



HOKKAIDO UNIVERSITY

Title	Metakaolin-based Geopolymer for Immobilizing Concentrated Cs Generated by Volume Reduction of ^{137}Cs -contaminated Waste
Author(s)	Ichikawa, Tsuneki; Watanabe, Sadayuki; Arai, Hiroyuki et al.
Citation	環境放射能除染学会誌, 8(1), 3-16
Issue Date	2020-03
Doc URL	https://hdl.handle.net/2115/79155
Type	journal article
File Information	2020SRRCEV8N1-P3-16_Ichikawa.pdf



Metakaolin-based Geopolymer for Immobilizing Concentrated Cs Generated by Volume Reduction of ^{137}Cs -contaminated Waste

ICHIKAWA Tsuneki^{1, 2*}, WATANABE Sadayuki³, ARAI Hiroyuki², HAGA Kazuko⁴, and YAMADA Kazuo²

● **Summary** ● Cs-loaded geopolymer, cation exchangeable amorphous aluminosilicate prepared by mixing metakaolin, water glass and water-soluble CsCl at ambient temperature, was found to immobilize Cs strongly and to release it very slowly into sea water. The leaching test of geopolymer containing 9.1% by mass of Cs showed that geopolymer prepared from 10 : 15 weight ratio of metakaolin and water glass held more than 97% of Cs after prolonged immersion in deionized water. The leaching restarted in seawater, though the effective diffusion coefficient for Cs leaching was as low as $1.96 \times 10^{-5} \text{ cm}^2/\text{h}$. The theoretical analysis of the leaching process including ionic diffusion and ion exchanging revealed that the slow release was due to the high selectivity coefficient of cation exchange sites for Cs^+ adsorption and much higher concentration of adsorbed cations in the pore solution of geopolymer than that of cations penetrated from sea water. The low leaching ratio in deionized water and the slow leaching rate in seawater indicate that geopolymer is possible to be used as an immobilizer-solidifier for concentrated Cs generated by volume reduction of ^{137}Cs -contaminated waste.

Key Words: radioactive waste, decontamination, ^{137}Cs , volume reduction, geopolymer, immobilizer, metakaolin, water glass

1. Introduction

Since the Fukushima Daiichi Nuclear Power Plant Accident on March 11 of 2011¹⁻⁴⁾, an enormous amount of ^{137}Cs -contaminated wastes such as ^{137}Cs -contaminated top soil and ^{137}Cs -enriched municipal solid waste incinerator fly ash have been collected and temporally stored as a result of decontamination works⁵⁾. To find land space wide enough for the final disposal of the contaminated wastes is now a social issue in Japan.

One of feasible ways to solve the problem is the volume reduction by decontamination. Several attempts have been made for the volume reduction. Takeshita *et al.* have proposed the decontamination of top soil by hydrothermal treatment^{6,7)}. We have proposed a super volume reduction system composed of pyroprocessing and

ion chromatographic decontaminations^{8,9)}. In any case, the decontamination work generates new ^{137}Cs -enriched waste containing a significant amount of Cs that is generally water-soluble. The solidification-immobilization of Cs enriched waste is therefore inevitable for the final disposal.

Vitrification with borosilicate glass is the safest way of immobilizing Cs for a long period, though it is very costly¹⁰⁾. Cement solidification is a simple and low cost solidification process and has been widely used for radiologically contaminated waste. Cement solidification is generally attained by mixing waste, hydraulic binder and water under alkaline conditions. Portland cement is commonly used as a binder, though it has no ability of immobilizing Cs^+ ions. Geopolymer is an alkali-ac-

Received October 18, 2019; Accepted December 20, 2019

*Corresponding author: E-mail: tsuneki@eng.hokudai.ac.jp

¹Hokkaido University, Home address: 8-1-27 Tonden 3, Kita-ku, Sapporo, Hokkaido 002-0853, Japan

²National Institute for Environmental Studies, Fukushima Branch, 10-2 Fukasaku, Miharu, Fukushima 963-7700, Japan

³Tokyo Metropolitan Industrial Technology Research Institute, 2-4-10, Aomi, Koto-ku, Tokyo 135-0064, Japan

⁴Taiheiyo Consultant, Co. Ltd., 2-27-8 Nihonbashi, Chuou-ku, Tokyo 103-0004, Japan

Table 1. Composition of source materials used for the preparation of geopolymer samples

Component	Al ₂ O ₃ (mol/kg)	SiO ₂ (mol/kg)	Na ₂ O (mol/kg)	TiO ₂ (mol/kg)	H ₂ O (% by mass)
Metakaolin	4.37	8.65	0.32	0.24	0.1
Water glass	0	6.11	2.84	0	45.8

tivated aluminosilicate that has been extensively studied in recent years as a substitute of Portland cement¹¹⁾. Geopolymer can be solidified by mixing powdered aluminosilicates such as metakaolin, coal fly ash and blast furnace slug with alkali silicate and/or alkaline solutions at ambient temperature to give chemically, thermally and mechanically stable materials. Due to its stability, cation adsorption capacity and tolerance to ionizing radiations, geopolymer is an attractive candidate for the solidification and immobilization of radioactive wastes¹²⁻¹⁷⁾.

Several attempts have been made for utilizing geopolymer as a Cs⁺ immobilizer¹⁸⁻²³⁾. These results suggested that the leaching resistance of geopolymer was induced by the suppression of ionic diffusion arising from narrow pore diameters and by ionic adsorption by aluminosilicate cation exchange sites to form (CsAlO₂)(SiO₂)_{1+x}. Although these studies showed that geopolymer had enough ability of suppressing the leaching of Cs to deionized water, the leaching to sea water has scarcely been studied. Intrusion of sea water might be possible to take place during the long storage period by tsunami and storm surges. Since sea water is an electrolyte solution composed of alkali and alkaline earth metal cations, chloride and sulfate anions, and so on, the cations penetrated into geopolymer are possible to exchange with Cs⁺ to cause the leaching of Cs. In the previous work, we studied the leaching of Cs from geopolymer prepared from copper ferrocyanide-loaded silica gel as a spent Cs adsorbent, metakaolin and a NaOH solution, and found no leaching both in deionized water and in sea water⁹⁾. However, the content of Cs in the geopolymer was as low as 0.5% by mass of the geopolymer. Since the final volume reduction factor is proportional to the content of Cs in a final disposable product, to increase the content of Cs in geopolymer is desirable for attaining a higher volume reduction factor. In the present study, the leaching of Cs from metakaolin-based geopolymer containing 9.1% Cs by mass of Cs to deionized water and sea water was studied for certifying the long-term soundness of geopolymer as a Cs-immobilizer. The physicochemical properties

of the geopolymer were also studied for clarifying the mechanism of Cs-immobilization.

2. Materials and Methods

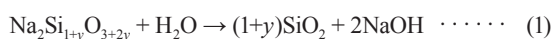
(1) Materials

Metakaolin used was Satintone SP33 supplied by BASF, USA. Table 1 shows the chemical composition of the metakaolin. The metakaolin (general formula = Al₂O₃(SiO₂)_x) was chosen as a source material of geopolymer because this was easily solidified at ambient temperature by adding an alkaline solution. Several metakaolin samples and other aluminosilicates tested were not solidified at ambient temperature. Alkaline solutions used were the aqueous solution of sodium silicate (water glass: general formula = Na₂Si_{1+y}O_{3+2y}·zH₂O) and/or the aqueous solution of NaOH. The chemical composition of water glass supplied by Junsei Chemicals is also shown in Table 1. Cs⁺ ions may be incorporated in geopolymer either as an alkaline salt such as CsOH or Cs₂O or as a neutral salt such as CsCl or Cs₂CO₃. When an alkaline salt is added, as mentioned in the following section, OH⁻ ions generated from the salt are consumed to generate geopolymer and the counterpart Cs⁺ ions are incorporated as adsorbed ions of the resultant geopolymer. When a neutral salt is added, the anions and at least a part of Cs⁺ ions are dissolved in the pore solution of geopolymer as free ions. To use a neutral salt as a Cs source is therefore less desirable for preventing the leaching of Cs. In the present study, for examining the ability of suppressing Cs leaching under a severe condition, CsCl was used as a Cs source and ¹³⁷CsCl was used as a radioactive tracer.

