Development of Composite Adsorbents for LLW Treatment and Their Adsorption Properties for Cs and Sr – 13127

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ABSTRACT

In this study, the composite adsorbents (KCoFC-NM (NM: natural mordenite), KCoFC-SG (SG: porous silica gel), AMP-SG and so on) were prepared by impregnation-precipitation methods. As for the distribution properties, the largest $K_d,Cs$ value of $3.8 \times 10^4$ cm$^3$/g was obtained for KCoFC-SG (Davi.) composite. KCoFC-SG (NH, MB5D) and T-KCFC also had relatively large $K_d,Cs$ values above $1.0 \times 10^4$ cm$^3$/g. The uptake rate of Cs$^+$ ions was examined by batch method. KCoFC-SG (NH, MB5D) and AMP-SG (Davi.) had relatively large uptake rate of Cs$^+$, and the uptake attained equilibrium within 1 h. The maximum uptake capacity of Cs$^+$ ions was estimated to be above 0.5 mmol/g for KCoFC-NM and KCoFC-CP composites. KCoFC-X composite had a relatively large uptake capacity of Cs$^+$ ions (0.23 mmol/g > 0.17 mmol/g (T-KCFC)) and this composite also had a selectivity towards Sr$^{2+}$ ions; KCoFC-X is effective adsorbent for both Cs$^+$ and Sr$^{2+}$ ions. The largest value of $K_d,Sr$ was estimated to be 218 cm$^3$/g for titanic acid-PAN. Titanic acid-PAN had the largest uptake rate of Sr$^{2+}$ ions, and the uptake attained equilibrium within 8 h. Adsorbability of other nuclides was further examined by batch method. All adsorbents had adsorbability for Rb$^+$ and RuNO$_3^+$ ions. KCoFC-SG (NH), KCoFC-CP and T-KCFC had higher selectivity towards Cs$^+$ than other adsorbents; these adsorbents had adsorbability to Cs$^+$ ions even in the presence of Ba$^{2+}$, Ca$^{2+}$ and Mg$^{2+}$ ions. The separation factor of $K_d,Sr/K_d,Ba$ for titanic acid-PAN was about 1, indicating that the $K_d,Sr$ for titanic acid-PAN tends to decrease with Ba$^{2+}$ concentration. As for the breakthrough properties, the largest 5 % breakthrough and 5 % breakthrough capacity of Cs$^+$ ions were estimated to be 47.1 cm$^3$ and 0.07 mmol/g for the column of KCoFC-SG (NH), respectively. The order of 5 % breakthrough capacity of Cs$^+$ is as follows; KCoFC-SG (NH) > KCoFC-NM > KCoFC-SG (Q-10) > T-KCFC > KCoFC-X > KCoFC-CP. From the results of batch and column experiments, the composite adsorbent of KCoFC-SG (NH) was effective for the uptake of Cs$^+$ ions, and KCoFC-X composite was useful for the uptake of both Cs$^+$ and Sr$^{2+}$ ions.
The estimation of irradiation stability and the uptake properties using the actual wastes are further essential for the practical operation.

**INTRODUCTION**

The radioactive waste treatment by co-precipitation, ultrafiltration and adsorption methods (Fig. 1) are planned in LWTF for the low level liquid wastes generated from Tokai-reprocessing facility. The target liquid wastes consist of highly concentrated sodium nitrate containing low level radioactive Cs and Sr. In the operation process, the chemical durability and irradiation stability are important characteristics; conventional adsorbents have some problems in the maximum uptake capacity, irradiation resistance and cost efficiency.

![Diagram of adsorption system in LWTF](Image)

Insoluble ferrocyanides (cobalt-ferrocyanides (KCoFC), nickel-ferrocyanides (KNiFC)) and heteropolyacid salts (ammonium molybdophosphate (AMP), ammonium tungstophosphate (AWP)) (Fig. 2) are well known to have strong adsorbability for Cs\(^+\) ions, however, these adsorbents are fine crystalline powders and cannot be used directly to the column separation process[1, 2, 3, etc.]. Considering the stable granulation of these adsorbents, novel composite adsorbents using impregnation-precipitation methods have been developed by Tohoku University and JAEA; these fine crystals are loaded in the macropores of porous silica gels and zeolites. The present study deals with the preparation of composite adsorbents, their characterization, and adsorption properties of Cs\(^+\), Sr\(^{2+}\) and other metal ions in the presence of highly concentrated sodium nitrate (5 M NaNO\(_3\)) by batch and column methods.
EXPERIMENTAL

