Leaching Characteristics of Cs from the Decomposed Cu Ferrocyanide Adsorbent Solidified by Portland Cement and Geopolymer

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Abstract. The use of cement technology is under investigation for the disposal of ^{137}Cs, which is a type of radioactive waste and which was dispersed as a result of the accident. Here, we present the results of a study on the leaching characteristics of Cs from solidified bodies. Combustible materials contaminated with radioactive Cs released by the accident at the TEPCO's Fukushima Daiichi NPS are incinerated to reduce their volume, and the incineration residue is further reduced by melting treatment. Cs exists as water-soluble salts in the molten fly ash. The Cs can be transferred to the liquid phase by washing, and the Cs can be further concentrated by ion-exchange chromatography using Cs adsorbents such as ferrocyanide transition metal salts. The adsorbent used must be stabilized for final disposal. We present an example of using copper ferrocyanide as an adsorbent in this process. Copper ferrocyanide was calcined and decomposed, then solidified with Portland cement or metakaolin geopolymer. Since cement hydrate has no cation exchange property, all Cs leached into pure water, but copper ferrocyanide, after pyrolysis, became cation exchangeable in the alkaline environment of Portland cement, resulting in a Cs leaching rate of only 20%. The Cs leaching rate from the geopolymer solidified body was 2% because the geopolymer is an ion exchanger and has a large Cs ion selectivity for Na ions. However, from the viewpoint of workability during mixing, there was an upper limit to the amount of material to be treated, and cement solidification was superior in terms of volume reduction.

Keywords: Cs · leaching · geopolymer · ferrocyanide · disposal · radioactive wastes · solidification

1 Introduction

Nuclear power is one way to reduce CO_2 emissions. However, problems associated with nuclear power include the disposal of radioactive waste and the seriousness of accidents once they occur, even if they are extremely rare. While the main problem of radioactive waste disposal may be the consensus building of the public, one of the technical

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challenges is the control of elemental leaching from the waste body. In cement solidification, a typical method of waste body preparation, many multivalent metal cations are precipitated as hydroxides because cement creates an alkaline atmosphere generally speaking, metal elements that become an oxo-anions in alkaline conditions can be made to insoluble Ca salts by pH control, and anions can be fixed in the ion exchanger cement hydrates such as AFm to a certain extent. The only alkali metal ions that are not expected to be immobilized are those that do not interact with the cement hydrates, except in the Ca dissolved or carbonated state; the pH of the porewater decreases with the addition of SCMs, but this is due to the consumption of OH^- in the hydration reaction of the SCMs and the resulting alkali metals adsorption on low Ca/Si ratio C-S-H surface and at the Al sites in C-A-S-H, but there is no effect that changes the concentration of alkali metal ions concentration by more than one order of magnitude like other elements.

As an example of a radiation disaster, the TEPCO Fukushima Daiichi nuclear power plant accident is considered. As a result of this accident, a large area of eastern Japan was contaminated by radioactive Cs (r-Cs). Due to the nature of the accident, only highly volatile Cs are the only radionuclides to be considered in environmental contamination, as radionuclides were diffused from the reactor with steam. Other radio-nuclides detected in environments are the same order of magnitude of fall out by past atmospheric nuclear test [1], therefore the only radioactive contamination from that accident can be considered to be radioactive Cs. Decontamination activities to achieve the additional exposure dose due to the accident set by the government have resulted in the generation of removed soil and contaminated waste being delivered to an interim storage facility. It is estimated that 13 million m^3 of removed soil and 380,000 m^3 of contaminated waste have been transferred to the interim storage facility [2]. Government policy states that due to the huge amount of contaminated material, a maximum reduction in the disposal volume is required for final disposal [3].

Cs is strongly adsorbed by clay minerals, so Cs hardly moves from the soil in general environments, but Cs in contaminated waste such as incineration ash has a high water soluble fraction, which needs to be taken care of. Of the contaminated waste, combustible materials are incinerated and reduced in volume, and incineration residues are further treated in melting furnaces, where r-Cs is concentrated in molten fly ash of much smaller volume, and slag with reduced r-Cs concentration is generated [4]. The majority of r-Cs in molten fly ash is water soluble and can be further reduced in volume by ion exchange chromatographic concentration after fly ash washing. The spent adsorbent is further stabilized in some way and made into a disposal body. Studies have shown that the maximum volume reduction of Cs from the original waste to the disposal body is 1 in 60,000 [5]. The best performing adsorbent used in ion exchange chromatography is ferrocyanide transition metal salts, but after adsorption treatment, there is the possibility of dissolution of ferrocyanide ions meaning of the release of r-Cs once fixed, and this final disposal requires the decomposition of ferrocyanide ions in Japan, which has restrictions regarding total cyanide in the environment [6]. Furthermore, the volume reduction rate depends on how the radioactive Cs is stabilized after decomposition and final disposal.