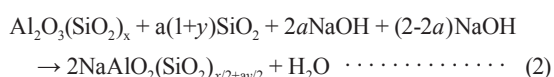
(2) Sample preparation

Geopolymer was prepared by thoroughly hand-mixing metakaolin, CsCl, water glass and/or a NaOH solution for three minutes and then poured into a plastic petri dish with inside dimensions of 3.4 cm diameter and 1 cm height or into an air-tight laminated bag. For obtaining a flat surface and avoiding a carbonation reaction, geopolymer in the petri dish was tightly covered with a plastic

sheet and the cap of the dish, and stored in an air-tight laminated bag. After waiting for one day for setting, the samples were cured for two weeks at 60°C. Geopolymer discs in the dishes were used for leaching tests without demolding, whereas those poured in the bag were used for chemical analyses after crashing into powder. Since the chemical reaction of geopolymer formation is expressed as



and



the amounts of water glass and NaOH added to metakaolin were adjusted in such a way that the total molar amount of Na atoms in the mixture was the same as that of the Al atoms. The amount of water glass added to 10 grams of metakaolin was either 0, 5, 10 or 15 grams. They will be called GP10-0, GP10-5, GP10-10 and GP10-15, respectively. The amount of water added was adjusted in such a way that the total weight of water was equal to that of metakaolin. Unless otherwise stated, the content of Cs in geopolymer was fixed to 9.1% by mass (wt%) of geopolymer (0.685 mol/kg or 10 wt% by the outside ratio).

(3) Analytical methods

The Cation exchange capacity (CEC) of geopolymer was determined by measuring the amount of free OH^- ions in powdered geopolymer by an acid-base titration. Subtraction of the amount of free OH^- ions from the total amount of Na^+ ions added for the solidification gave the amount of alkali metal ions adsorbed on cation exchange sites AlO_2^- . Five grams of powdered geopolymer was mixed with 50 grams of deionized water in a centrifugal tube. After stirring for six hours, the solution was centrifuged for 15 minutes at 4000 rpm and the supernatant solution was sucked through a 0.2 μm pore syringe filter and served for an acid-base titration. After adding a 0.1 mol/dm³ (M) HCl solution, the solution was back-titrated

with a 0.1 M NaOH solution using methyl orange as an indicator.

X-ray diffraction (XRD) analyses were carried out with a Rigaku SmartLab X-ray diffractometer equipped with Studio II software for XRD analysis. Solid state MAS NMR spectra were measured with a JNM-ECA600 FT NMR spectrometer. The porosity of geopolymer was determined by measuring the volume and the weight loss of geopolymer by drying at 110°C. The weight loss was assumed to be equal to the volume of free water filling the pores in geopolymer. The distribution of the pore diameter was measured with a Shimadzu Autopore II9200 mercury intrusion porosimeter.

The selectivity coefficient of Cs^+ adsorption for GP10-10 was determined by measuring the fraction of Cs that was leached out from the powdered geopolymer into deionized water, sea water, a 0.6 M NaCl solution or a 1 M CsCl solution. Table 2 shows the chemical composition of sea water used for leaching tests. About 0.5 g of weighed GP10-10 powder labelled with ca. 7000 Bq/g of ^{137}Cs was mixed with one of the solution, and was stirred for two days for attaining an adsorption equilibrium condition. The suspension was then centrifuged at a speed of 4000 rpm for 15 minutes, and filtrated with a 0.2 μm pore syringe filter. Two cm³ of the filtrate was transferred in a plastic petri dish with inside dimensions of 3.4 cm diameter and 1 cm height. For preventing uneven distribution of the filtrate due to surface tension between the filtrate and the plastic bottom, a paper filter of 3.3 cm in diameter was placed on the bottom of the dish before the transfer. The dish was then transferred into a γ -ray measuring apparatus with a NaI crystal scintillator of 5.08 cm diameter and 5.08 cm height. The radioactivity of ^{137}Cs was determined under the secular equilibrium condition. Since the content of Cs in the 1 M CsCl solution was more than 100 times larger than that in GP10-10, the amount of Cs leached into the CsCl solution was equal to the initial amount of Cs in GP10-10. The amount Cs leached into deionized water gave the amount of Cs that was not bound to the cation exchange sites of GP10-10. The difference

Table 2. Chemical composition of artificial sea water used for leaching test

Ionic species	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Total cation	Cl ⁻	Br ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Total anion
Concentration/mM	465	9.87	53.3	9.98	0.096	601*	543	0.839	27.6	2.33	601*

*meq/dm³

between the amounts of Cs leached into the 1M CsCl solution and into deionized water gave the amount of Cs bound to the cation exchange sites.

(4) Leaching test

Cs leaching tests were carried out by measuring the intensity of γ -rays emitted from ^{137}Cs in geopolymer discs after immersing them in deionized water, sea water, a 0.6 M NaCl solution or a 0.6 M CsCl solution at 30°C. For preventing the back diffusion of leached Cs, the solutions were renewed every time after the measurements. The intensity of γ -rays was measured by placing the NaI detector on the open surface of the disc. The detected intensity of γ -rays is generally not the same as the amount of Cs remaining in the geopolymer. The intensity I from the disc with thickness L is a function of the concentration of Cs at distance z from the surface of the disc, $C(z)$, the geometrical efficiency of detecting γ -rays generated at z , $g(z)$, and the attenuation factor of the γ -rays that can be approximately given by $\exp(-az)$, where a is an attenuation coefficient, as

$$I = \int_0^L C(z)g(z)\exp(-az)dz \quad (3)$$

To know the functional shape of $g(z)\exp(-az)$ (detection efficiency) is therefore necessary for determining the total content of Cs from the observed radiation intensity. The functional shape was determined by measuring the radioactivity of a ^{137}Cs -doped thin paper disc of 3.4 cm diameter that was sandwiched between aluminum plates of 3.4 cm diameter with the total thickness of 1 cm. Fig. 1 shows the detection efficiency as a function of the distance from the surface. The detection efficiency at the bottom of a 1 cm geopolymer disc was also shown in Fig. 1. Although the density and therefore the attenuation coefficient of geopolymer was lower than those of aluminum, the sensitivity coefficient at 1 cm was not much

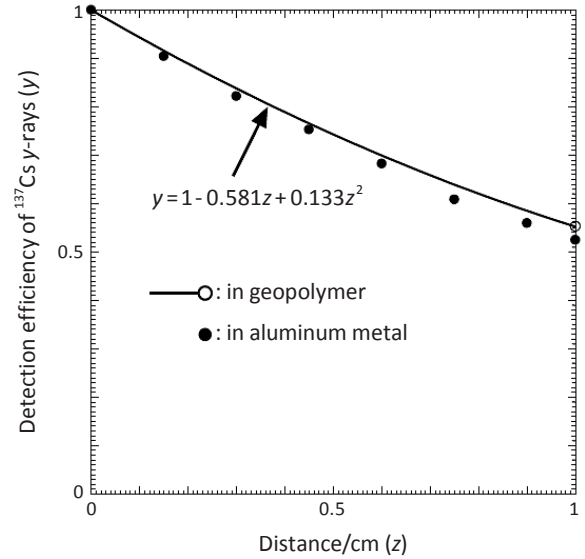


Fig. 1. Detection efficiency of ^{137}Cs γ -rays as a function of distance z between the surface of γ -ray shielding material and ^{137}Cs γ -ray source

different. The main factor contributing to the detection efficiency was therefore the geometrical efficiency. The detection efficiency for geopolymer was approximately expressed by function $1 - 0.581z + 0.133z^2$.

