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Ion Chromatographic Decontamination of ^{137}Cs -enriched Fly Ash Using Poly (vinyl alcohol)-bound Copper Ferrocyanide as Cs Adsorbent

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● **Summary** ● Poly(vinyl alcohol)-bound granulated copper ferrocyanide was found to be a Cs adsorbent suitable for ion chromatographic elimination of Cs from the water extract of ^{137}Cs -enriched fly ash that was generated by pyroprocessing decontamination of ^{137}Cs -contaminated solid wastes. The troublesome leakage of cyanide compounds during the chromatographic process was suppressed by the use of the organic binder. The adsorbent adsorbed 67 g/kg of Cs from the extract of the fly ash containing 10^5 times of Na^+ ions and 3×10^4 times of K^+ ions with respect to Cs^+ ions. Since ^{137}Cs -enriched fly ash contained 11 mg/kg of Cs and most of Cs was water-soluble, the ion chromatographic elimination reduced the weight of the radioactive waste by a factor of more than 5,000. ^{137}Cs -contaminated solid wastes before pyroprocessing decontamination generally contains a few ppm of Cs, so that the total weight reduction factor of more than 10,000 can be easily attained by pyroprocessing decontamination and subsequent ion chromatographic decontamination using poly(vinyl alcohol)-bound copper ferrocyanide as a Cs adsorbent.

Key Words: ^{137}Cs decontamination, volume reduction, ion chromatography, pyroprocessing, copper ferrocyanide, poly(vinyl alcohol), antioxidant

1. Introduction

The Fukushima Daiichi Nuclear Power Plant accident induced by the East Japan earthquake and tsunami of March 11, 2011 released approximately 1.5×10^{16} Bq of ^{137}Cs ¹⁻⁴⁾, which contaminated plants, soils, houses and so on around the reactor site. The decontamination work after the accident generated an enormous amount of ^{137}Cs -contaminated wastes such as ^{137}Cs -enriched municipal solid waste incineration fly ash and ^{137}Cs -contaminated top soil that have been collected and stored on temporary storage sites⁵⁾. To find land space wide enough for the final disposal of the contaminated wastes is now a social issue in Japan. Volume or weight reduction of the contaminated wastes is one of the feasible ways for solving the problem. We have studied the possibility of volume

reduction to less than one thousandth by the combination of pyroprocessing decontamination and Cs ion chromatography⁶⁾. Pyroprocessing decontamination is the distillation of stable Cs and ^{137}Cs which uses calcium chloride and calcium carbonate as Cs expeller and evaporation agent, and heat treatment over 1300°C with a melting furnace or a rotary kiln. Cs and the other alkali metals in soil and ash are generally captured in silicate and/or aluminosilicate as bound ions. The calcium ions react with these compounds at high temperature to expel alkali metal ions including ^{137}Cs . The alkali metal ions then react with chloride ions to convert to volatile alkali metal chlorides. The evaporated chlorides are cooled and completely trapped in bag filter systems to give ^{137}Cs -enriched fly ash. The decontaminated wastes can be used as construc-

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tion materials⁷⁻⁹). The decontamination factor (the ratio of initial specific radioactivity to final specific radioactivity resulting from a decontamination process) and the weight reduction factor (the weight ratio of the initial waste to final one to be disposed as radioactive waste) are estimated to be 26 and 13 for melt processing, and are more than 1000 and 20 for kiln processing, respectively¹⁰.

Although pyroprocessing is a powerful method of ¹³⁷Cs decontamination, the weight reduction factors are not enough for such a huge amount of contaminated waste. Moreover, since ¹³⁷Cs in the ash is highly water soluble, addition of Cs immobilizing agent is necessary for the safe disposal, which reduces the reduction factor. Further weight reduction can be attained by removing Cs from the ash with ion chromatography. Washing of ¹³⁷Cs-enriched fly ash with water causes the dissolution of stable Cs⁺ and ¹³⁷Cs⁺ ions into water together with the other soluble ions such as Na⁺ and K⁺. The insoluble residue is transferred to a furnace to convert to construction materials, if the decontamination is not enough for disposing the residue as nonradioactive waste. The aqueous solution containing ¹³⁷Cs is introduced into an ion exchange column packed with a highly selective Cs adsorbent, and the ¹³⁷Cs-free eluate is discharged as a nonradioactive solution.

The weight reduction factor for the ion chromatographic decontamination process is given by the content of Cs in a Cs adsorbent divided by the content of Cs in ¹³⁷Cs-enriched fly ash. The content of Cs in the adsorbent is in turn determined by the cation exchange capacity and selectivity coefficients of Cs⁺ ion adsorption against the other competing cations. The higher the cation exchange capacity and the selectivity coefficients are, the higher the content is. For attaining the high weight reduction factor, it is therefore necessary to use a Cs adsorbent with high cation exchange capacity and high selectivity coefficient of Cs adsorption.

Several cation exchangers have been studied and used for the selective adsorption of Cs from ¹³⁷Cs-contaminated aqueous solutions by ion chromatography. Vermiculite, a natural clay mineral with a layered structure, has been studied as a fixed bed material for the ion chromatography¹¹⁻¹⁵). Although vermiculite initially shows a high selectivity of Cs adsorption with respect to the other metal cations, the selectivity coefficient of the Cs adsorption steeply decreases with increasing the amount of adsorbed Cs^{12,15}). The Cs adsorption capacity

of vermiculite in the mixed solution of Cs⁺ and the other cations is therefore not high enough for the weight reduction of ¹³⁷Cs-enriched fly ash.

