Radioactive Cesium Removal from Ash-Washing Solution with High pH and High K⁺-Concentration Using Potassium Zinc Hexacyanoferrate

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ABSTRACT

The effectiveness of $K_2Zn_3[Fe(CN)_6]_2$ (KZnHCF) for the radioactive Cesium (R-Cs) decontamination from wood ash extract is studied. Because the ash-washing solution is of high pH and high K^+ -concentration, adsorbent with high pH tolerance and selectivity for Cs^+ over coexistent K^+ is required. For this purpose, we evaluated the effectiveness of KZnHCF, Prussian blue (PB), and zeolite. With 10,000 mg/L of K^+ -concentration, the distribution coefficient, K_d of KZnHCF, PB, and zeolite were 719, 4400, and 210 mL/g, respectively. Regarding the pH-effect, KZnHCF shows good Cs adsorption even at pH 12, in contrary, PB is effective only at pH < 9. Actually for the decontamination of ash washed solution with 212 Bq/L of total R-Cs activity and 1,000 mL/g of solution to adsorbent ratio, only KZnHCF could reduce the radioactivity to less than 60 Bq/L, the standard of ^{134}Cs for public waters in Japan. In addition, a theory for predicting the R-Cs adsorption ratio based on the initial concentration of K^+ , by using the equilibrium coefficient $K_{eq} = 71.6$ for the ion-exchange between K^+ and Cs^+ in KZnHCF is proposed.

1. INTRODUCTION

Decontamination of radioactive cesium (R-Cs), majority of which are ^{134}Cs and ^{137}Cs , has become one of the serious environmental issues after the nuclear power plant accidents such as Chernobyl¹ and Fukushima.²⁻⁵ The contaminated materials can be grouped into three main classes: waters such as river and underground water; minerals such as soil and mud; and combustibles such as wood, plant and domestic waste. Among them, the contaminated solid materials, the minerals and the combustibles, make huge mass of estimated about $15\text{-}28 \times 10^6 \text{ m}^3$.⁶ For the safe disposal of such wastes, volume reduction has become necessary.

A study conducted by the International Atomic Energy Agency (IAEA) for the treatment of contaminated combustibles has suggested incineration as one of the suitable methods.⁷ They provided more than 10 treatment methods including incineration and chemical processes. For the solid wastes, incineration is advantageous with respect to the byproduct volume, against the chemical processes such as acid digestion and molten salt oxidation.

The volume of combustible contaminated materials can be reduced by incineration. Actually it is reported that the mass of the ash obtained by the incineration of R-Cs contaminated wood bark and garbage is only about 1-5 % of the original mass.⁸ However, in connection with the safe storage of such ash, two important issues must be addressed. The first is the enriched concentration of R-Cs. And the second is the ease of washing out the R-Cs with water. Especially fly ash collected at the filters of exhaust gas meets the condition of high R-Cs concentration and ease of washing with water.⁹

Most promising method for the safe storage of contaminated ash in the waste sites is extraction of washable R-Cs with water followed by enrichment of the later using Cs selective

adsorbent. By doing so, the chances of gradual leaching of R-Cs from the storage site can be sharply reduced. In addition, overall radioactivity in the solid waste to be stored can be decrease leading to the ease of handling and depending upon the residual R-Cs permanent landfilling of it can even be considered .⁸⁻¹⁰

In general, the ash extract is basic because of the alkali metal oxide and hydroxide.^{11,12} In order for avoiding the need of the neutralization prior to passing the extract to the adsorbent, an adsorbent with high Cs selectivity as well as stability in alkaline solution is required. Various types of the Cs adsorbents were studied for decontamination, for example, selective cation adsorbent such as crown ether^{13,14}, natural or synthesized minerals such as zeolite^{15,16}, and metal hexacyanoferrate (MHCF) such as Prussian blue(PB)^{17,18}. Among these, based on the cost factor, zeolite or MHCF prepared with common metals are preferred.