3. Results and Discussion

(1) Characterization

Table 3 shows the composition of geopolymer samples used for physicochemical characterizations. Within two hours after mixing the ingredients, GP10-0, GP10-5 and GP10-10 were fluid enough for filling petri dishes for molding without giving vibration. GP10-15 was too viscous to fill the mold without giving vibration. The setting times of all the samples were less than 15 hours at ambient temperature. The density of geopolymer increased with increasing the content of water glass added for the preparation. The porosity decreased with increasing the content of water glass. Fig. 2 shows the distribution of

Table 3. Composition and characteristics of geopolymer samples

Sample	Al (mol/kg)	Si/Al (mol/mol)	Cs (wt%)	CEC* (eq/kg)	(Na+Cs)**/CEC	Density	Porosity
GP10-0	3.34	0.99	9.1	3.18	1.29	1.68	0.60
GP10-5	3.13	1.34	9.1	2.88	1.35	1.73	0.59
GP10-10	2.94	1.69	9.1	2.74	1.34	1.78	0.54
GP10-15	2.75	2.04	9.1	2.63	1.33	1.82	0.52

*Cation exchange capacity

**Total molar amount of Na^+ and Cs^+ ions in 1 kg of geopolymer.

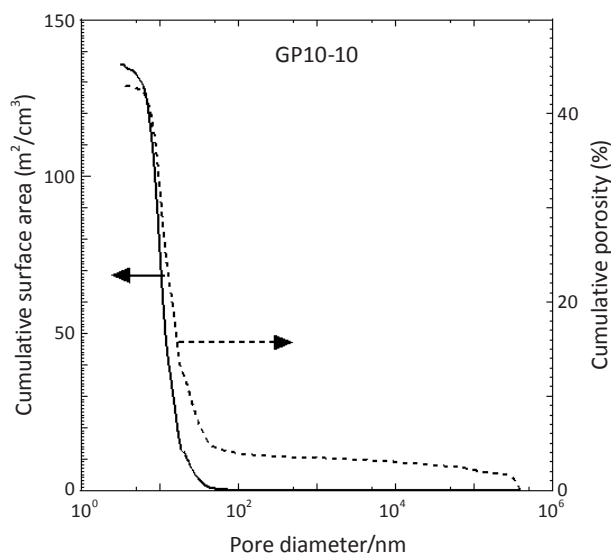


Fig. 2. Cumulative distribution of pore diameter in geopolymer GP10-10

pore diameter for GP10-10. The volume-averaged diameter was 12.8 μm whereas the surface area-averaged diameter was 12.6 nm. The cation exchange sites were therefore located on the surface of micro pores with the average diameter of 12.6 nm.

As shown in Table 3, the CEC of geopolymer samples were close to the amount of Al, which indicates that most of Al atoms were used for preparing cation exchange sites AlO_2^- . Fig. 3 shows the solid-state MAS NMR spectra of ^{27}Al , ^{29}Si , ^{23}Na and ^{133}Cs in GP10-10. The ^{27}Al NMR spectrum can be assigned to the Al atom coordinating four $-\text{O}-\text{Si}-$ groups and acting as a cation exchange site²⁴⁾, which accords with the fact the CEC was close to the content of Al atoms. The ^{29}Si NMR spectrum can be assigned to Q^4 species coordinating four $-\text{O}-\text{Si}-$ and/or $-\text{O}-\text{Al}-$ groups, which indicates that three-dimensional silica networks were developed in geopolymer. The NMR chemical shifts of ^{23}Na and ^{133}Cs were slightly changed by changing the molar ratio of Cs to Na, which suggests that the strength of electrostatic field generated by cation exchange sites changed site by site.

Fig. 4 shows the XRD patterns of geopolymer samples. GP10-0 indicates the formation of both amorphous and zeolite phases. The latter phase was assignable to zeolite Cs-F²⁵⁾. GP10-5, GP10-10 and GP10-15 did not show the presence of a crystalline phase, which suggests that the formation of crystalline phase was suppressed by adding viscous water glass.

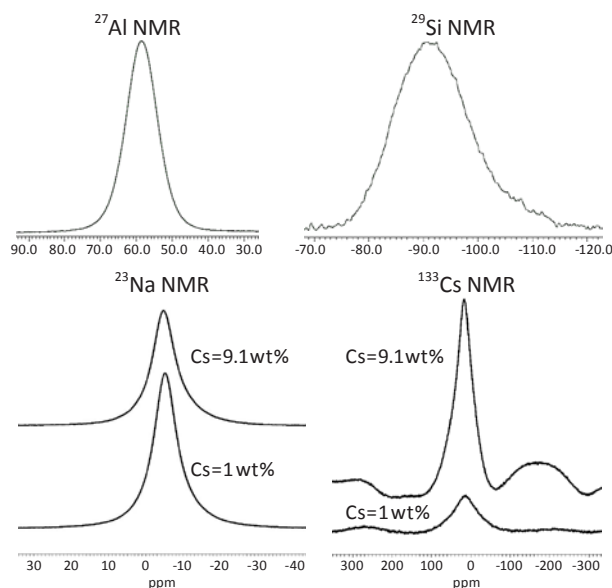
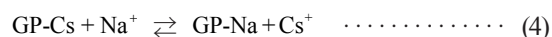


Fig. 3. Solid state MAS NMR spectra of ^{27}Al , ^{29}Si , ^{23}Na and ^{133}Cs in geopolymer GP10-10

The resistance of geopolymer toward Cs leaching arises from the adsorption of Cs^+ ions on the cation exchange sites. The stronger the adsorption is, the slower the leaching is. The strength of the adsorption can be expressed with an ionic selectivity coefficient. When geopolymer is immersed in the solution of electrolyte such as NaCl solution, the ion exchange reaction takes place between adsorbed Cs^+ ions and Na^+ ions in the solution, as



where GP-X denotes X^+ cations adsorbed on the cation exchange sites of geopolymer. Under the equilibrium condition, we obtain

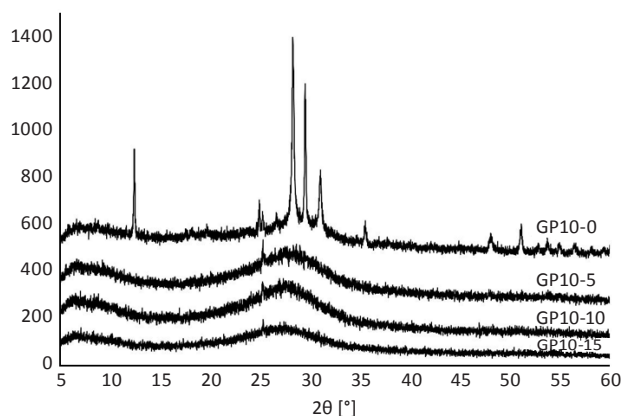


Fig. 4. XRD patterns of geopolymer samples containing Cs. See Table 3 for the compositions of the samples

$$K_{\text{Cs/Na}} = \frac{[\text{Na}^+][\text{GP-Cs}]}{[\text{Cs}^+][\text{GP-Na}]} \dots\dots\dots (5)$$

where $K_{\text{Cs/Na}}$ is the Cs selectivity coefficient of the ion exchanger against Na^+ ions, $[\text{GP-Cs}]$ and $[\text{GP-Na}]$ are the molar amounts of adsorbed Cs^+ and Na^+ ions, $[\text{Cs}^+]$ and $[\text{Na}^+]$ are the molar amounts of unbound free Cs^+ and Na^+ ions in the solution, respectively. Using the law of mass valance, Eq. (5) is rewritten as

$$K_{\text{Cs/Na}} = \frac{([\text{Na}^+]_0 + [\text{Cs}^+]_0 - [\text{Cs}^+])([\text{GP-Cs}]_0 + [\text{Cs}^+]_0 - [\text{Cs}^+])}{[\text{Cs}^+](\text{CEC} - [\text{GP-Cs}]_0 + [\text{Cs}^+] - [\text{Cs}^+]_0)} \dots\dots\dots (6)$$

Here $[\text{Na}^+]_0$ and $[\text{GP-Cs}]_0$ are the initial amounts of $[\text{Na}^+]$ and $[\text{GP-Cs}]$, respectively, $[\text{Cs}^+]_0$ is the initial amount of Cs^+ that is in geopolymer but is not adsorbed, and CEC is the cation exchange capacity. Eq. (6) indicates that the selectivity coefficient is determined by measuring the amount of Cs^+ ions released into the solution.