Materials

The composite adsorbents (KCoFC-NM (NM: natural mordenite), KCoFC-SG (SG: porous silica gel), AMP-SG and so on) were prepared by impregnation-precipitation methods (Figs. 3 and 4). The characteristics are illustrated in Fig. 2. For example, the preparation procedure of KCoFC-NM is as follows. Two grams of NM was dried (3 h, 200°C), and then impregnated with 1 M Co(NO₃)₂ under reduced pressure (3 h). The impregnated NM was washed and dried (3 h, 90°C). The dried NM was then impregnated with 0.5 M K₄[Fe(CN)₆] under reduced pressure (3 h) and dried (3 h, 90°C). The KCoFC fine crystals were loaded in the macropores of natural mordenite matrices, as the following synthetic reaction formula;

\[
K_4[Fe(CN)_6] + Co(NO_3)_2 = K_2[CoFe(CN)_6] + 2 KNO_3 \quad (Eq. 1)
\]

Synthetic reaction formula for AMP is as follows.

\[
H_3Mo_{12}O_{40}P + 3 NH_4NO_3 \rightarrow (NH_4)_3PMo_{12}O_{40} + 3 HNO_3 \quad (Eq. 2)
\]

Fig. 2. Schematic view of the structure of composites, zeolite matrices and ion exchangers.
Uptake Experiment of Cs and Sr by Batch Methods

The distribution and uptake rate of Cs\(^+\) and Sr\(^{2+}\) ions for zeolites and composites was estimated by batch method. An aqueous solution (5 cm\(^3\)) containing 0.1 ppm Cs\(^+\) and Sr\(^{2+}\) ions, 400 g/L NaNO\(_3\) and 4.3 g/L Na\(_2\)SO\(_4\) was contacted with 50 mg of zeolites and composites at 25±1°C up to 1 d, which was found to be sufficient for attaining equilibrium. The concentrations of Cs\(^+\) and Sr\(^{2+}\) ions were estimated by isotope tracer technique (NaI(Tl) scintillation counter (Chiyoda Technol, JDC-715)). The uptake percentage (\(R\), %) of metal ions removed from the solution and the distribution coefficient (\(K_d\), cm\(^3\)/g) are defined as:

\[
R = \frac{(C_i - C_f)}{C_i} \times 100 \quad \text{(%),} \quad \text{(Eq. 3)}
\]

\[
K_d = \frac{(C_i - C_f)}{C_i} \times \frac{V}{m} \quad \text{(cm\(^3\)/g),} \quad \text{(Eq. 4)}
\]

where \(C_i\), \(C_f\) (cpm/cm\(^3\)) are the radioactivity counts of nuclides at initial and at equilibrium, respectively; \(m\) (g) the weight of solid sample; \(V\) (cm\(^3\)) the volume of aqueous phase.
Determination of Maximum Adsorption Amount of Cs and Sr

The maximum uptake amount ($Q_{\text{max}}$, mmol/g) of Cs$^+$ and Sr$^{2+}$ ions for composite adsorbents was estimated by batch method. An aqueous solution (5 cm$^3$) containing 0.1 mol/L Cs$^+$ or Sr$^{2+}$ ions was contacted with 50 mg of composite adsorbents at 25±1°C up to 1 d. The adsorption amount of Cs$^+$ and Sr$^{2+}$ ions were estimated by isotope tracer technique as follows.

$$Q_{\text{max}} = C_{f}/C_{i} \times C_{s} \times V/m \times 1000 \quad \text{(mmol/g), \quad (Eq. 5)}$$

where $C_{i}$, $C_{f}$ (cpm) are the radioactivity counts of solution at initial and adsorbent at equilibrium, respectively; $C_{s}$ (mol/L) is the concentration of metal ions at initial; $V$ (L) the volume of aqueous phase; $m$ (g) is the weight of adsorbent.

Uptake Experiment for Other Nuclides by Batch Methods

The distribution of Ba$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, Rb$^+$ and RuNO$^{3+}$ ions for composites was estimated by batch method. An aqueous solution (5 cm$^3$) containing 10 ppm Ba$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, Rb$^+$ or RuNO$^{3+}$ ions was contacted with 50 mg of composites at 25±1°C up to 1 d. The concentrations of metal ions were measured by atomic absorption spectrometer (AAS, Jarrell AA890) and ICP-AES (SII, SPS 7800).

Column Test

The composite adsorbents (1 g) were densely packed into a glass column (5 mmΦ×200 mm long). Figure 5 shows the apparatus for the column experiments. A feed solution ([Cs$^+$] = 200 ppm, [NaNO$_3$] = 400 g/L, [Na$_2$SO$_4$] = 4.3 g/L) was passed through the column at a flow rate of 0.16 ~ 0.22 cm$^3$/min. Every 2.0 cm$^3$ of the effluent was then taken by a fraction collector. A breakthrough curve was obtained by plotting the
breakthrough ratio \((C/C_0)\) against the effluent volume, where \(C_0\) and \(C\) (ppm) are the concentrations of the initial solution and the effluent, respectively. The concentrations of \(Cs^+\) were estimated by isotope tracer technique.