Various solidification methods can be applied for stabilization. The simplest is cement solidification [7, 8]. However, ferrocyanide transition metal salts decompose in an alkaline atmosphere, Cs is no longer immobilized in the cement hardened body, which is an alkaline atmosphere, Cs is released into the liquid phase and, as mentioned earlier, cement has no cation exchange capacity and it cannot fix alkali metal ions [9], so only a reduced diffusion coefficient due to the dense structure of the hardened cement is expected. Geopolymers can also be applied [10, 11]. Geopolymers partially replace the silica backbone by a four-coordinated alumina, which compensates for the lack of one charge of Al compared to Si, so that cations are adsorbed and cation-exchange properties occur. This is beneficial for Cs fixation.

This report describes the results of an evaluation of the Cs leaching behavior of Cs removed from molten fly ash washings by ion exchange chromatography using copper ferrocyanide, after calcination and decomposition of the copper ferrocyanide and solidification with Portland cement or geopolymers. The nature of radioactive waste management is that the safety of disposal is evaluated as a comprehensive system that includes the solidified body, the structure of the disposal facility, and the geologic environment of the disposal site. Therefore, although there is no specific requirement for the leaching behavior of Cs, it is important to understand its leaching behavior.

2 Experiments

2.1 Materials

The solidification object is a simulated spent copper ferrocyanide adsorbent containing 0.5 mol/kg Cs (labelled 4 kBq/meq-Cs for ^{137}Cs) as saturated adsorption, calcined and decomposed at around 400 °C in air, with a cation composition of almost $Cs_{0.2}K_{0.8}Cu_{1.5}Fe$, iron oxide, copper oxide, alkali metal carbonates and nitrites (abbreviated as Calcined Spent Adsorbent, CSA). Two binders for solidification were selected: ordinary Portland cement (OPC), which conforms to JIS R 5210–2019, and geopolymer. The geopolymer was synthesized from metakaolin and water glass; Metakaolin used was Satintone SP33 supplied by BASF, USA. Water glass used was supplied by Junsei Chamicals, Japan. The molar ratios of Si/Al and Na/Al are important in the preparation of the geopolymers and are therefore listed so that the molar ratios could be understood (Table 1).

Table 1. Chemical compositions of metakaolin and water glass.

Component	Al_2O_3	SiO_2	Na_2O	TiO_2	H_2O
	mol/kg				mass%
Metakaolin	4.37	8.65	0.32	0.24	0.1
Water glass	0	6.11	2.84	0	45.8

2.2 Mixture Proportion

Mixing ratios for cement solidification and geopolymer solidification are shown in Tables 2 and 3 respectively. For cement solidification, the mixture of CSA and OPC with about 40% water was filled into plastic petri dishes 35 mm in diameter and 10 mm thick and sealed and cured at 40 °C for 4 weeks. Density was measured by gravimetric measurements in water.

A sample with CSA replaced by CsCl (CsCl/OPC = 1/5.9) was prepared by the same method. This corresponds to the case of direct cement solidification of molten fly ash. The main components of the molten fly ash are KCl and NaCl, with CsCl on the order of 1 ppm, but here only CsCl was added for comparison with Cs adsorbed on copper ferrocyanide.

In the case of geopolymer solidification, a mixture of 2 metakaolin to 3 water glass and a small amount of water by mass, plus CSA, was filled into the same petri dish and sealed and cured at 40 °C for 4 weeks. The mixing ratio was based on the composition of the geopolymer as $NaAlO_2.SiO_2$. The geopolymer is an amorphous aluminosilicate, with four-coordinated AlO_2 partially replacing SiO_2. The Na/Al in the geopolymer was designed to be 1.0, as Al is accompanied by a + 1 charge cation for charge compensation.

Table 2. Mixture proportions of cement solidification.

Sample	Mass ratio				Cs	Density
	CSA	OPC	W	CSA/OPC	mass%	g/cm^3
PC-1	3.06	12.2	5	1/4	1.49	2.10
PC-2	4.03	12.0	5	1/3	1.89	2.11
PC-3	5.53	11.0	5	1/2	2.53	2.12
PC-4	8.06	8.06	5	1/1	3.78	2.11

Table 3. Mixture proportions of geopolymer solidification.