Since sea water contains several minor cations other than Na^+ ions, the selectivity coefficient of Cs^+ adsorption is not able to be expressed by a simple function. However, assuming that the effect of minor cations on the Cs^+ adsorption is replaceable with Na^+ ions of equivalent concentration (*e.g.* 10 mM of Ca^{2+} is equivalent to 20 mM of Na^+), the selectivity coefficient for sea water can be expressed with Eq. (6) by replacing $[\text{Na}^+]_0$ with the total amount of cations in sea water. Fig 5 shows the selectivity coefficients of Cs^+ adsorption for GP10-10 in sea water and in a 0.6 M NaCl solution. With increasing the amount of adsorbed Cs, the selectivity coefficient decreased toward the lowest value of 16. This is because of the inhomogeneity of the cation exchange sites. Since Cs^+ ions were preferentially adsorbed on the exchange sites with higher selectivity coefficient, the average selectivity coefficient gradually decreased with increasing the amount of adsorbed Cs. The inhomogeneity of the cation exchange sites caused the concentration-dependent chemical shifts of ^{23}Na and ^{133}Cs NMR spectra shown in Fig. 3. The selectivity coefficient in sea water was approximately the same as that in the NaCl solution, which certifies the validity of the assumption that the effect of minor cations in sea water on the selectivity coefficient of Cs^+ adsorption is replaceable with equivalent Na^+ ions.

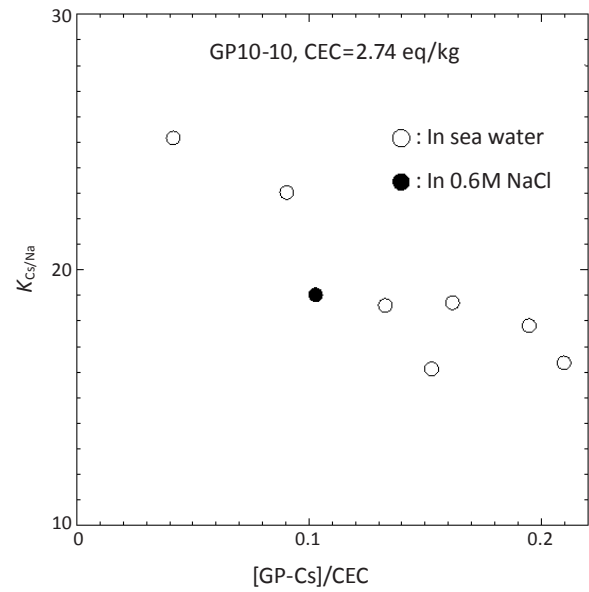


Fig. 5. Selectivity coefficient $K_{\text{Cs/Na}}$ of Cs^+ adsorption for geopolymer GP10-10 against Na^+ ions in 0.6 M NaCl solution or all cations in sea water. $[\text{GP-Cs}]$ and CEC denote the amount of adsorbed Cs^+ ions and the cation exchange capacity, respectively. Sea water is regarded to be equivalent to a 0.6 M NaCl solution

(2) Cs leaching from geopolymer

Fig. 6 shows the leaching of Cs from geopolymer discs to deionized water at 30°C . As shown in Table 3, the total amounts of Na^+ and Cs^+ ions were about 30% higher than the cation exchange capacities, which imply that about 30% of alkali metal ions were not fixed to the

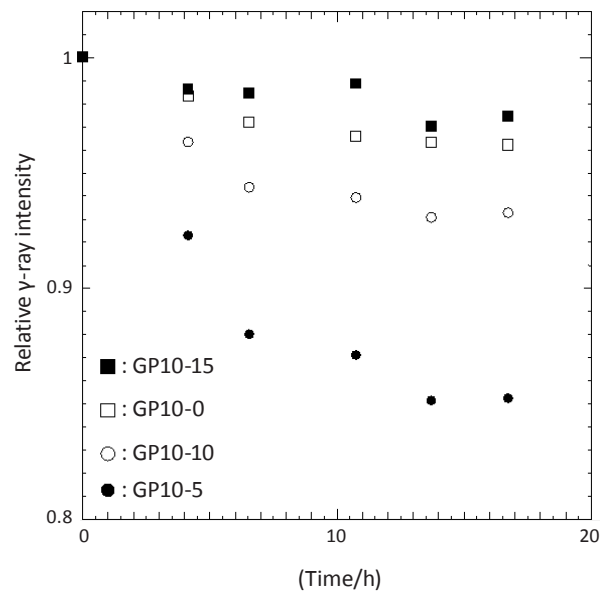


Fig. 6. Decrease of ^{137}Cs γ -rays from geopolymer samples by the leaching of Cs to deionized water at 30°C . See Table 3 for the compositions of the samples

cation exchange sites but were dissolved in the pore solutions of geopolymer as free ions. The leaching of Cs in deionized water was less than 15% for all the samples and was terminated within one week. The leaching of less than 15% of Cs indicates that Cs^+ ions were preferentially adsorbed in geopolymer. The leaching followed the square-root time law, which implies that the leaching was a diffusion-controlled process.

As mentioned in chapter 2(4), the detected intensity of γ -rays from a geopolymer disc is not necessarily proportional to the amount of Cs remained in the disc, because the detection sensitivity depends on the location of ^{137}Cs in the disc. To know the spatial distribution of Cs in the disc during the leaching is therefore necessary for obtaining the residual amount of Cs from the observed intensity of γ -rays. Assuming that the leaching of Cs is a simple diffusion-controlled process, the spatial distribution of Cs in a geopolymer disc with thickness L is obtained by solving a diffusion equation of

$$\frac{\partial C(z)}{\partial t} = D_e \frac{\partial^2 C(z)}{\partial z^2} \quad \dots\dots\dots (7)$$

where D_e is the effective diffusion coefficient for Cs leaching. The solution of Eq. (7) under the boundary conditions of

$$[C(z)]_{z=0} = 0 \quad \dots\dots\dots (8)$$

and

$$[\partial C(z) / \partial z]_{z=L} = 0 \quad \dots\dots\dots (9)$$

is given by

$$C(z) = C_0 \sum_{n=0}^{\infty} \frac{2 \sin[(n+1/2)\pi z / L]}{(n+1/2)\pi} \exp[-(n+1/2)^2 \pi^2 D_e t / L^2] \quad \dots\dots\dots (10)$$

Substitution of Eq. (10) into Eq. (3) gives the detected intensity of γ -rays emitted from ^{137}Cs in geopolymer. The amount of Cs in the disc is in turn given by

$$S \int_0^L C(z) dx = SLC_0 \sum_{n=0}^{\infty} \frac{2 \exp[-(n+1/2)^2 \pi^2 D_e t / L^2]}{(n+1/2)^2 \pi^2} \quad \dots\dots\dots (11)$$

where S is the cross section of the disc and C_0 is the ini-

tial concentration of Cs that can be finally leached out. At $[4\pi D_e t / (\pi L^2)]^{1/2} < 0.3$, the relative amount of Cs remaining in the disc is approximately expressed by

$$S \int_0^L C(z) dx / (SLC_0) \approx 1 - \sqrt{4D_e t / (\pi L^2)} \quad \dots\dots\dots (12)$$

The amount of Cs remaining in a geopolymer disc is thus obtained from the observed intensity of γ -rays. Fig. 7 shows the relation between the relative intensity of γ -rays, x , and the fraction of Cs remaining in a geopolymer disc, y . The relation can be expressed very well with a function $y = (1 + 0.321x - 0.321x^2)x$, which indicates that the relative intensity of γ -rays is close to the relative amount of remaining Cs. Since the relative difference between the γ -ray intensity and the amount of remaining Cs is less than 8%, the relative intensity of γ -rays is regarded as the relative amount of remaining Cs.