Crystalline silicotitanate or sodium titanate is another mineral adsorbent which can selectively adsorb Cs⁺ ions under the presence of the other cations¹⁶⁻²¹). Although the selectivity coefficient of Cs adsorption²¹) is not as high as those of transition metal ferrocyanates which will hereinafter be mentioned, it can be used under highly alkaline condition. Another advantage of silicotitanate is that the solidification-immobilization of adsorbed Cs is easily attained by heating the spent silicotitanate¹⁶), which makes the final disposal process very easy.

A Cs adsorbent for the decontamination of Cs-enriched fly ash is used under the condition that the concentration of interfering alkali metal cations is more than 10⁴ times higher than that of Cs⁺ ions, so that the Cs selectivity coefficient of more than 10⁴ is desirable for attaining the high volume reduction factor. Within known Cs adsorbents, only transition metal ferrocyanides (MeFeCN, where Me and FeCN denote transition metal and ferrocyanide, respectively) satisfy this requirement²²). Some of them were developed and used for removing radioactive cesium scattered by the Fukushima Daiichi Nuclear Accident²³⁻²⁶). Transition metal ferrocyanides are nonstoichiometric crystalline compounds with various metal to ferrocyanide molar ratio. Moreover, their Cs adsorption ability depends on the condition of the preparation. Slow growth or prolonged heating of the crystals increases the tolerance to alkali attack, though their Cs adsorption ability decreases²⁶). It is therefore difficult to uniquely determine the Cs adsorption ability of transition metal ferrocyanides. The slurry of transition metal ferrocyanide generated by rapid mixing of the solutions of ferrocyanide and transition metal ions generally shows the highest ability of Cs adsorption. Table 1 shows the Cs adsorption ability of MeFeCN slurry thus obtained. Within transition metal ferrocyanides examined, CoFeCN, NiFeCN and CuFeCN showed the selectivity coefficient of more than 10⁴. We used CuFeCN as a Cs adsorbent for the decontamination of ¹³⁷Cs-enriched fly ash because of its high cation exchange capacity, high selectivity coefficient of Cs adsorption, low toxicity, low cost, and no legal restriction on manufacturing and using a large amount of CuFeCN. According to the Japanese Chemical Substances Control Law and the Industrial Safety and Health Act, to manufacture and use a large amount of transition metal

Table 1. Cs adsorption ability of transition metal ferrocyanide slurry

Transition metal ion	CEC*	$K_{Cs/K}$ *
Mn ²⁺	0.83	3,900
Fe ³⁺	0.53	7,500
Co ²⁺	0.99	50,000
Ni ²⁺	1.04	48,000
Cu ²⁺	1.55	46,000
Zn ²⁺	1.77	2,900

* cation exchange capacity (CEC, equivalent unit) per unit ferrocyanide and the selectivity coefficient of Cs⁺ ion adsorption with respect to K⁺ ions ($K_{Cs/K}$) at the K⁺ to Cs⁺ molar ratio of around 30,000.

ferrocyanides other than FeFeCN and CuFeCN necessitate the detailed investigation on their toxicity. FeFeCN and CuFeCN necessitate no investigation because they are categorized as existing chemical substances.

Although MeFeCN have high ability of Cs adsorption, they are fine powders and not suitable for column application. Sorbent particles for column chromatography should be large and rigid enough for maintaining the smooth flow of an aqueous solution containing ¹³⁷Cs ions, and have high specific surface area for fast and efficient ion exchange reaction. MeFeCN can be used as Cs adsorbents only after granulated with binders or loaded on solids with large surface area²⁷. Several methods have been proposed for the granulation or loading of CuFeCN²⁸⁻³⁰. We prepared CuFeCN-loaded silica gel as a Cs adsorbent and showed that the combination of pyroprocessing and ion chromatographic decontaminations with CuFeCN-loaded silica gel was possible to reduce the weight of the final contaminated waste to less than 1/1,000 of the original ¹³⁷Cs-contaminated waste. However, the weight reduction factor of 1,000 may not be enough for treating the stored ¹³⁷Cs-contaminated wastes of more than one million tons. The ¹³⁷Cs-contaminated waste of 100 tons or 1 m×10 m×10 m in size would be very easy to be disposed, if the weight reduction factor of more than 10,000 is attained.

A factor preventing the increase of the weight reduction factor was the low cation exchange capacity of CuFeCN-loaded silica gel. Although CuFeCN-loaded silica gel showed a high Cs selectivity coefficient of more than 20,000, the exchange capacity was as low as 0.29 eq/kg. This is because of the low loading ratio of CuFeCN. After several attempt to increase the exchange capacity, we concluded that low exchange capacity was inevitable

as long as loading was used for preparing the granulated adsorbent. To prepare granulated CuFeCN with a small amount of binder is necessary for increasing the exchange capacity. In the present study, poly(vinyl alcohol) was used as a binder of CuFeCN to increase the exchange capacity to *ca.* 2 eq/kg. Another problem for CuFeCN-loaded silica gel was the continuous leakage of cyanide during the ion chromatographic process. Although the concentration of leaked cyanide was far less than the waste water standard of 1mg CN/dm³, to use a Cs adsorbent without leakage is desirable for treating large amount of ¹³⁷Cs-enriched fly ash. The leakage of cyanide was found to be suppressed by the use of poly(vinyl alcohol) as a binder for CuFeCN.

2. Materials and Methods

Three types of granulated CuFeCN were used for comparing the ability of Cs adsorption in an aqueous solution that was obtained by washing Cs-enriched fly ash with water. One was CuFeCN-loaded silica gel (CuFeCN-SiO₂) and the other two were granulated CuFeCN supplied by Kanto Chemical Co. Inc. The latter two, tentatively named MC-CuFeCN and Cica-CuFeCN, were prepared by using calcium alginate and poly(vinyl alcohol) as binders, respectively. The molar ratio of Cu to FeCN was 1.5 : 1 for both the CuFeCN.