MHCF prepared using common metals, Iron(PB), copper(CuHCF), and zinc(ZnHCF) hexacyanoferrate were previously studied for the adsorption of Cs.¹⁹⁻²¹ Results show that one of the important physical properties of the adsorbent is the particle size. Generally, the adsorbent with larger particle size is preferred for the ease of solid-liquid separation. Also, the larger particles can be precipitated by coagulation techniques. Immobilization onto some substrate also becomes easy for larger particles²². However, the material with smaller particle size has the advantage of faster adsorption rate. Therefore, the particle size should be chosen appropriately as per the purpose.

In this paper, we discussed the R-Cs adsorption properties of potassium zinc hexacyanoferrate (KZnHCF)²³⁻²⁷, a type of ZnHCF. Different from other commonly used analogues, CuHCF and PB, the primary particle sizes of which is less than 30 nm^{28,29}, particle size of ZnHCF is more

than 200 nm.³⁰ This material is cheaper for being prepared using an abundant metal salt, and more importantly, offers high working pH, stable in alkaline solution, and high Cs-selectivity. Using real extraction solution of wood ash, we demonstrated that KZnHCF can decrease the R-Cs radioactivity below the national effluent standard only by the addition at the rate of 1,000 mg/L. In contrast, zeolite and PB were found to be unsuitable for decontamination from alkaline extract, for the lack of Cs-selectivity and instability in high-pH solution, respectively. Additionally, a relationship for the prediction of the Cs-adsorption performance of KZnHCF based on the amount of adsorbent and the K⁺ concentration in the solution is proposed.

2. MATERIALS AND METHODS

2.1 Synthesis and Characterization

KZnHCF was synthesized in batch as follows:

For this, 24 mL of 0.5 mol/L ZnCl₂ (pure grade, Wako Pure Chemical Industries, Ltd.) solution adjusted to pH 2.0 with HCl and 16 mL of 0.5 mol/L K₄[Fe(CN)₆] (pure grade, Wako Pure Chemical Industries, Ltd.) solution were mixed in 50 mL centrifuge tube. After mixing well by hand shaking, it was centrifuged. The product was washed at least five times with pure water for removing the byproducts. The product named as KZnHCF was dried at 60 °C using evaporator.

The chemical composition of KZnHCF was evaluated by total dissolution using sample preparation system (MW, Multiwave 3000, Perkin Elmer, Inc.) followed by measurement using

Inductively Coupled Plasma - Mass Spectrometry (ICP-MS: NexIon300D, Perkin Elmer, Inc.) or Microwave Plasma Atomic Emission Spectroscopy (MP-AES: 4100 MP-AES, Agilent Technologies, Inc.). The water content was evaluated with Thermogravimetry - Differential Temperature Analysis (TG-DTA: Thermo Plus EVO 2, Rigaku Corp.). Crystal structure of KZnHCF was evaluated by using powder X-ray diffractometer (XRD: D2 phaser, Bruker Corp.), using Cu-K α X-ray ($\lambda = 0.154$ nm, 30 kV, 10 mA), with the Rietveld analysis software (TOPAS, Bruker Corp.). The size and shape of KZnHCF particles were determined using Scanning Electron Microscope (SEM: S-4800, Hitachi High-technologies Corp.).

For comparison, Cs-adsorption properties of PB and zeolite were also studied. For PB, PB60 (hereafter PB) purchased from Kanto Chemical Co., Inc., spray-dried powder of Fe₄[Fe(CN)₆]₃ with the grain size of 60 μ m was used. For zeolite, mordenite mined in Ayashi, Sendai, Miyagi prefecture, Japan, purchased from Shin-Tohoku Chemical Industry Co., Ltd., was used.

2.2 Cs-Adsorption from pseudo-washing solution

The Cs adsorption performance of KZnHCF was evaluated with batch-shaking method using the solution of non-radioactive ¹³³Cs (NR-Cs) and the extract solution containing R-Cs prepared by washing contaminated ash.