Sample	Mass ratio					Hardening at 1day			Cs	Density
	CSA	Met.K	W.Glass	W	CSA/GP	RT	40 °C	60 °C	mass%	g/cm^3
MGP-1	1.6	8	12	3.2	1/12.5	X	O		0.69	1.72
MGP-2	2.1	7	10.5	2.8	1/8.3	X	O		1.01	1.74
MGP-3	3.0	6	9	2.4	1/5	X	O		1.58	1.77
MGP-4	6.0	6	9	3	1/2.5	X	X	O	2.69	1.89

X: Not hardened, O: Hardened

2.3 Measurement of Cs Leaching

The Cs leaching from the solidified body was assessed by measuring the γ-rays due to ^{137}Cs from the specimen using an NaI scintillator detector. The measurement time was 3 min and repeated three times. The change in this count from the value before the leaching test was used to determine the percentage of Cs remaining.

Hardening was judged by whether the material deformed when pressed with a finger. The compressive strength required for the waste body after radioactive Cs stabilization is 1 MPa, which is about the same as soil, and if it does not deform at all when pressed with a finger, it can be judged that sufficient strength has been achieved, so strength measurements were not performed.

3 Results

3.1 OPC Solidification

The Cs leaching characteristics when solidified with OPCs is shown in Fig. 1: when CsCl is cement solidified, leaching progresses to a Cs residual of 0.4 within 150 h and eventually all Cs is released. However, when cement solidified with calcined ferrocyanide copper adsorbent CSA, Cs is initially leached out, but after two months (1440 h), leaching is completed and just under 80% of the Cs is retained in the solidified product. CSA acted as a cation exchanger in the alkaline atmosphere, and Cs was adsorbed and retained as $Cu_{1.5}FeO_{2.5}(OK)_{0.64}(OCs)_{0.16}$, based on the estimated chemical composition of CSA. In this reaction, considerable amounts of alkali (OH^-) from $Ca(OH)_2$ are assumed to be consumed. Then, free Ca^{2+} is generated and react with carbonate and nitrite anions originally brought in this system from Cs carbonate or nitrite. Instead, Cs is absorbed by hydrated CSA. However, still some parts of Cs are considered to exist as nitrite and hydroxide and the leaching of 20% Cs may be due to its presence in the cement hardened body pore water in a non-adsorbed state. Once the Cs^+ ions in this pore water are leached out, they are not leached out in pure water anymore because they are adsorbed by the cation exchanger. However, when exposed to salt water with low Cs concentrations, such as seawater, the entire amount of Cs is expected to be ion-exchanged with another alkali

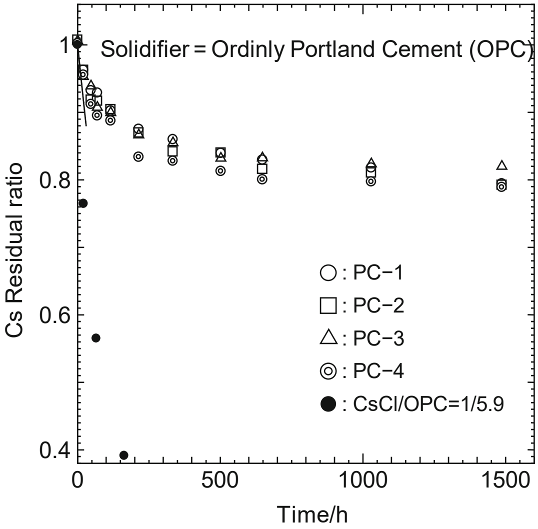

Fig. 1. Cs leaching behavior from OPC solidified specimens.

metal ions and released, even if the transition metal hydroxide salt has some Cs^+ ion selectivity because the K/Cs molar ration of sea water is around 1 million.

Increasing CSA up to the same weight as OPC did not significantly change the workability during mixing procedure, the strength, or Cs retention capacity of the solidified product. There is a possibility to further increase the amount of CSA added.

Since Cs is considered to be immobilized by ion exchange in the OPC-CSA solidified body, we can predict that when this solidified body is immersed in salt water, Cs will be ion-exchanged with the cations in the salt water and leached out.