¹³⁷Cs-enriched fly ash from a melt furnace was used for evaluating the Cs adsorption characteristics of these adsorbent. Table 2 shows the chemical composition of the ash determined by X-ray fluorescence and ICP-MS analyses. Table 3 shows the composition of water-soluble components determined by analyzing the water extract of the ash with ICP-MS, ICP-AES and ion chromatography. Comparison of Table 2 and 3 shows that most of Cs and K in the ash are water soluble. The ion chromatographic characteristics of the Cs adsorbents were measured by using aqueous solutions with chemical compositions similar to those in Table 3.

For measuring the cation exchange capacity (CEC, equivalent unit) of a granulated Cs adsorbent, 5 cm³ of the solution of 0.1 mol/dm³ (M) CsCl containing 1,000 Bq/cm³ of ¹³⁷CsCl was added to the weighed Cs adsorbent with CEC of *ca.* 0.2 meq in a centrifugal tube. The suspension was stirred with a tube rotator for two days, centrifuged at a speed of 4,000 rpm for 15 minutes, and then filtrated with a 0.2 μm pore syringe filter. Two cm³ of the filtrate was transferred in a plastic petri dish with inside

Table 2. Chemical composition of ¹³⁷Cs-enriched fly ash (% by mass)

Cs	Na ₂ O	K ₂ O	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	TiO ₂
0.0011	25.75	11.09	1.67	0.34	0.45	13.26	0.14	6.84	0.01
P ₂ O ₅	MnO	Cl	F	Cr ₂ O ₃	NiO	CuO	ZnO	Br	Rb ₂ O
0.07	0.02	29.45	0.155	0.009	0.006	0.78	3.721	0.321	0.014
SrO	Y ₂ O ₃	ZrO ₂	MoO ₃	Ag ₂ O	CdO	SnO ₂	Sb ₂ O ₃	TeO ₂	PbO
0.008	0	0	0.001	0.002	0.019	0.113	0.07	0.003	0.624

Table 3. Water-soluble components in ¹³⁷Cs-enriched fly ash

Ion	Cs ⁺	Na ⁺	K ⁺	Ca ²⁺	Sr ²⁺	Cl ⁻	SO ₄ ²⁻	OH ⁻
% by mass	0.00106	17.99	9.72	1.40	0.0035	30.0	4.67	0.43
mol/kg	0.00008	7.83	2.49	0.35	0.0004	8.46	0.73	0.25

dimensions of 34 mm diameter and 10 mm height. For preventing uneven distribution of the filtrate due to surface tension between the filtrate and the plastic bottom, a paper filter of 33 mm in diameter was placed on the bottom of the dish before the transfer. The petri dish with the filtrate was then transferred into a γ -ray measuring apparatus with a NaI crystal scintillator of 50.8 mm diameter and 50.8 mm height. The radioactivity of ¹³⁷Cs was determined under the secular equilibrium condition. The amount of adsorbed Cs was determined by comparing the intensities of γ -rays before and after the addition of the Cs adsorbent. Since the initial amount of Cs in the solution was more than two times larger than the CEC, the amount of adsorbed Cs was regarded as the CEC of the adsorbent.

The selectivity coefficient of Cs adsorption was determined by measuring the fraction of Cs that was adsorbed from the mixed solution of CsCl and the other ions in Table 3. The amount of an adsorbent added to the solution was adjusted in such a way that the CEC of the adsorbent was comparable to the molar amount of Cs⁺ ions in the solution. The molar ratio of Cs⁺ to K⁺ ions in the mixed solution was 1/10,000. The experimental procedure of determining the fraction of adsorbed Cs was the same as that used for measuring CEC. The selectivity coefficient of Cs⁺ adsorption against another ion M⁺, $K_{Cs/M}$, was determined by plotting the amount of adsorbed Cs⁺ ions [X-Cs] as a function of the concentration ratio of M⁺ to Cs⁺ ions in the solution, [M⁺]/[Cs⁺]. Since the molar amount of M⁺ ions was much larger than the CEC, [M⁺]/[Cs⁺] was obtained by using the relation of

$$[M^+]/[Cs^+] = [M^+]_0 / ([Cs^+]_0 - [X-Cs]) \quad \dots \dots \quad (1)$$

where [M⁺]₀ and [Cs⁺]₀ are the molar amounts of M⁺ and Cs⁺ ions in the solution before the addition of the adsorbent.

Ion exchange column chromatography was carried out using Cica-CuFeCN as a Cs adsorbent. The aqueous slurry of 1 g of Cica-CuFeCN was poured into an ion exchange column with an inner diameter of 9 mm. The height of the resultant bed was 32 mm so that the bulk density of the adsorbent was 0.5. Breakthrough curves for Cs adsorption were acquired by passing a solution containing 3.0 M NaCl, 0.9 M KCl, and 0.02 M CsCl with 500 Bq/cm³ of ¹³⁷Cs through the column at constant linear velocities of 14.6 cm/h to 37.2 cm/h. The radioactivity of Cs in the effluent was measured in the same manner as that for measuring CEC.