Table 4 summarizes the relative amounts of Cs leached into deionized water and the effective diffusion coefficients for Cs leaching to deionized water, $D_{e,d}$. Although the amount of leachable Cs strongly depended on the sample, the diffusion coefficient was not much different and was an order of $10^{-2} \text{ cm}^2/\text{h}$. Since the leached Cs was free Cs^+ ions in pore solutions that were in equilibrium with adsorbed Cs^+ , the diffusion coefficient in deionized water was not affected by ion exchanging. The best geopolymer for the suppression of Cs leaching was GP10-15. The amount of leachable Cs was less than

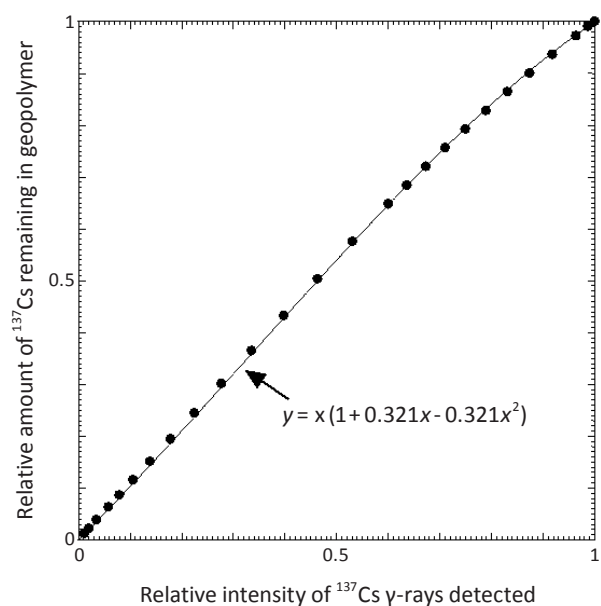


Fig. 7. Relation between detected intensity of γ -rays from geopolymer disc, x , and the amount of ^{137}Cs in the disc, y

Table 4. Effective diffusion coefficients of Cs leaching into deionized water and into sea water

Sample name	GP10-0	GP10-5	GP10-10	GP10-15
Relative amount of total Cs ⁺ leached into deionized water	0.0380	0.148	0.069	0.029
$D_{e,d}^*$ (cm ² /h)	0.972×10^{-2}	1.20×10^{-2}	1.22×10^{-2}	0.64×10^{-2}
$D_{e,s}^{**}$ (cm ² /h)	8.25×10^{-5}	9.99×10^{-5}	6.62×10^{-5}	1.96×10^{-5}
$D_{e,d}/D_{e,s}$	118	120	185	328

* Effective diffusion coefficient of Cs⁺ ion leaching into deionized water** Effective diffusion coefficient of Cs⁺ ion leaching into sea water

3% and the effective diffusion coefficient was 0.64×10^{-2} cm²/h. The amount of unbound and therefore leached Cs⁺ ions should be lowered by increasing the selectivity coefficient of C⁺ adsorption, so that the selectivity coefficient for GP10-15 might be the highest. The diffusion coefficient of 0.64×10^{-2} cm²/h is about 20 times larger than that for hardened OPC cement paste²⁶⁾. The larger diffusion coefficient may arise from higher porosity of geopolymer than that of the cement paste (porosity ≈ 0.3). The leaching of Cs from the cement paste is much slower, though most of Cs might be finally leached out.

Although the leaching of Cs into deionized water was terminated within one week, it was restarted in sea water. Fig. 8 shows the leaching of Cs from geopolymer samples into sea water at 30°C. The rate of Cs leaching was defined as the fraction of leached Cs per unit time with respect to the total amount of leachable Cs. Although the amount of leachable Cs in sea water was much higher

than that in deionized water, the leaching rate was much lower than that in deionized water, because the leaching necessitated the exchange of adsorbed Cs⁺ ions with cations in sea water. The leaching followed the square-root time law, which implies that the leaching was a diffusion-controlled process and the ion exchange process was much faster than the diffusion process. The effective diffusion coefficients for Cs leaching to sea water, $D_{e,s}$, is also summarized in Table 4. GP10-15 was also the best geopolymer for the suppression of Cs leaching into sea water. The half-life of Cs in GP10-15 with a thickness of 10 cm is estimated to be more than one hundred years by substituting $D_{e,s} = 1.96 \times 10^{-5}$ cm²/h and $L = 10$ cm into Eq. (12), which is long enough for reducing the radioactivity to less than one-tenth of the original intensity.

Since the leaching of Cs in sea water is induced by ion exchange, the leaching rate should be changed by changing the kind of cations in an aqueous solution. Fig.

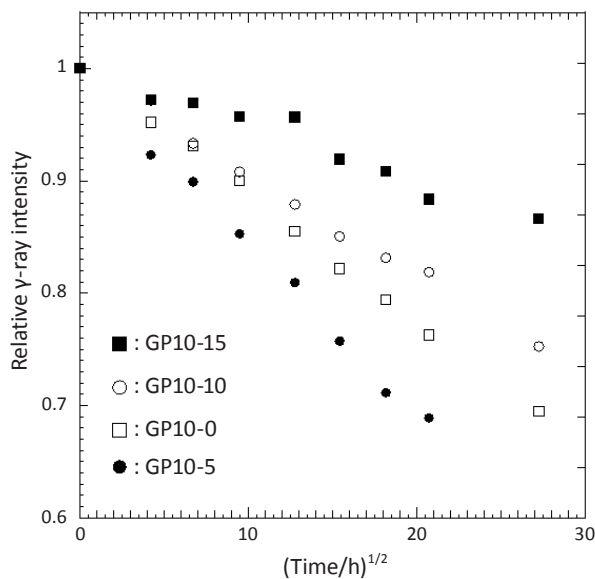


Fig. 8. Leaching of Cs from geopolymer samples to sea water at 30°C.
See Table 3 for the compositions of the samples

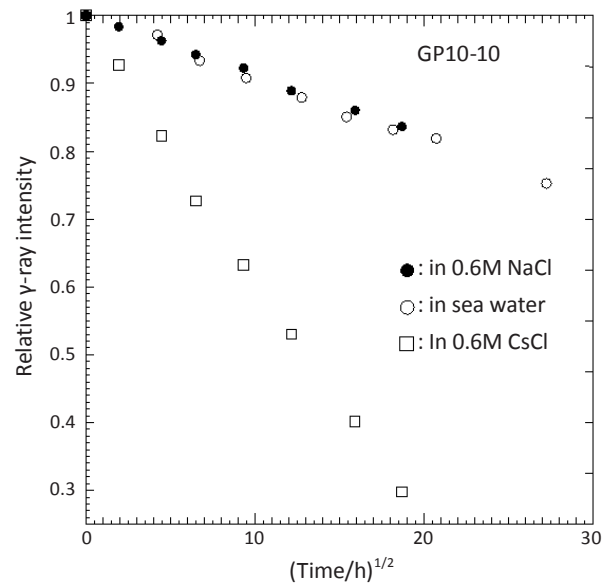


Fig. 9. Leaching of Cs from geopolymer GP10-10 to seawater, 0.6 M NaCl and 0.6 M CsCl solutions at 30°C

9 compares the rates of Cs leaching from GP10-10 into sea water, 0.6 M NaCl and 0.6 M CsCl solutions. The leaching rate in the 0.6 M NaCl solution was the same as that in sea water, which again certifies the validity of the assumption that the effect of minor cations in sea water on the adsorption/desorption of Cs^+ ions is replaceable with equivalent Na^+ ions. The leaching in the 0.6M CsCl solution was much faster than that in sea water, because the selectivity coefficient between adsorbed Cs^+ ions and free Cs^+ ions in the pore solution was unity. The diffusion coefficient of Cs leaching in the CsCl solution was $D_{e,\text{CsCl}} = 115 \times 10^{-5} \text{ cm}^2/\text{h}$, which was 17 times larger than that in sea water. Since the leaching in the CsCl solution still necessitated the desorption of Cs^+ ions, the leaching rate was much slower than that in deionized water.