For the NR-Cs test, 10 mg of KZnHCF was added to 10 mL aqueous solution of CsNO₃. After shaking the tubes using multi shaker (SI-300C, AZ-ONE) at 600 rpm at 25°C, the supernatant was separated by centrifuging. The concentration of Cs and K in the supernatant was evaluated

by ICP-MS and MP-AES, respectively. The Cs adsorption rate (A) and distribution coefficient (K_d) are calculated according to eq (2) and (3), respectively.

$$A = \frac{[A-Cs]_{eq}m}{[Cs^+]_iV} = \frac{[Cs^+]_i - [Cs^+]_{eq}}{[Cs^+]_i} \quad (2)$$

$$K_d = \frac{[A-Cs]_{eq}}{[Cs^+]_{eq}} = \frac{[Cs^+]_i - [Cs^+]_{eq}}{[Cs^+]_{eq}} \times \frac{V}{m} \quad (3)$$

Here, $[A-Cs]$, $[Cs]$, m , and V represent concentration of Cs in adsorbent, concentration of Cs in solution, mass of the adsorbent, and volume of the solution, respectively. The subscript ‘eq’ and ‘i’ indicate the equilibrium and the initial states, respectively.

Effect of pH on the Cs-adsorption performance was investigated in batch taking 1 mg/L solution of NR-Cs at pH 5-13 and mixing for 12 hours. Solutions of weakly basic ranges were prepared with pH-buffers; for pH 8.6, Tris (hydroxymethyl)aminomethane and HCl ; for pH 9.4 and 10.1 H_2CO_3 and $NaHCO_3$. Solutions of pH 11, 11.5, 12.5, 13, and 13.5 were adjusted with NaOH. To investigate the effect of the co-existing ion, adsorption tests were performed taking 1 mg/L NR-Cs solution with 1– 10,000 mg/L K^+ ion.

2.3 Cs-Adsorption from real washing solution

For knowing the R-Cs adsorption performance of KZnHCF, R-Cs contaminated bottom ash was obtained by the incineration of broadleaf trees. The R-Cs contaminated broadleaf trees, such as cherry blossom, oak, Japanese apricot etc. were logged in Fukushima area, Japan. After incineration with a biomass boiler (Gasifire, Arc Inc.), the bottom ash was collected from the

incinerator. The ash was characterized with power X-ray diffractometer (X'pert, PANalytical) using Cu-K α X-ray ($\lambda = 0.154$ nm) and X-ray Fluorescence Analysis (ZSX prius, Rigaku Corp.).

For preparing the ash extract solution, 110 g of the ash and 1100 g of ultra-pure water were mixed and stirred for 1 hour in a flask at 80°C. After stirring, the mixture was filtered through 0.45 μ m membrane and diluted 5 times with ultra-pure water. The radioactivity of R-Cs in extracted solution was measured with NaI scintillator (LB2045, BERTHOLD TECHNOLOGIES GmbH & Co. KG). The other elements in the solution were measured with ICP-MS and MP-AES.

3 RESULT AND DISCUSSION

3.1 Characterization

Chemical composition of the KZnHCF was determined as $K_{1.98}Zn_{2.94}[Fe(CN)_6]_{2.00} \cdot 6.2H_2O$. The XRD pattern of KZnHCF shown in Figure S1 indicates that the space group of the crystal structure is R-3c. The composition and XRD pattern are consistent with the previous report^{31,32}. From the Rietveld analysis, the structural parameters are obtained as, $a = 12.5345(15)$, $c = 32.1020(39)$, $\alpha = \beta = 90^\circ$, and $\gamma = 120^\circ$. SEM image shown in Figure S2 reveals that the KZnHCF particles have mainly flat rectangular shape and their size ranges between 200 – 700 nm.

3.2 Adsorption Performance with NR-Cs solution

At first, taking the NR-Cs solution, Cs adsorption performance of KZnHCF in the presence of K^+ ion was compared with those of PB and zeolite.

The Cs adsorption rates A and the distribution coefficients K_d of the adsorbents are shown in Figure 1. In case of 10 mg/L of K^+ -concentration, $K_d(KZnHCF)$ was more than 10^5 mL/g, highest of all. Even with K^+ -concentration, of as high as 10,000 mg/L, $K_d(KZnHCF)$ was about 719 mL/g, a rather higher value, although it was 4,400 mg/L for PB. The result reveals the highest adsorption ratio of KZnHCF in the absence of K^+ , and the best Cs-selectivity of PB in the presence of K^+ ion. In contrary, zeolite was poor with or without K^+ , a less suitable material for the decontamination of ash-washing solution with high K^+ -concentration.