MeFeCN with Me ranging from Mn²⁺ to Zn²⁺ were prepared for measuring the oxidation resistance of MeFeCN. MeFeCN was synthesized by mixing 20 cm³ of 0.02 M K₄Fe(CN)₆ solution and an equivolume solution of 0.03 M transition metal chloride in a centrifugal tube while stirring vigorously. The precipitate of MeFeCN was centrifuged at a speed of 4000 rpm for 15 minutes. After removing the supernatant solution, the precipitate was mixed with distilled water and centrifuged again. This cycle was repeated until the supernatant solution did not show any optical absorption arising from Fe(CN)₆⁴⁻ and Fe(CN)₆³⁻ ions (between 290 nm to 600 nm). The optical absorption spectrum was measured with Shimadzu UV-1800 spectrophotometer. The precipitate was then mixed with 50 cm³ of distilled water in a beaker, and was left for one week. The mixture was then centrifuged, and the optical absorption spectrum of the supernatant solution was measured after filtrating with a 0.2 μ m

pore syringe filter. Transition metal ferricyanides (MeFe3CN) with Me ranging from Mn²⁺ to Zn²⁺ were prepared for identifying the dissolved species in the filtrate of MeFeCN. The method of MeFe3CN preparation was similar except for the method of washing the precipitate. Since most of MeFe3CN was slightly water soluble, except for FeFe3CN, the precipitate generated by mixing 0.02 mol/dm³ of K₃Fe(CN)₆ and 0.02 M of MeCl₂ was washed until the absorption spectrum of the supernatant solution was unchanged. The solubility of FeFe3CN prepared from 0.02 mol/dm³ of K₃Fe(CN)₆ and 0.02 M of FeCl₃ was higher than 0.02 M, so that the mixed solution was diluted five times with distilled water to measure the absorption spectrum.

3. Results and Discussion

(1) Cation exchange capacity and selectivity coefficient of Cs adsorption

The maximum amount of adsorbed Cs in an adsorbent under an ion chromatographic condition is determined by the cationic composition of an incoming aqueous solution and the selectivity coefficients of Cs⁺ adsorption against the other ions in the solution. The selectivity coefficient of Cs⁺ ion adsorption against ion with valence z_i is given by

$$K_{Cs/M_i} = \frac{[X-Cs]^{z_i} [M_i^{z_i+}]}{[Cs^+]^{z_i} [X_{z_i}-M_i]} \dots\dots\dots (2)$$

where [X-Cs] and [X_{z_i}-M_i] are the molar amounts of adsorbed Cs⁺ and M_i^{z_i+} ions, and [Cs⁺] and [M_i^{z_i+}] are the molar amounts of Cs⁺ and M_i^{z_i+} ions in the solution, respectively. Eq. (2) is rewritten as

$$[X_{z_i}-M_i] = \frac{[X-Cs]^{z_i} [M_i^{z_i+}]}{K_{Cs/M_i} [Cs^+]^{z_i}} \dots\dots\dots (3)$$

The CEC of the adsorbent is constant, so that

$$CEC = [X-Cs] + \sum_{i=1}^N z_i [X_{z_i}-M_i] = [X-Cs] \left(1 + \sum_{i=1}^N z_i \frac{[X-Cs]^{z_i-1} [M_i^{z_i+}]}{K_{Cs/M_i} [Cs^+]^{z_i}} \right) \dots\dots\dots (4)$$

where N denotes the number of the kind of cations other than Cs⁺. Eq. (4) indicates that [X-Cs] is comparable in magnitude to CEC only when the value of K_{Cs/M_i} is comparable in magnitude to the value of [M^{z_i+}]/[Cs⁺]^{z_i}. As shown in Table 3, the amount of divalent cations in the solution is much smaller than the total amount of monovalent cations, so that Eq. (4) is simplified as

Table 4. Cs adsorption characteristic of granulated copper ferrocyanide

Adsorbent	CuFeCN-SiO ₂	MC-CuFeCN	Cica-CuFeCN
CEC (eq/kg)	0.305	2.31	2.20
Adsorbed Cs (mol/kg)*	0.125	0.294	0.617
K _{Cs/K}	21,500	12,500	14,000
CEC at K _{Cs/K} (eq/kg)	0.30	1.0	1.94

* Equilibrium amount of adsorbed Cs in a mixed solution of CsCl and KCl with the molar ratio of 1/30,000.

$$[X-Cs] = \frac{CEC}{1 + ([Na^+]/[Cs^+])/K_{Cs/Na} + ([K^+]/[Cs^+])/K_{Cs/K} \dots\dots\dots (5)}$$

The values of [Na⁺]/[Cs⁺] and [K⁺]/[Cs⁺] are 100,000 and 30,000, respectively. The weight reduction factor for ¹³⁷Cs-enriched fly ash is proportional to the amount of adsorbed Cs, so that large CEC and selectivity coefficients of Cs adsorption are required for attaining the large reduction factor. Table 4 summarizes the CEC of three CuFeCN adsorbents. CuFeCN-SiO₂ showed the lowest CEC, because the main component in CuFeCN-SiO₂ was SiO₂. Since MC-CuFeCN and Cica-CuFeCN were granulated with a small amount of organic binders, their CEC were more than seven times larger than that of CuFeCN-SiO₂. To use MC-CuFeCN or Cica-CuFeCN in ion chromatographic elimination of Cs is therefore advantageous for attaining a large weight reduction factor.

Since the adsorption of a N⁺ ion from an aqueous solution into transition metal ferrocyanide accompanies the dehydration of the ion and the concomitant hydration of an desorbed ion M⁺, and vice versa, the selectivity coefficient of N⁺ ion adsorption against M⁺ ion is given by⁽²⁶⁾

$$K_{NM} = \exp\left(\frac{\Delta G_{D,M} - \Delta G_{D,N}}{RT}\right) \exp\left(\frac{\Delta G_{R,N} - \Delta G_{R,M}}{RT}\right) \dots\dots (6)$$

where ΔG_{D,M} and ΔG_{D,N} are dehydration free energies of hydrated M⁺ and N⁺ ions, and ΔG_{R,N} and ΔG_{R,M} are free energies for removing dehydrated N⁺ and M⁺ ions from the adsorption site, respectively. The dehydration energy of Cs⁺ ions (ΔG_{D,Cs} = 314.2 kJ/mol⁽³¹⁾) is the lowest among alkali and alkaline earth metal ions, so that Cs⁺ ions are selectively adsorbed by transition metal ferrocyanide even the free energy for removing the dehydrated ion from the adsorption site is lower than that of the other ions. The dehydration energy of K⁺ ions (ΔG_{D,K} = 359.8