(3) Suppression mechanism of Cs leaching

The suppression mechanism of Cs leaching from geopolymer to sea water can be understood by solving a reaction-diffusion equation including cation exchange reactions. For avoiding the mathematical complexity, we assume that the diffusion coefficients D of Na^+ , Cs^+ and the counterpart anions are the same. We also assume that the effect of minor cations in sea water is replaceable with equivalent Na^+ ions. The reaction-diffusion equation of ions in a geopolymer disc with thickness L is then expressed as

$$\frac{\partial[\text{Cs}^+]}{\partial t} + \frac{\partial[\text{GP-Cs}]}{\partial t} = D \frac{\partial^2[\text{Cs}^+]}{\partial z^2} \quad \dots\dots\dots (13)$$

$$\frac{\partial[\text{Na}^+]}{\partial t} + \frac{\partial[\text{GP-Na}]}{\partial t} = D \frac{\partial^2[\text{Na}^+]}{\partial z^2} \quad \dots\dots\dots (14)$$

Here z is the distance measured from the surface of the disc, $[\text{Cs}^+]$ and $[\text{Na}^+]$ are the concentrations of Cs^+ and Na^+ ions in the pore solution of geopolymer, and $[\text{GP-Cs}]$ and $[\text{GP-Na}]$ are the concentrations of Cs^+ and Na^+ ions which are bound to the cation exchange sites but are movable in the pore solution, respectively. The cation ex-

change capacity of geopolymer is constant, so that

$$[\text{GP-Cs}] + [\text{GP-Na}] = \rho \text{CEC} / \phi = E_0 \quad \dots\dots\dots (15)$$

Here ρ and ϕ are the density and the porosity of geopolymer, respectively. The value of E_0 for GP10-10 is estimated from these values in Table 3 to be 9 M. Defining C as the total concentration of Cs in geopolymer,

$$C = [\text{Cs}^+] + [\text{GP-Cs}] \quad \dots\dots\dots (16)$$

Eq. (13) is rewritten as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2[\text{Cs}^+]}{\partial z^2} \quad \dots\dots\dots (17)$$

The initial value of C in GP10-10 is estimated from the amount of Cs remaining after dipping in deionized water to be $0.23 E_0$. Defining B as the total concentration of free Cs^+ and Na^+ ions in the pore solution,

$$[\text{Cs}^+] + [\text{Na}^+] = B \quad \dots\dots\dots (18)$$

the sum of Eq. (13) and Eq. (14) gives

$$\frac{\partial B}{\partial t} = D \frac{\partial^2 B}{\partial z^2} \quad \dots\dots\dots (19)$$

Eq. (19) indicates that the total concentration of free ions is not affected by ion exchanging. The diffusion coefficient D is therefore equal to $D_{e,d}$ in Table 4. Since the leaching of Cs to deionized water is much faster than that into sea water, and is terminated within one week, it is reasonable to assume that B becomes a constant immediately after immersing geopolymer into sea water, or $B = B_0$. Since the leaching of Cs^+ ions is a diffusion-controlled reaction, it is also possible to assume that Eq. (5) is always established in geopolymer (assumption of instantaneous equilibrium). $[\text{Cs}^+]$ in Eq. (17) is then given by

$$[\text{Cs}^+] = \frac{K_{\text{Cs/Na}}(E_0 - C) + B_0 + C}{2(K_{\text{Cs/Na}} - 1)} \left[\sqrt{1 + 4(K_{\text{Cs/Na}} - 1)B_0 C / [K_{\text{Cs/Na}}(E_0 - C) + B_0 + C]^2} - 1 \right] \quad \dots\dots\dots (20)$$

The value of B_0 is not necessarily the same as that of sea water or 0.6M, because the surface charge on the pore walls changes the chemical potentials of positive and negative ions in the pore solution and therefore changes the concentrations of the ions. Although the effect of surface

charge on the chemical potential of ions has been calculated microscopically by using molecular dynamic simulations²⁷⁾, as far as we know, no attempt has been made to calculate the chemical potentials rigorously and explicitly as a function of macroscopic parameters such as concen-

tration of ions, pore diameter and surface charge density. The value of B_0 is also possible to be calculated by using the theory of electrical double layer²⁸⁾. However, the calculation is not rigorous and the theoretical foundation of the calculation is unclear. We therefore constructed an explicit thermodynamic theory for estimating the chemical potentials from the macroscopic parameters.

We treat a simple case that a solid sample with a cylindrical pore of radius R is immersed in an electrolyte solution composed of monovalent ions. The surface of the pore is negatively charged to adsorb positive ions. The density of the surface charge is given by σ . The chemical potentials of positive and negative ions, μ_+ and μ_- , respectively, are given by the sum of the free energy of dilution and the electrostatic energy, as

$$\mu_+ = kT \ln(n_+) + eV \quad \dots\dots\dots (21)$$

$$\mu_- = kT \ln(n_-) - eV \quad \dots\dots\dots (22)$$

where k is the Boltzmann constant, T is the absolute temperature, n_+ and n_- are the number densities of positive and negative ions, respectively, e is the elementary charge, and V is the electrostatic potential generated by the surface charge and positive and negative ions in the pore solution. Here the standard chemical potentials of the ions are omitted for simplicity. Under an equilibrium condition, the chemical potential of identical particles is the same everywhere in the solution, so that

$$n_+ = \exp\left(\frac{\mu_+}{kT}\right) \exp\left(-\frac{eV}{kT}\right) \equiv n_{+0} \exp\left(-\frac{eV}{kT}\right) \quad \dots\dots (23)$$

$$n_- = \exp\left(\frac{\mu_-}{kT}\right) \exp\left(\frac{eV}{kT}\right) \equiv n_{-0} \exp\left(\frac{eV}{kT}\right) \quad \dots\dots\dots (24)$$

where n_{+0} and n_{-0} are constants. The total numbers of positive and negative ions per unit length are given by

$$N_+ = 2\pi \int_0^R n_+ r dr = 2\pi n_{+0} \int_0^R \exp\left(-\frac{eV}{kT}\right) r dr \quad \dots\dots (25)$$

$$N_- = 2\pi \int_0^R n_- r dr = 2\pi n_{-0} \int_0^R \exp\left(\frac{eV}{kT}\right) r dr \quad \dots\dots\dots (26)$$

The principle of electrical neutrality is then expressed as

$$N_- - N_+ = 2\pi R(\sigma / e) \quad \dots\dots\dots (27)$$

Ions in the pore solution are in equilibrium with ions in the outer solution (sea water) with chemical potential $kT \ln(n_0)$, where n_0 is the number density of positive or

negative ions in the outer solution ($0.6 \text{ M} = 0.3614/\text{nm}^3$). Due to the principle of electrical neutrality, a positive ion migrates from the outer solution in pair with a negative ion, so that the relation of

$$kT \ln(n_{+0}) + kT \ln(n_{-0}) = 2kT \ln(n_0) \quad \dots\dots\dots (28)$$

is established under the equilibrium condition. Eq. (28) gives the relation of $n_{+0} = n_0^2/n_{-0}$.

For determining the values of n_{+0} and n_{-0} , it is necessary to determine the electrostatic potential V as a function of r and σ . The electrostatic potential can be obtained from the Gauss' law or so-called Poisson-Boltzmann equation

$$\begin{aligned} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial V}{\partial r} \right) &= -\frac{e(n_+ - n_-)}{\varepsilon} \\ &= \frac{en_0}{\varepsilon} \left[(n_{-0}/n_0) \exp\left(\frac{eV}{kT}\right) - (n_{+0}/n_0) \exp\left(-\frac{eV}{kT}\right) \right] \end{aligned} \quad \dots\dots\dots (29)$$

where ε is the dielectric constant of water. Spatial integration of Eq. (29) under the condition of Eq. (27) gives a commonly-used boundary condition of

$$\left(\frac{\partial V}{\partial r} \right)_{r=R} = \frac{\sigma}{\varepsilon} \quad \dots\dots\dots (27')$$

Eq. (27') is therefore equivalent to Eq. (27). Since the condition of electrical neutrality is completely fulfilled at $r = 0$, provided that the electrostatic potential of the outside of the pore is zero, it is possible to set

$$[V]_{r=0} = 0 \quad \dots\dots\dots (30)$$

and

$$\left[\frac{\partial V}{\partial r} \right]_{r=0} = 0 \quad \dots\dots\dots (31)$$

The theory of electrical double layer assumes $[V]_{r=0} = V_0 \neq 0$ and $n_{+0} = n_{-0} = n_0$ ²⁸⁾, which implies that the chemical potentials of positive and negative ions at $r = 0$ are composed of the identical free energy of dilution, $kT \ln(n_0)$, and different electrostatic energies of eV and $-eV$, respectively. The present theory claims that the chemical potentials of positive and negative ions at $r = 0$ are composed of solely the free energies of dilution, $kT \ln(n_{+0})$ and $kT \ln(n_{-0})$, respectively. Although the two theories give the same result, because the sum of the chemical poten-

tials of positive and negative ions gives the same value of $2kT\ln(n_0)$, the thermodynamic implications of the chemical potential are quite different.

