	3.239×10^{-11}	5.845×10^{-11}
k (sec^{-1})	7.164×10^{-22}	1.293×10^{-23}
W (mg/mg)	3.650×10^{-3}	6.620×10^{-3}

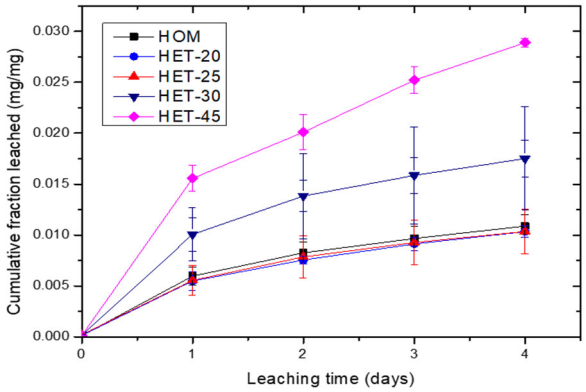

Fig. 1. CFL from short-term leaching test

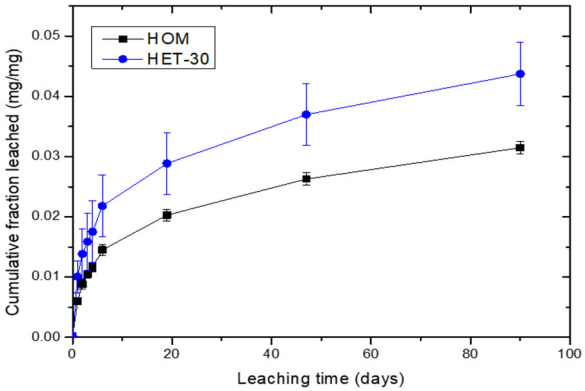

Fig. 2. CFL from long-term leaching test

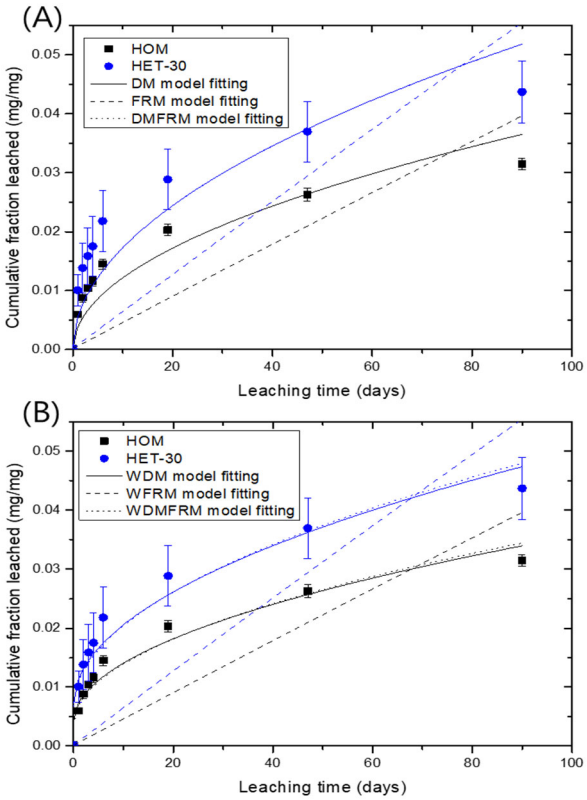

Fig. 3. Results of leaching model fitting (A) models without wash-off and (B) models with wash-off

4. Conclusions

This study investigated the effect of heterogeneity on Cs leaching from geopolymer waste form containing spent IERs. Comparing the Cs leaching test results of homogeneous and heterogeneous samples, it can be determined that it is possible that heterogeneity increases Cs leaching, but the effect would only appear in waste forms with very high level of heterogeneity (over heterogeneity of HET-30, 0 wt% + 30 wt%). As the result of fitting the CFL of Cs leaching test using leaching model equations applying diffusion and first-order dissolution reaction mechanisms, it was concluded that Cs leaching for both homogeneous and heterogeneous samples is controlled by mainly diffusion with minor initial wash-off processes.

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