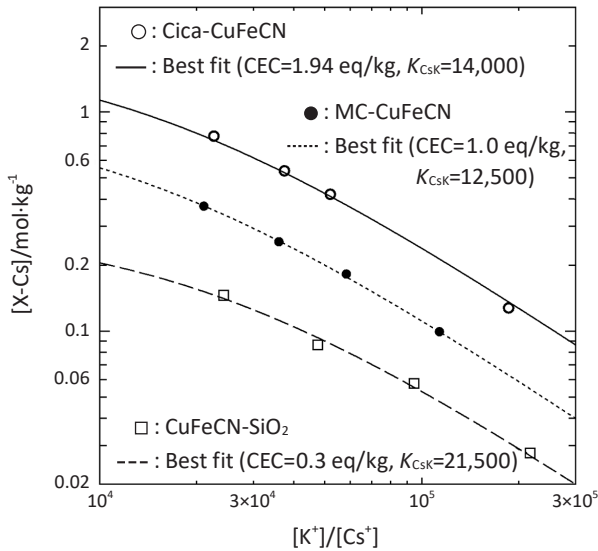


Fig. 1. Equilibrium amount of Cs⁺ ions [X-Cs] adsorbed in granulated copper ferrocyanides in solution composed of 0.9 M KCl and dilute CsCl as a function of concentration ratio of K⁺ to Cs⁺ ions [K⁺]/[Cs⁺]

kJ/mol) is the second lowest among cations in Table 3, so that K⁺ ions are the most effective suppressor for the adsorption of Cs⁺ ions. Fig. 1 compares the equilibrium amounts of adsorbed Cs in a mixed solution of 0.9 M KCl and dilute CsCl as a function of the equilibrium concentration ratio of K⁺ to Cs⁺ ions in the solution, [K⁺]/[Cs⁺]. The amount of the adsorbed Cs at [K⁺]/[Cs⁺] =

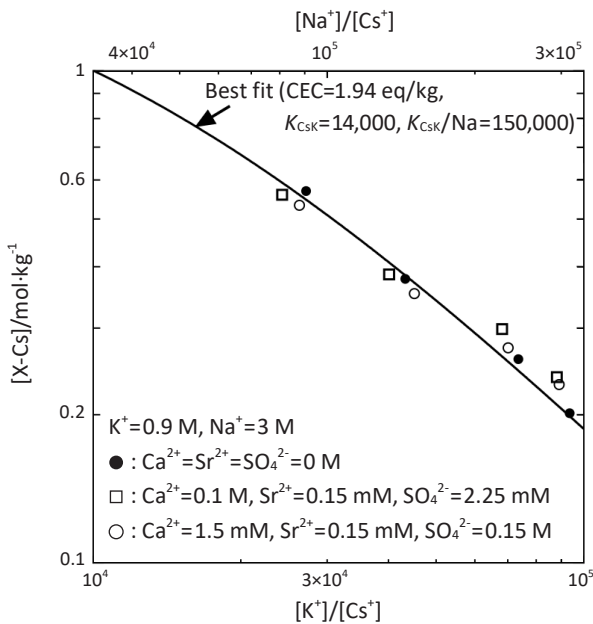


Fig. 2. Equilibrium amount of Cs⁺ ions [X-Cs] adsorbed in granulated copper ferrocyanide Cica-CuFeCN in solution containing dilute CsCl, 0.9 M KCl, 3.0 M NaCl and the other minor ions as a function of concentration ratio of K⁺ and Na⁺ to Cs⁺ ions, [K⁺]/[Cs⁺] and [Na⁺]/[Cs⁺], respectively

30,000, the concentration ratio of the ions in water extract of the ¹³⁷Cs-enriched fly ash, was the highest for Cica-CuFeCN, so that Cica-CuFeCN was the best Cs adsorbent among the granulated adsorbents examined. Fig. 2 also shows the values of $K_{Cs/K}$ obtained from the best fits of the experimental data. The best fits also give the values of CEC, which are different from those determined by the CEC measurements. This difference arises from the distribution of the value of $K_{Cs/K}$ in a Cs adsorbent. The $K_{Cs/K}$ of a part of Cs adsorption sites is much smaller than that of average $K_{Cs/K}$ determined by the best fit within the range of $[K^+]/[Cs^+] = 2 \times 10^4$ to 2×10^5 , so that the value of CEC determined by the best fit is always smaller than the entire CEC. Table 4 summarizes the Cs adsorption characteristics of CuFeCN-SiO₂, MC-CuFeCN and MC-CuFeCN thus determined. The difference of dehydration energies between K⁺ and Cs⁺ is 45.6 kJ/mol, so that the value of the first exponential term in the right side of Eq. (6) is 1.34×10^8 . Since the observed $K_{Cs/K}$ are much smaller than 1.34×10^8 , the values of the second exponential term are much less than unity. The ion adsorption affinity of the cation exchange site is much lower to a dehydrated Cs⁺ ion than to a dehydrated K⁺ ion.