RESULTS AND DISCUSSION

Characterization

Figure 6 shows the digital microscope images of typical composite adsorbents. The practical sizes of composites were estimated to be \(300 \sim 1,300 \mu m\). Figures 7 and 8 show typical X-ray diffraction (XRD) patterns of KCoFC-SG (Q-10) and AMP-SG (NH MB-10), respectively. In the XRD patterns of KCoFC-SG (Q-10) and AMP-SG (NH MB-10), the loading of KCoFC and AMP crystals in the amorphous SG matrices were confirmed.

Fig. 6. Digital microscope images of composite adsorbents.
Distribution and Uptake Rate of Cs$^+$

As for the distribution properties, the largest $K_{d,Cs}$ value of $3.8 \times 10^4$ cm$^3$/g was obtained for KCoFC-SG (Davi.) composite (Fig. 9). KCoFC-SG (NH, MB5D) and T-KCFC also had relatively large $K_{d,Cs}$ values above $1.0 \times 10^4$ cm$^3$/g. Most of composites had $K_{d,Cs}$ values nearly equal to that of T-KCFC. The uptake rate of Cs$^+$ ions was examined by batch method (Fig. 10). KCoFC-SG (NH, MB5D) and AMP-SG (Davi) had relatively large uptake rate of Cs$^+$, and the uptake attained equilibrium within 1 h. The order of uptake rate of Cs$^+$ ions is as
Maximum Adsorption Capacity of Cs$^+$

**Figure 11** shows the maximum uptake capacity of Cs$^+$ ions. The maximum uptake capacity of Cs$^+$ ions was estimated to be above 0.5 mmol/g for KCoFC-NM and KCoFC-CP composites. It is well known that natural mordenite and natural clinoptilolite also has adsorbability for Cs$^+$; both KCoFC and matrices part (NM and CP) in these two composites have adsorbability for Cs$^+$. Thus, these large maximum uptake capacities of Cs$^+$ were obtained for KCoFC-NM and KCoFC-CP composites. KCoFC-X composite had a relatively large uptake capacity of Cs$^+$ ions (0.23 mmol/g > 0.17 mmol/g (T-KCFC)) and this composite also had a selectivity towards Sr$^{2+}$ ions; KCoFC-X is an effective adsorbent for both Cs$^+$ and Sr$^{2+}$ ions.
Radiation Stability

As for the radiation stability test, KCoFC-NM composites were irradiated by 60Co-γ ray up to 2.75 MGy (Japan Atomic Energy Agency), and the uptake ability of Cs⁺ for the irradiated specimens was estimated by the batch method. Irradiation of composites was conducted in the solution containing 400 g/L NaNO₃ and 4.3 g/L Na₂SO₄. Irradiation conditions were summarized in Table I. Relatively large $K_{d,Cs}$ values above $10^3$ cm³/g and large maximum adsorption amount of Cs above 0.7 mmol/g are obtained even after irradiation at 2.75 MGy as shown in Figs. 12 and 13.

<table>
<thead>
<tr>
<th>Adsorbed Dose [MGy]</th>
<th>KN3</th>
<th>KN1</th>
<th>KN4</th>
<th>KN5</th>
<th>KN8</th>
<th>KN10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Immersion (Irradiation) Time [h]</td>
<td>104</td>
<td>268</td>
<td>506</td>
<td>887</td>
<td>268</td>
<td>887</td>
</tr>
</tbody>
</table>

Fig. 12. Distribution properties of Cs for irradiated specimens. [Cs⁺]: 0.1 ppm; [Sr²⁺]: 0.1 ppm; [NaNO₃]: 400 g/L; [Na₂SO₄]: 4.3 g/L; $V/m$: 100cm³/g; shaking time: 1 d; 25°C.

Fig. 13. Maximum uptake capacity of Cs for irradiated specimens. [Cs⁺]: 0.1 mol/L; [NaNO₃]: 400 g/L; [Na₂SO₄]: 4.3 g/L; $V/m$: 100cm³/g; shaking time: 1 d; 25°C.