The average concentration of unbound free cations exchangeable with adsorbed cations, B_0 , can be estimated in the following way. The electrostatic potential V at an arbitrary value of n_0/n_0 is obtained by numerically solving Eq. (29) with the Runge-Kutta method under the boundary conditions of Eq. (30) and Eq. (31). Substitution of thus obtained V into Eq. (25) and Eq. (26) gives the values of N_+ and N_- , respectively. Substitution of N_+ and N_- into Eq. (27) gives the value of σ . The calculation should be repeated with different n_0/n_0 until the value of σ accords with the surface charge density of the pore wall. The average concentration is finally calculated as

$$B_0 = \frac{N_+ + 2\pi R(\sigma/e)}{\pi R^2} = \frac{N_-}{\pi R^2} \quad \dots\dots\dots (32)$$

For carrying out the above calculations, it is necessary to determine the value of the radius of pores, R , and the density of surface charge, σ . The average pore radius of GP10-10 was already determined by the porosity measurement to be 6.3 nm. Assuming that the length of pores in geopolymer is much longer than the radius, the density of the surface charge of GP10-10 is estimated from the cation exchange capacity of 4.88 meq/cm³, the porosity of 0.54 cm³/cm³ and the average pore radius of 6.3 nm to be $-\sigma/e = 17.1/\text{nm}^2$. Fig. 10 shows the average concentration

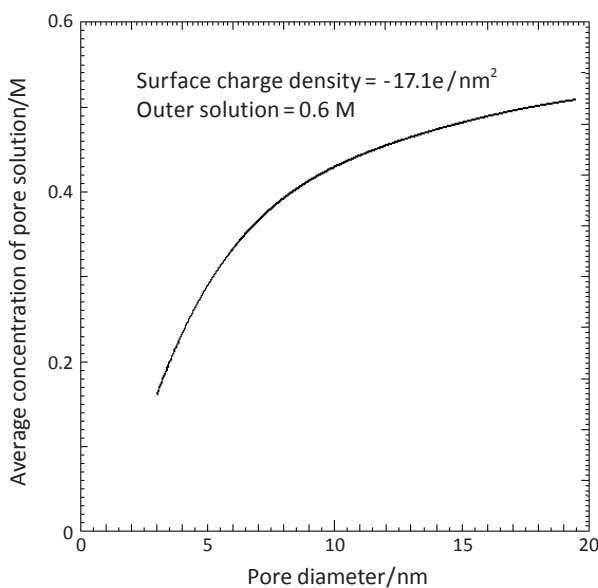


Fig. 10. Effect of surface charge on the concentration of pore solution in geopolymer GP10-10 immersed in 0.6 M NaCl solution

of free cations in GP10-10 that is immersed in a 0.6 M NaCl solution. The average concentration is lower than that of the outer solution and decreases with decreasing the pore diameter. The average concentration at the average diameter of 12.6 nm is 0.46 M, which implies that B_0 for GP10-10 is 0.46 M even the concentration of the outer solution is 0.6 M.

Since the values of E_0 , C_0 and B_0 have been determined, it is now possible to calculate Eq. (20). Under the condition of $K_{\text{Cs/Na}} \gg 1$, substitution of $E_0 = 9 \text{ M}$, $C = C_0 = 0.23E_0$ and $B_0 = 0.46 \text{ M}$ into the second term in the square root term in Eq. (20) gives

$$4(K_{\text{Cs/Na}} - 1)B_0C / [K_{\text{Cs/Na}}E_0 - (K_{\text{Cs/Na}} - 1)C + B_0]^2 \ll 1 \quad \dots\dots\dots (33)$$

Eq. (20) is then possible to be simplified by using a first-order Taylor series approximation of the square root term as

$$[\text{Cs}^+] \approx \frac{C}{K_{\text{Cs/Na}}E_0/B_0 - (K_{\text{Cs/Na}} - 1)C/B_0 + 1} \approx \frac{C}{K_{\text{Cs/Na}}E_0/B_0 + 1} \quad \dots\dots\dots (34)$$

The relation of $C < C_0 \ll E_0$ has been used for deriving the rightmost term in Eq. (34). Since Eq. (34) is also the exact solution for $K_{\text{Cs/Na}} = 1$, Eq. (34) is valid irrespective of the value of $K_{\text{Cs/Na}}$. The effective diffusion coefficient for Cs leaching to sea water or a 0.6 M NaCl solution is finally expressed as a function of observed parameters as

$$D_{e,s} \equiv \frac{D_{e,d}}{K_{\text{Cs/Na}}\rho\text{CEC}/(\phi B_0) + 1} \quad \dots\dots\dots (35)$$

were ρ and ϕ are the density and the porosity of geopolymer, respectively. The solutions of Eq. (17) is then given by replacing D_e in Eq. (10) and Eq. (12) with $D_{e,s}$ in Eq. (37). The ratio of $D_{e,d}/D_{e,\text{CsCl}}$ for GP10-10 can be obtained by substituting $K_{\text{Cs/Na}} = 1$ and $\rho\text{CEC}/(\phi B_0) = 20$ into Eq. (37) to be 21, which can be compared with the observed value of $D_{e,d}/D_{e,\text{CsCl}} = 11$. Assuming that the value of $\rho\text{CEC}/(\phi E_0)$ is 11 for GP10-10, the value of $K_{\text{Cs/Na}}$ is estimated from the observed value of $D_{e,d}/D_{e,s} = 185$ to be 17, which compares well with the experimental value of $K_{\text{Cs/Na}} \approx 20$. The theory developed here therefore explains the suppression mechanism of Cs leaching into sea water. The slow leaching is due to the higher concentration of adsorbed cations than that of unbound free cations in geopolymer and the higher selectivity of adsorption for

Cs⁺ ions than that for the other ions in sea water. Within amorphous geopolymer, the ability of suppressing Cs leaching to sea water increased with increasing the Si/Al molar ratio. Since the value of $\rho\text{CEC}/\varphi$ is not much different within the amorphous geopolymer, the increase may be due to the increase of the selectivity coefficient with increasing Si/Al ratio.

4. Conclusion

It was revealed that the solidification of water-soluble Cs compounds with metakaolin and water glass and/or an alkaline solution was a very efficient way of immobilizing a large amount of Cs including ¹³⁷Cs. The mixed material was fluid enough within a few hours after the mixing, so that it was easily poured into a mold. The mixture was solidified within one day at ambient temperature. The chemical and solid state NMR analyses of the resultant geopolymer showed that more than 90% of Al atoms possess the structural unit of NaAlO₂ or CsAlO₂. Geopolymer thus prepared was therefore a cation exchanger with very high cation exchange capacity.

The XRD analysis of geopolymer samples showed that water glass was an efficient suppressor for the formation of zeolite crystals, and helped the formation of three-dimensional amorphous networks.

The Cs leaching tests of geopolymer samples containing 9.1 wt% of Cs showed that GP10-15 with Si/Al molar ratio of 2.04 showed the highest ability of suppressing the Cs leaching. Although more than 33% of alkali metal cations were not bound to GP10-15, the amount of Cs leached into deionized water was less than 3%. The leaching continued in sea water, though the leaching was slow enough to use the geopolymer as a solidifier-immobilizer for radioactive Cs. The retardation of Cs leaching in sea water was due to higher concentration of adsorbed cations than that of free cations in the pore solution of geopolymer and the higher selectivity of the adsorption for Cs⁺ ions than those for the other ions in sea water.