Fig. 2 shows the effect of ions other than K⁺ on the equilibrium amount of Cs adsorbed by Cica-CuFeCN in the solution composed of dilute CsCl, 3 M NaCl, 0.9 M NaCl and other minor ions. Except for Cs⁺, Ca²⁺ and SO₄²⁻ ions, the molar ratios among each ion were adjusted to reproduce the ionic composition of the water extract of the ¹³⁷Cs-enriched fly ash. Since the amounts of Ca²⁺ and SO₄²⁻ in Table 3 exceeded the solubility limit of CaSO₄, the equilibrium amount of adsorbed Cs was measured in a solution in which the amount of Ca²⁺ or SO₄²⁻ was adjusted to reproduce the composition of the water extract. As shown in Fig. 2, ionic species other than K⁺ and Na⁺ did not affect the adsorption of Cs⁺ ions. The amount of adsorbed Cs was determined solely by the molar ratio of K⁺ and Na⁺ ions to Cs⁺ ions, [K⁺]/[Cs⁺] and [Na⁺]/[Cs⁺], respectively. The selectivity coefficient of Cs⁺ adsorption against Na⁺ ions was determined from the best fit of the experimental data to be $K_{Na/Cs} = 150,000$. The selectivity coefficient is much larger than $K_{K/Cs}$, because the dehydration energy of Na⁺ ions is much larger than that of K⁺ ions ($\Delta G_{D,Na} = 431.8$ kJ/mol). Substitution of CEC = 1.94 eq/kg, $K_{K/Cs} = 14,000$, $K_{Na/Cs} = 150,000$, [K⁺]/[Cs⁺] = 30,000 and [Na⁺]/[Cs⁺] = 100,000 into Eq. (5) gives the equilibrium amount of adsorbed Cs to be 0.509 mol/kg or 6.34%

by mass of Cica-CuFeCN. Since the ^{137}Cs -enriched fly ash contained 11 ppm of Cs, the weight reduction factor of 5,763 was attained by the ion chromatographic elimination of Cs. The pyroprocessing decontamination of ^{137}Cs -contaminated waste with a melt furnace concentrates Cs ten times in the fly ash, so that the overall weight reduction factor for the original ^{137}Cs -contaminated waste is as high as 57,630.

The equilibrium Cs adsorption capacity of 0.509 mol/kg is not much different from the Cs adsorption capacity of 0.617 mol/kg at $[\text{K}^+]/[\text{Cs}^+]=30,000$ and $[\text{Na}^+]/[\text{Cs}^+]=0$, which implies that the weight reduction factor is mainly determined by the molar ratio of K^+ to Cs^+ ions in a water extract. Since the molar ratio of K^+ to Cs^+ ions depends on the molar ratio in ^{137}Cs -enriched fly ash, which in turn depends on the chemical composition of ^{137}Cs -contaminated waste before pyroprocessing decontamination, the overall weight reduction factor by pyroprocessing and ion chromatographic decontaminations depends on the chemical composition of original ^{137}Cs -contaminated waste. Suppose ^{137}Cs -contaminated standard soil⁽³²⁾ containing 6 ppm Cs, 13,600 ppm K and 6,300 ppm Na is pyroprocessed to transfer all K and Cs into ^{137}Cs -enriched fly ash as water-soluble compounds, the amount of adsorbed Cs is estimated from $[\text{K}^+]/[\text{Cs}^+]=7,704$, $\text{CEC}=1.94$ eq/kg and $K_{\text{K/Cs}}=14,000$ to be 14.3% by mass of Cica-CuFeCN. The overall weight reduction factor is therefore 23,833. Similarly, pyroprocessing and ion chromatographic decontaminations of municipal solid waste incineration fly ash containing 4 ppm of Cs and 5% of K on average^(33,34) gives the overall weight reduction factor of 15,000. The weight reduction factor of more than 10,000 is therefore not difficult to be attained by pyroprocessing decontamination and subsequent ion chromatographic decontamination with Cica-CuFeCN as a Cs adsorbent.

(2) Ion chromatography

The ion chromatographic decontamination of ^{137}Cs -enriched fly ash is practical only if the decontamination process is fast enough for handling a large amount of the water extract. The processing rate depends on the volume flow velocity of a solution passing through an ion exchange column to eliminate dissolved Cs^+ ions. The volume flow velocity is in turn given by a product of the cross section of the column and the liner flow velocity of the solution, so that it is important to measure the break-

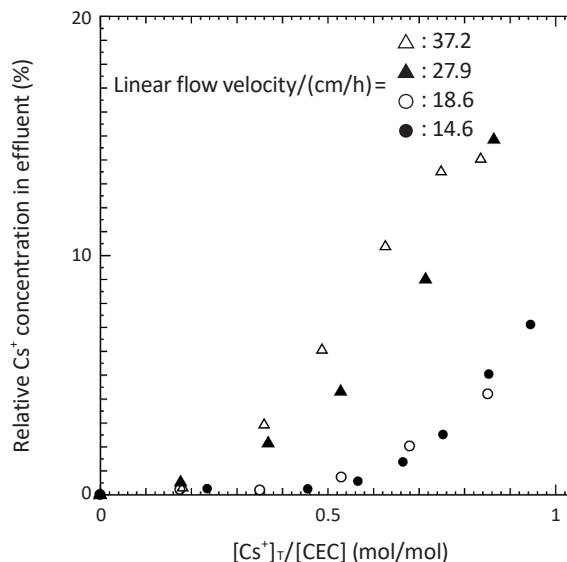


Fig. 3. Breakthrough curves in Cs^+ ion adsorption of adsorbent Cica-CuFeCN from solution containing 3 M NaCl, 0.9 M KCl and 0.02 M CsCl as a function of linear flow velocity. $[\text{Cs}^+]_T$ denotes the total molar amount of Cs^+ ions passing through Cica-CuFeCN with cation exchange capacity [CEC]