Uptake of Sr

Figures 14(a)–(c) show the adsorption properties of Sr²⁺. The largest value of $K_{d,Sr}$ was estimated to be 218 cm³/g for titanic acid-PAN. The $K_{d,Sr}$ value for KCoFC-A (2.3 cm³/g) was smaller than that for A-type zeolite (15 cm³/g). This result indicates the possibility that a part of macropores of A-type zeolite were filled with KCoFC crystals. The relatively small $K_{d,Sr}$ value for KCoFC-CP composite was obtained, indicating the poor adsorbability of Sr²⁺ ions for this composite. Titanic acid-PAN had the largest uptake rate of Sr²⁺ ions, and the uptake attained
equilibrium within 8 h. The maximum uptake capacity of Sr$^{2+}$ ions was estimated to be above 0.2 mmol/g for KCoFC-X composite. The order of maximum uptake capacity of Sr$^{2+}$ ions is as follows.

KCoFC-X > KCoFC-A > titanic acid-PAN

Adsorbability of Other Metal Ions

Adsorbability of other metal ions was further examined by batch method (Fig. 15). All adsorbents had adsorbability for Rb$^+$ and RuNO$_3^+$ ions. KCoFC-SG (NH), KCoFC-CP and T-KCFC had higher selectivity to Cs$^+$ than other adsorbents; these adsorbents had adsorbability to Cs$^+$ ions even in the presence of Ba$^{2+}$, Ca$^{2+}$ and Mg$^{2+}$ ions. The separation factor of $K_{d, Sr}/K_{d, Ba}$ for titanic
acid-PAN was about 1, indicating that the $K_{d,\text{Sr}}$ of titanic acid-PAN tends to decrease in the presence of $\text{Ba}^{2+}$.

**Breakthrough Properties**

As for the breakthrough properties, the largest 5% breakpoint and 5% breakthrough capacity of $\text{Cs}^+$ ions were estimated to be 47.1 cm$^3$ and 0.07 mmol/g for the column of KCoFC-SG (NH), respectively (Figs. 16 and 17). The order of 5% breakthrough capacity of $\text{Cs}^+$ is as follows.

KCoFC-SG (NH) > KCoFC-NM > KCoFC-SG(Q-10) > T-KCFC > KCoFC-X > KCoFC-CP.

From the results of batch and column experiments, the composite adsorbent of KCoFC-SG (NH) was effective for the uptake of $\text{Cs}^+$ ions, and KCoFC-X composite was useful for the uptake of both $\text{Cs}^+$ and $\text{Sr}^{2+}$ ions (Table II).
CONCLUSIONS

The composite adsorbents (KCoFC-NM (NM: natural mordenite), KCoFC-SG (SG: porous silica gel), AMP-SG and so on) were prepared by impregnation-precipitation methods. The uptake behaviours of Cs$^+$ and Sr$^{2+}$ in the presence of about 5 mol/L NaNO$_3$ were examined using composites. As for the distribution properties, the largest $K_{d,\text{Cs}}$ value of $3.8 \times 10^4$ cm$^3$/g was obtained for KCoFC-SG (Davi.) composite. KCoFC-SG (NH, MB5D) and T-KCFC also had relatively large $K_{d,\text{Cs}}$ values above $1.0 \times 10^4$ cm$^3$/g. KCoFC-SG (NH, MB5D) and AMP-SG (Davi.) had relatively large uptake rate of Cs$^+$, and the uptake attained equilibrium within 1 h. The maximum uptake capacity of Cs$^+$ ions was estimated to be above 0.5 mmol/g for KCoFC-NM and KCoFC-CP composites. KCoFC-X composite had a relatively large uptake capacity of Cs$^+$ ions ($0.23$ mmol/g > $0.17$ mmol/g (T-KCFC)) and this composite also had a selectivity towards Sr$^{2+}$ ions; KCoFC-X is effective adsorbent for both Cs$^+$ and Sr$^{2+}$ ions. Adsorbability to other metal ions was further examined by batch method. KCoFC-SG (NH), KCoFC-CP and T-KCFC had higher selectivity to Cs$^+$ compared to other adsorbents; these adsorbents had adsorbability to Cs$^+$ ions even in the presence of Ba$^{2+}$, Ca$^{2+}$ and Mg$^{2+}$ ions. As for the breakthrough properties, the largest 5% breakpoint and 5% breakthrough capacity of Cs$^+$ ions were estimated to be 47.1 cm$^3$ and 0.07 mmol/g for the column of KCoFC-SG (NH), respectively. From the results of batch and column experiments, the composite adsorbent of KCoFC-SG (NH) was effective for the uptake of Cs$^+$ ions, and KCoFC-X composite was useful.
for the uptake of both Cs$^+$ and Sr$^{2+}$ ions. The estimation of irradiation stability and the uptake properties using the actual wastes are further essential for the practical operation.

REFERENCES