3.2 Geopolymer Solidification

The Cs leaching behavior of CSA solidified with geopolymer is shown in Fig. 2. The geopolymer used for solidification is a cation exchanger with composition $NaAlO_2.2SiO_2$ and has a high selectivity for Cs^+ ion adsorption (see Appendix), so that more than 98% of Cs is retained in the geopolymer by replacing Na. In cement solidification, the leaching rate is higher because it is the K^+ ions that compete with the Cs^+ ions, which are more effective in inhibiting the adsorption of Cs^+ ions, while in geopolymers, in addition to having a higher ion exchange capacity, they compete with Na^+ ions, which are less effective in inhibiting the adsorption of Cs^+ ions. Hence, although there is no comparison of Cs^+ ion selectivities of hydrated CSA and geopolymer, the leaching of Cs^+ ions is considered to have been smaller in Na-containing geopolymer. As with cement solidification of CSA, once the Cs^+ ions in the pore water have been leached from geopolymer solidification body, no further leaching occurs from the ion exchanger, but all Cs^+ ions are ion-exchanged and released when exposed to salt water such as seawater with low Cs^+ ion concentrations as shown in Fig. 3 [12]. In artificial sea water and in 0.6 M NaCl solution, the leaching behaviors of Cs^+ ion are similar. In the same concentration 0.6 M but of CsCl, the leaching of Cs^+ ion was much faster. The leaching of Cs^+ ion was evaluated by ^{137}Cs in solidified body and it is possible to evaluated the isotope exchange. Because the Cs can much more than Na, the Cs^+ ion leaching was faster than NaCl. However, every leaching tendency showed linear to square root of time, and this means the leaching is controlled by diffusion.

Increasing the amount of CSA up from 1/12.5 to 1/5 of the solidified material weight does not significantly change the strength or Cs retention capacity of the solidified product, but if the amount exceeds 1/2.5 (MGP-4), solidification becomes difficult because of the low workability for molding.

3.3 Comparison of Cement and Geopolymer Solidifications

The characteristics of cement and geopolymer solidification of the above-mentioned calcined spent ferrocyanide calcined copper adsorbent CSA are summarized in Table 4. In cement solidification, a larger amount of CSA can be added, resulting in a big volume reduction of 1/27,000 from the original wastes, which is combustible contaminated wastes. Geopolymer solidification, on the other hand, has a limited amount of CSA added in terms of workability during mixing, resulting in a volume reduction rate of 1/9,000, which is 1/3 of the efficiency of cement solidification.

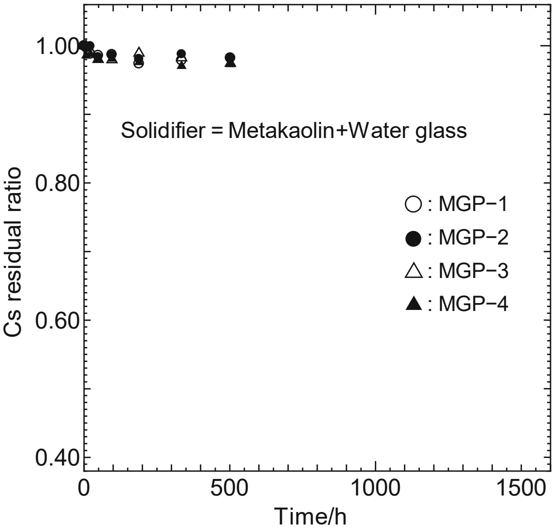

Fig. 2. Cs leaching behavior from geopolymer solidified specimens.

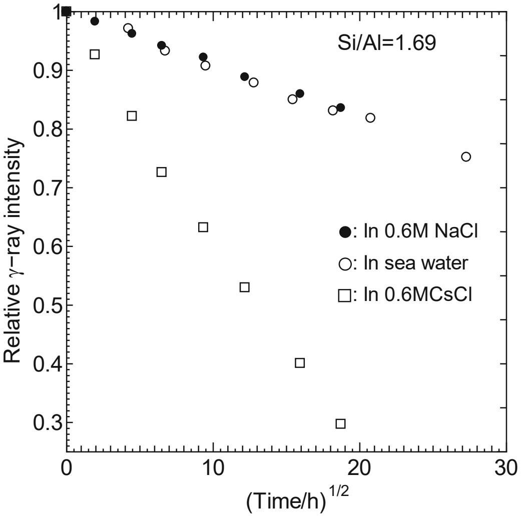

Fig. 3. Cs + ion leaching behaviors in saline solutions [12].

However, the geopolymer has an advantage in terms of leaching into water: 20% for cement solidification, compared to 2% for geopolymer solidification. Therefore, cement solidification requires more careful consideration for migration by rainwater and groundwater in disposal facilities. However, migration is a diffusion control phenomenon from the surface of the solidified body and can therefore be quantitatively assessed.

Both cannot retain Cs^+ ions to seawater, so care must be taken to ensure that salt water does not seep into the disposal facility. Since neither can retain Cs + ions relative to seawater, care must be taken to prevent saltwater penetration into the disposal facility, and in environments where the disposal facility is exposed to saltwater or dilute but groundwater penetration, the risk of exposure must be assessed by calculating the leaching rate in the safety assessment.