through curve for Cs adsorption as a function of the linear flow velocity. The Cs breakthrough curves were measured by passing a solution containing 3.0 M NaCl, 0.9 M KCl, and 0.02 M of CsCl through a cylindrical column packed with 1 g of Cica-CuFeCN (overall CEC=2.20 meq) at constant linear flow velocities of 14.6 cm/h to 37.2 cm/h. The cross section and the height of the packed Cs adsorbent were of 0.636 cm² and 3.2 cm, respectively. For shortening the time of the measurement, the relative concentration of Cs^+ ions in the solution was increased 667 times higher than that in the water extract of the ^{137}Cs -enriched fly ash. Fig. 3 compares the breakthrough curves under different linear flow velocities. The breakthrough curve was identical at the flow velocity of less than 18.6 cm/h, which implies that the flow was slow enough to attain complete ion exchange equilibrium between the adsorbent and the solution. The flow velocity of 18.6 cm/h was very close to the flow velocity of 18.2 cm/h for CuFeCN-SiO₂⁽⁶⁾, which implies that the ion exchange rate of Cica-CuFeCN was comparable with that of CuFeCN-SiO₂. The amount of adsorbed Cs at the breakthrough point was about 50% of the CEC of the adsorbent. The breakthrough point shifted to 20% at the flow velocity of 37.2 cm/h, because the solution passed through the adsorbent before attaining the ion exchange equilibrium. The ion chromatographic separation of specific ions from a solution is generally carried out under the condition that

the flow velocity is faster than the rate of ion exchange between aqueous and solid phases, which causes the shift of the breakthrough point toward 0%. Multi-column ion chromatography with longer flow path is therefore necessary for attaining the maximum weight reduction factor.

(3) Elution of cyanide

Ion chromatographic elimination of Cs with MeFeCN as a Cs adsorbent occasionally accompanies the elution of cyanide. Although ferrocyanide and ferricyanide ions are harmless, the elution of cyanide is generally undesirable. An additional apparatus for trapping the eluted cyanide is then necessary for using MeFeCN as a Cs adsorbent. To suppress the elution of cyanide is therefore desirable for using MeFeCN as a Cs adsorbent. Since the solubility of MeFeCN is low enough to detect no MeFeCN in the supernatant solution of MeFeCN by UV-visible absorption spectroscopy, the elution of cyanide implies the chemical decomposition of MeFeCN. Fig. 4 shows the UV-visible absorption spectra of filtrates obtained from suspensions of MeFeCN after standing for one week in air at ambient temperature. FeFeCN, CuFeCN and ZnFeCN with no binder showed strong absorptions assignable to ferricyanide ions $\text{Fe}(\text{CN})_6^{3-}$, which suggests that $\text{Fe}(\text{CN})_6^{4-}$ ions in MeFeCN were oxidized to generate water-soluble transition metal ferricyanides MeFe3CN. Although CuFeCN

without binder was oxidized to release CuFe3CN, Cica-CuFeCN with poly(vinyl alcohol) as a binder did not release CuFe3CN, which indicates that poly(vinyl alcohol) prevented the oxidation of CuFeCN. The formation of CuFe3CN from Cica-CuFeCN was not observed even after standing for two months. Ion chromatographic elimination of Cs with Cica-CuFeCN as an adsorbent does not necessitate the additional apparatus for the elimination of eluted cyanide and therefore simplifies the decontamination system.

Observation of no MeFe3CN in the supernatant solution implies either MeFeCN was not oxidized or the solubility of generated MeFe3CN was too low to be detected. MeFe3CN was therefore prepared to know the solubility of MeFe3CN. Fig. 5 shows the UV-visible absorption spectra of the saturated solutions of MeFe3CN. The solubility of MeFe3CN was approximately 1.1 mM for MnFe3CN, 0 mM for CoFe3CN, 1.25 mM for NiFe3CN, 0.41 mM for CuFe3CN and 0.50 mM for ZnFe3CN. Since MeFe3CN other than CoFe3CN was water soluble, formation of no MeFe3CN from MnFeCN, NiFeCN and Cica-CuFeCN implies that these MeFeCN were tolerant to the oxidation. The solubility of FeFe3CN was more than 20 mM and was too high to be observed with UV-visible absorption spectroscopy, so that the absorption spectrum of the diluted FeFe3CN solution is shown in Fig. 5. Too

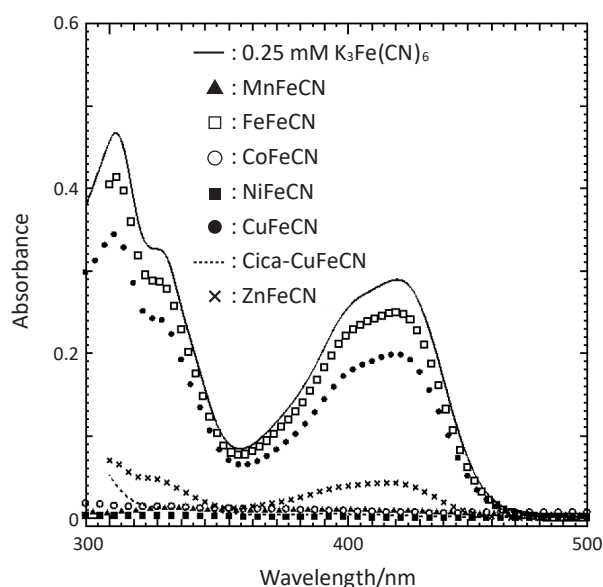


Fig. 4. UV-visible absorption spectra of filtrates obtained from suspensions of insoluble transition metal ferrocyanides MeFeCN, where Me indicates transition metal, after standing for one week in air at ambient temperature. The absorption spectrum of potassium ferricyanide $\text{K}_3\text{Fe}(\text{CN})_6$ is shown for comparison