References

- 1) S. Mizokami, Y. Kumagai: Chapter 2. Event Sequence of the Fukushima Daiichi Accident. In "Reflections on the Fukushima Daiichi Nuclear Accident. Toward Social-Scientific Literacy and Engineering Resilience", Eds. by J. Ahn, C. Carson, M. Jensen, K. Juraku, S. Nagasaki, S. Tanaka, Springer Open, pp 21-50 (2015).
- 2) Y. Morino, T. Ohara, M. Nishizawa: Atmospheric behavior, deposition, and budget of radioactive materials from the Fukushima Daiichi nuclear power plant in March 2011. *Geophys Res Lett.* **38**, L00G11 (2011).
- 3) Y. Morino, T. Ohara, M. Watanabe, S. Hayashi, M. Nishizawa: Episode Analysis of Deposition of Radiocesium from the Fukushima Daiichi Nuclear Power Plant Accident. *Environ Sci Technol.*, **47**, 2314-2322 (2013).
- 4) S. Tanaka, S. Kado: Chapter 3. Analysis of Radioactive Release from the Fukushima Daiichi Nuclear Power Station. In "Reflections on the Fukushima Daiichi Nuclear Accident. Toward Social-Scientific Literacy and Engineering Resilience" Eds. by J. Ahn, C. Carson, M. Jensen, K. Juraku, S. Nagasaki, S. Tanaka, Springer Open, pp 51-84 (2015).
- 5) Ministry of Environment, Japan, Environmental Remediation in Affected Areas in Japan http://josen.env.go.jp/en/pdf/environmental_remediation_1908.pdf (2019).
- 6) X. Yin, H. Takahashi, Y. Inaba, K. Takeshita: Desorption of Cesium Ions from Vermiculite with Sea Water by Hydrothermal Process. *Chem. Lett.*, **45**, 256–258 (2015).
- 7) X. Yin, X. Wang, H. Wu, T. Ohnuki, K. Takeshita: Enhanced desorption of cesium from collapsed interlayer regions in vermiculite by hydrothermal treatment with divalent cations. *J. Hazard. Mater.*, **326**, 47–53 (2017).
- 8) Center for Material Cycles and Waste Management Research (National Institute for Environmental Studies): Technical evaluation of the pyroprocessing of removed soil etc. containing radioactive Cs. http://www.nies.go.jp/fukushima/pdf/cs_heat-treatment_201510.pdf (2015). [in Japanese]
- 9) T. Ichikawa, K. Yamada, M. Osako, K. Haga: Super Volume Reduction of ¹³⁷Cs-contaminated Solid Waste by Ion Chromatographic Elimination of Cs from ¹³⁷Cs-enriched Dust Generated by Pyroprocessing decontamination. *J. Soc. Remed. Radioact. Contam. Environ.*, **6**, 73-80 (2018).
- 10) NukeText: Spent Fuel Treatment and Disposal. http://www.nuketext.org/shiyouzumi_eng.html#glass (2009).
- 11) K. Komnitsaa, D. Zaharaki: Geopolymerization: A review and prospect for minerals industry. *Mater.*

- Eng.*, **20**, 1261-1277 (2007).
- 12) V. Cantarel, T. Motooka, I. Yamagishi: Geopolymers and Their Potential Applications in the Nuclear Waste Management Field - A Bibliographical Study -. *JAEA-Review*, 2017-014 (2017). <http://jolissrch-inter.tokai-sc.jaea.go.jp/pdfdata/JAEA-Review-2017-014.pdf>, and references therein.
 - 13) S. Ukritnukun, C.C. Sorrell, D. Gregg, E.R. Vance, P. Koshy: Potential Use of Ambient-Cured Geopolymers for Intermediate Level Nuclear Waste Storage. *MRS Advances*, **3**, 1123-1131 (2018).
 - 14) L. Leay, A. Potts, T. Donoclift: Geopolymers from fly ash and their gamma irradiation. *Mater. Lett.*, **227**, 240-242 (2018).
 - 15) N. Deng, H. An, H. Cui, Y. Pan, B. Wang: Effect of gamma-ray irradiation on leaching of simulated ^{133}Cs radionuclides from geopolymer wasteforms. *J Nucl Mater.*, **459**, 270-275 (2015).
 - 16) X. Liu, Y. Ding, X. Lu: Immobilization of simulated radionuclide ^{90}Sr by fly ash-slag-metakaolin-based geopolymer. *J. Nucl. Technol.*, **198**, 64-69 (2017).
 - 17) X. Zhonghui, J. Zao, W. Dandan, X. Peng, Y. Xu, N. Li, Y. Qiu, P. Li: Immobilization of strontium-loaded zeolite A by metakaolin-based geopolymer. *Ceram. Int.*, **43**, 4434-4439 (2017).
 - 18) Q. Li, Z. Sun, D. Tao, Y. Xu, P. Li, H. Cui, J. Zhai: Immobilization of simulated radionuclide ^{133}Cs by fly ash-based geopolymer. *J. Hazard. Mater.*, **262**, 325-331 (2013).
 - 19) S. Berger, F. Frizon, C. Jousset-Dubien: Formation of caesium based and caesium containing geopolymers. *Adv. Appl. Ceram.*, **108**, 412-417 (2009).
 - 20) C. Kuenzel, J.F. Cisneros, T.P. Neville, L.J. Vandeperre, S.J.R. Simons, J. Bensted, C.R. Cheeseman: Encapsulation of Cs/Sr contaminated clinoptilolite in geopolymers produced from metakaolin. *J. Nucl. Mater.*, **466**, 94-99 (2015).
 - 21) N.K. Lee, H. Khalid, H.K. Lee: Adsorption characteristics of cesium onto mesoporous geopolymers containing nano-crystalline zeolites. *Microporous Mesoporous Mater.*, **242**, 238-244 (2017).
 - 22) M.R. El-Naggar, M. Amin, Impact of alkali cations on properties of metakaolin and metakaolin/slag geopolymers. Microstructures in relation to sorption of Cs-134 radionuclides. *J. Hazard. Mater.*, **344**, 913-924 (2018).
 - 23) M.A. Haddad, E. Ofer-Rozovski, G. Bar-Nes, E.J.C. Borojovich, A. Nikolski, D. Mogiliansky, A. Katz: Formation of zeolites in metakaolin-based geopolymers and their potential application for Cs immobilization. *J. Nucl. Mater.*, **493**, 168-179 (2017).
 - 24) M.G. Blackford: Transmission electron microscopy and nuclear magnetic resonance studies of geopolymers for radioactive waste immobilization. *J. Am. Ceram. Soc.*, **90**, 1193-1199 (2007).
 - 25) A.M. Taylor, R. Roy: Zeolite studies IV: Na-P zeolites and the ion-exchanged derivatives of tetragonal Na-P1. *Am. Mineral.*, **49**, 656-682 (1964).
 - 26) M. Mihara, S. Harasawa, K. Torii: Apparent diffusion coefficients of Cs and I in hardened cement paste using mineral admixtures. *Genshiryoku Bakuendo Kenkyu*, **26**, 15 – 23 (2019). [in Japanese, available from <https://nuce.aesj.or.jp/jnuce/vol26/Jnuce-Vol26-1-p15-23.pdf>]
 - 27) Y. Matsuura: Ion Selectivity Mechanism of an Ion Channel Studied by Molecular Dynamics Simulation. Ph.D. Thesis, *Tokyo University of Science Repository for Academic Resources*, 1262-A (2014), and references therein.
 - 28) S.A. Safran: Chapter 5-5. Electrostatic Interactions. In "Statistical Thermodynamics of Surfaces, Interfaces, and Membranes", CRC Press, pp. 151-164 (1994).

報 文 (英語論文)

¹³⁷Csで汚染された廃棄物の減容化で生じた濃縮Csを固定化する材料としての メタカオリン由来ジオポリマー

市川 恒樹*, 渡邊 禎之, 新井 裕之, 芳賀 和子, 山田 一夫

【要 約】 メタカオリンと水ガラスや苛性ソーダなどのアルカリ源に水溶性のCsClを加えて室温で固化したカチオン交換性非晶質アルミノケイ酸塩であるCs担持ジオポリマーは、Csを固定化するとともに、海水中でも非常にゆっくりとしかCs放出をしないことが分かった。メタカオリンと水ガラスの混合比が10:15でCsを9.1重量%含むジオポリマーは脱イオン水中で97%以上のCsを永続的に保持する。海水中でのCs漏出は非常に遅く、漏出の実効拡散係数は $1.96 \times 10^{-5} \text{ cm}^2/\text{h}$ だった。漏出が非常に遅いのは、ジオポリマー細孔中での吸着カチオンの実効濃度が海水濃度に比べて非常に高く、かつジオポリマーのカチオン交換基のCsイオン選択係数が非常に高いので、海水イオン-吸着Csイオン間のイオン交換が非常に遅くなるためであることが分かった。漏出が非常に遅いため、ジオポリマーは¹³⁷Cs汚染廃棄物の減容処理で生じたCs濃縮物の固定化材として使用できることが判明した。

【キーワード】 放射性廃棄物、除染、¹³⁷Cs、減容、ジオポリマー、固定化材、メタカオリン、水ガラス

 2019年10月18日受付、2019年12月20日受理

*Corresponding author: (所属) 北海道大学・国立研究開発法人国立環境研究所、E-mail: tsuneki@eng.hokudai.ac.jp