3.3 Analysis of the effect of coexisting K^+

The effect of coexisting K^+ can be well analyzed with the theory of chemical equilibrium³³. The result implies that the realistic decontamination system can be designed, once the equilibrium constant (K_{eq}) is determined by the laboratory test. When the Cs-adsorption is driven by the ion exchange between K^+ and Cs^+ , the reaction formula and K_{eq} can respectively be described as,

$$K_{eq} = \frac{[A-Cs]_{eq}[K^+]_{eq}}{[A-K]_{eq}[Cs^+]_{eq}} \quad (5).$$

$[A-K]$ and $[K^+]$ represent the concentration of K^+ in adsorbent and solution, respectively. Equilibrium constant of KZnHCF is evaluated between 43 and 79 as shown in Figure 2(a), which is almost consistent with the previous report²³.

Because the present work is aimed for the removal of Cs from ash-washing solution, the system, both the solution and the adsorbent, contains much higher concentration of K^+ than Cs^+ ; with $[K^+]_i/[Cs^+]_i = 7 \times 10^5$ in the ash-washing solution used. In addition, when the amount of adsorbent used for the decontamination is sufficient, the amounts of K^+ and Cs^+ ions satisfy the relationship: $([A-K]_i \times m) / ([Cs^+]_i \times V) \gg 1$.

Then $[A-K]$ and $[K^+]$ can be approximated to be almost constant during adsorption, *i.e.*

$$[A-K]_{eq} = [A-K]_i, \quad (6)$$

$$[K^+]_{eq} = [K^+]_i. \quad (7)$$

In this case, the distribution coefficient K_d defined in Eq (3) can be expressed as,

$$K_d = K_{eq}[A - K]_i \times \frac{1}{[K^+]_i}. \quad (8)$$

Taking the logarithm,

$$\log(K_d) = -\log([K^+]_i) + \log(K_{eq}[A-K]_i). \quad (9)$$

From Eq (9), it becomes possible to obtain the information about the adsorption mechanism. When the ion-exchange between K^+ and Cs^+ occurs, the slope of $\log(K_d)$ versus $\log[K^+]_i$ becomes -1 . Actually, as observed in Figure 1(b), $\log(K_d)$ is the linear function of $\log[K^+]$ for all the adsorbents. The slopes for KZnHCF and Zeolite are -0.991 and -0.864 , respectively, indicating K^+ - Cs^+ ion exchange as the mechanism during the Cs -adsorption. Different from it, the slope of PB is -0.456 , which implies rather smaller role of K^+ - Cs^+ ion exchange in comparison with the other adsorbents. Ion exchange with H^+

is also important in Cs-adsorption onto PB as reported previously¹⁶. This additional role of H^+ is the reason of higher selectivity of PB against the coexistent K^+ .

With the same approximation, the adsorption rate A defined in Eq (2) is redefined into the function only as,

$$A = \frac{[A-Cs]_{eq}}{[Cs^+]_i} \times 100 = \frac{[A-Cs]_{eq} \times m \times 100}{[A-Cs]_{eq} \times m + [Cs^+]_{eq} \times V} = \frac{100}{1 + \frac{[Cs^+]_{eq} \times V}{[A-Cs]_{eq} \times m}} = \frac{100}{1 + \frac{1}{K_{eq}} \frac{[K^+]_i \times V}{[A-K]_i \times m}} \quad (10).$$

With Eqs (9) and (10), K_d and A are well fitted as functions of $[K^+]_i$ and $[A-K]_i$, as shown in Figure 2(b) with $K_{eq} = 71.6$. This outcome indicates that the adsorption rate can be predicted only with the given values of $[K^+]_i$, $[A-K]_i$, V and m , once the value of K_{eq} is known.