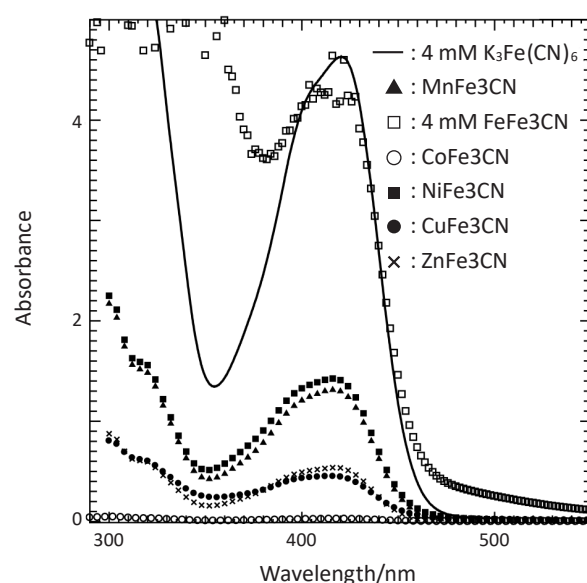
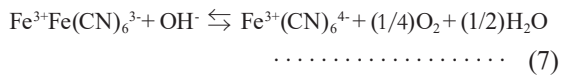


Fig. 5. UV-visible absorption spectra of saturated solutions of transition metal ferricyanides MeFe3CN, where Me denotes transition metals. The absorption spectrum of FeFe3CN was measured by diluting the solution. The absorption spectrum of potassium ferricyanide $\text{K}_3\text{Fe}(\text{CN})_6$ is shown for comparison

much dilution of the solution caused the conversion of FeFe_3CN to FeFeCN , which suggests that the following reaction took place in the solution.



4. Conclusion

It was revealed that poly(vinyl alcohol)-bound copper ferrocyanide was a Cs adsorbent suitable for ion chromatographic elimination of Cs from the water extract of ^{137}Cs -enriched fly ash that was generated by pyroprocessing decontamination of ^{137}Cs -contaminated solid wastes. The amount of adsorbed Cs from the wash solution of the fly ash was given by $1.94/\{([\text{K}^+]/[\text{Cs}^+])/1.4 \times 10^4 + ([\text{Na}^+]/[\text{Cs}^+])/15 \times 10^4\}$ mol/kg, where $[\text{K}^+]/[\text{Cs}^+]$ and $[\text{Na}^+]/[\text{Cs}^+]$ are molar ratio of K^+ and Na^+ ions to Cs^+ ions in the wash solution, and 1.4×10^4 and 15×10^4 are the selectivity coefficients of Cs^+ ion adsorption against K^+ and Na^+ ions, respectively. The values of $[\text{K}^+]/[\text{Cs}^+]$ and $[\text{Na}^+]/[\text{Cs}^+]$ in the present study were 3×10^4 and 10^5 , respectively, so that the amount of adsorbed Cs was 0.509 mol/kg or 6.34% by mass of CuFeCN . Since ^{137}Cs -contaminated waste before the pyroprocessing decontamination contained about 1.1 ppm of Cs, the overall weight reduction factor for the original contaminated waste was as high as 57,000. To attain the weight reduction factor of more than 10,000 is thus not difficult by the combination of pyroprocessing and ion chromatographic decontaminations. The weight reduction factor of 10,000 implies that one million tons of ^{137}Cs -contaminated waste is possible to be concentrated to 100 tons of radioactive waste that can be stored in one room. To use poly(vinyl alcohol) as a binder for CuFeCN granulation is advantageous not only for increasing the weight reduction factor but also for suppressing the troublesome cyanide leakage during the ion chromatographic process. Poly(vinyl alcohol) suppresses the oxidation of CuFeCN during the ion chromatographic process to prevent the formation of soluble CuFe_3CN , which makes it unnecessary to attach an additional equipment to the ion chromatographic system for trapping cyanide.

Since the spent adsorbent is fine grains containing a significant amount of ^{137}Cs , the stabilization of the adsorbent is necessary for the final disposal. Studies on the solidification-immobilization of Cs by using geopolymer³⁵⁾ or by making copper phosphate glass³⁶⁾ are under progress.

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報 文 (英語論文)

ポリビニルアルコールで造粒したフェロシアン化銅をCs吸着剤に用いた イオンクロマトグラフィーによる¹³⁷Cs濃縮飛灰の除染

市川 恒樹*, 山田 一夫, 岩井 良太, 金澤幸広

【要 約】 ポリビニルアルコールで造粒したフェロシアン化銅は、¹³⁷Cs汚染廃棄物を高温乾式除染して生じる¹³⁷Cs濃縮飛灰から、水洗および水洗液のイオンクロマトグラフィーによってCsを濃縮除去するのに適したCs吸着剤であることが分かった。イオンクロマトグラフィーの際に問題となるフェロシアン化銅からのシアン化物流出はポリビニルアルコールによって防止できた。水洗液からの飽和Cs吸着量は吸着剤1 kg当たり67 gに達した。¹³⁷Cs濃縮飛灰のCs含有量は11 ppmなので、放射性廃棄物としての減量係数は5千以上となった。元の¹³⁷Cs汚染廃棄物を基準にすると、高温乾式除染とイオンクロマトグラフィーによる減量係数は5万以上となった。¹³⁷Cs汚染廃棄物は通常数ppmのCsを含有するので、これの高温乾式処理とイオンクロマトグラフィー処理によって、最終放射性廃棄物の量を1万分の1以下にできることがわかった。

【キーワード】 ¹³⁷Cs除染、減容、イオンクロマトグラフィー、高温乾式処理、フェロシアン化銅、ポリビニルアルコール、抗酸化剤

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