Table 4. Comparison of characteristics of cement and geopolymer solidifications.

Solidification	Mass reduction	Volume reduction*	Leaching to water	Feature
OPC	1/13,000	1/27,000	20% (2 months)	Easy to operate
Geopolymer	1/5,200	1/9,00	2% (2 weeks)	High viscosity during mixing

* Assumptions: relative weight of melting fly ash is 1.0 and Cs concentration is 3 ppm.

4 Conclusions

CSA, a calcined and decomposed product of spent adsorbent copper ferrocyanide, was solidified by OPC and geopolymer, and the leaching behavior of Cs^+ ions from the solidified product was investigated.

When CsCl was simply cement solidified, Cs^+ ions leached rapidly and in total in pure water due to the lack of cation exchange properties in the cement hydrates.

When CSA was cement solidified, 20% of Cs^+ ions were leached in 2 months, although no further release occurred, as Fe and Cu become hydroxides in the alkaline atmosphere and are likely to have cation-exchange properties.

When CSA was geopolymer solidified, the Cs^+ ion leaching rate into pure water was 2% in 2 weeks and no further leaching occurred because the geopolymer is an ion exchanger and has a high Cs^+ ion selective adsorption for Na^+ ions.

Although geopolymer solidification was superior in terms of these leaching properties, cement solidification was superior in terms of volume reduction, as the CSA addition rate had to be limited due to workability limitations during geopolymer preparation.

Both of the two solidification methods, being ion exchangers, limit Cs^+ ion leaching into pure water but do not prevent leaching into seawater. In another study, solidification as transition metal phosphate salts was proposed [5], and although the solidification process involves high temperatures and bubbling, Cs^+ ion leaching into both pure and seawater can be eliminated because the transition metal phosphate salts are non-water soluble.

Appendix: Cs^+ Ion Selectivity of Geopolymer Against Na^+ and Cs Leaching in Saline Water

Cs adsorption by geopolymer (GP-) is caused by ion-exchanging reaction as shown in Eq. (A-1).

$$\mathrm{GP-Na+Cs^+} \Longleftrightarrow \mathrm{GP-Cs+Na^+} \tag{A-1}$$

Geopolymers are cation exchangers, but their cation exchange capacity is determined by the amount of four-coordinated Al. The alkali metal ions fixed in the geopolymer are equal to the number of moles of Al.

Cs^+ ion selectivity of geopolymer against Na^+ at the equilibrium is defined as Eq. (A-2).

$$K_{\mathrm{Cs/Na}} = \frac{[\mathrm{GP-Cs}][\mathrm{Na^+}]}{[\mathrm{GP-Na}][\mathrm{Cs^+}]} \tag{A-2}$$

[] means ion concentration in mol/kg for solid or in mol/L for solution. GP-X means X ion containing geopolymer.

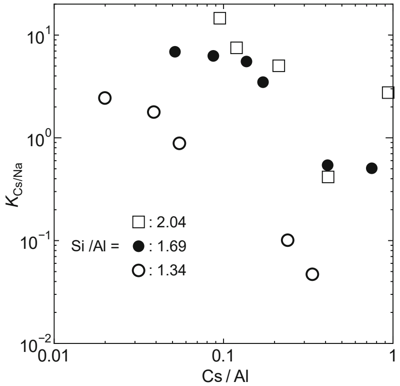

Fig. A-1. Cs^+ selectivity coefficient against Na^+ of geopolymer with various Si/Al ratios and at various Cs adsorption degree (Cs/Al) [13].

Three different geopolymers with different Si/Al molar ratios were synthesized from metakaolin and water glass. 27Al-NMR showed that all Al was four-coordinated. The three geopolymers were immersed in CsCl/NaCl mixtures of different concentrations and the KCs/Na was determined from the Cs + ion depletion from the liquid phase according to Eq. (A-2), as shown in Fig. A-1 KCs/Na was higher with a higher Si/Al molar ratio, i.e. a lower cation exchange capacity. However, it does not increase so much when Si/Al is increased from 1.69 to 2.04. KCs/Na also decreases with increasing Cs adsorption rate (Cs/Al). Both 23Na-NMR and 133Cs-NMR show a chemical shift change with increasing Cs adsorption, indicating that the ion exchange sites in the geopolymer have different Cs selectivities and are therefore filled by Cs in the order of sites with large Cs selectivities. The synthesized geopolymer is X-ray amorphous, but as type A zeolites with an Al/Si ratio of 1 and low Cs selectivity and phillipsite with an Al/Si ratio of 1.67 and high Cs selectivity are known, it is possible that local structures similar to both are mixed in the geopolymer.

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