3.4 Effect of pH on Cs-adsorption

KZnHCF shows better Cs adsorption at basic to alkaline pH, as shown in Figure 3. In general, the metal hexacyanoferrate decomposes into metal hydroxide and alkali metal hexacyanoferrate in high pH solution. The decomposition pH varies with the type of metal used. While decomposition of PB starts at around pH 10, KZnHCF was stable up to pH 12 making it a material offering wider working pH.

3.5 R-Cs removal from the ash-washing water

Cs-adsorption taking realistic R-Cs contaminated ash-washing solution was carried out mainly for two purposes. One is to reveal the applicability of KZnHCF for the R-Cs removal from the extract solution without neutralization. Another purpose is to examine the applicability of the theory postulated in the previous section for predicting the adsorption mechanism. Before testing the theory, the ash and the extract were characterized. From the investigation with the XRD and XRF (Figure S1 and S2), the bottom ash with the radioactivity of 28,000 Bq/kg is found to consist of mainly Ca, K, Al, and Si in carbonate, hydroxide and oxide forms. By washing with water, 42% of R-Cs was extracted to the solution phase. The concentration of R-Cs in the extract solution was 212 ± 23 Bq/kg.

The time dependence of R-Cs adsorption ratio by the adsorbents along with the prediction value for the equilibrium state is shown in Figure 4. For the first purpose, it is clearly found that KZnHCF shows the best performance among the adsorbents, i.e. 86.6 % of adsorption ratio in 60 minutes of mixing. In contrast, PB shows a decreasing trend with time. This decrease was caused by the gradual decomposition of PB due to high solution pH. Among the adsorbents, only KZnHCF could reduce the R-Cs concentration of the to below 60 Bq/L, the standard of ^{134}Cs for environmental water in Japan.

For the second purpose of examining the proposed theory, two conditions, $[\text{K}^+]/[\text{Cs}^+]_i \gg 1$, and $M_A(\text{K})/M_S(\text{Cs}) \gg 1$ were checked and were satisfied. For the adsorption test

with $[K^+]_i$ and $[Cs^+]_i$ in the ash-washing solution, as shown in Table 1, resulting $[K^+]_i/[Cs^+]_i$ was estimated as 7.1×10^5 . The value of $M_A(K)/M_S(Cs)$ was calculated as 8.8×10^4 . It is found that the observed R-Cs adsorption rate is asymptotic to the predicted value for both KZnHCF and Zeolite, reinforcing the applicability of the proposed theory.

CONCLUSION

This study demonstrates the effectiveness of KZnHCF for Cs adsorption from the ash-washed solution without neutralization. Therefore KZnHCF can be used for the in-line uptake of R-Cs during the decontamination of ash by washing as well as for the decontamination of R-Cs in leachate released from the disposal site. In addition, a theory for the postulation of the adsorption performance of KZnHCF is proposed which uses the initial concentration of K^+ , adsorbent/solution ratio, and the equilibrium constant $K_{eq} = 71.6$. Results demonstrate that the theory can indeed be of great application for postulating, for example, the adsorbent feed, while designing the decontamination schemes.

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Table 1. Concentration of each alkali metal cations in the ash-washing solution.

element	Concentration (mg/L)
Na	30.6 ± 0.6
K	775 ± 2.7
Rb	1.27 ± 0.10
^{133}Cs	0.0037 ± 0.0001

Figure 1. (a) Cs-adsorption rate A and (b) distribution coefficient K_d of KZnHCF, PB, and Zeolite as a function of K^+ concentration in the solution in equilibrium, $[K^+]_{eq}$.

Figure 2. (a) Equilibrium constant, K_{eq} , with different initial K^+ concentrations. (b) Adsorption rate A and distribution coefficient K_d of KZnHCF at different K^+ ion concentrations with the concentration at $C_s=1$ mL/g, and $V/m = 1,000$ mL/g. The solid and dotted lines represent the calculated values at $K_{eq} = 71.6$.

Figure 3. pH-dependence of the Cs adsorption rate of KZnHCF and that of PB

Figure 4. Adsorption rate of R-Cs versus shaking time in ash-washing solution.