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 3.8×10^4 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 1.0×10^4 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 % 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. 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.
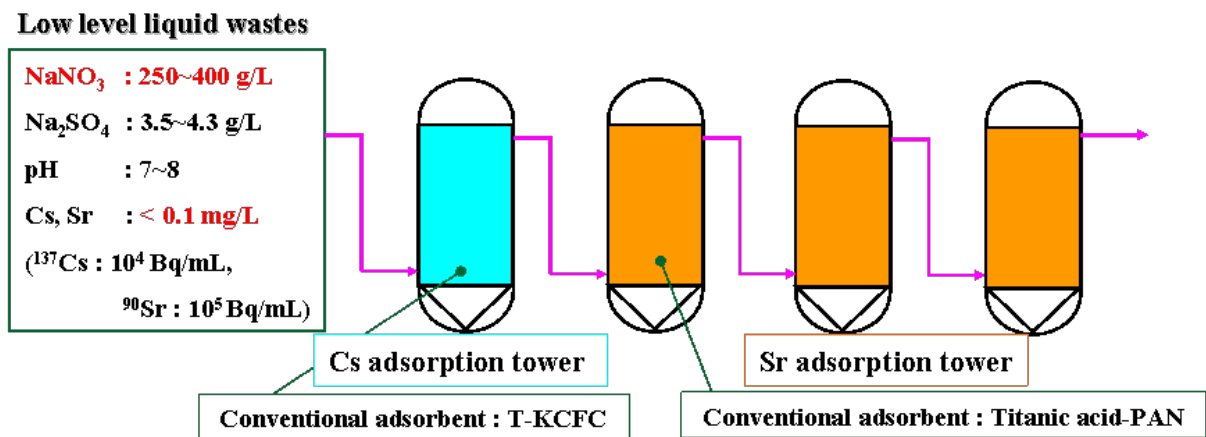
Fig. 1. Adsorption system in LWTF (Tokai-reprocessing facility).

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.
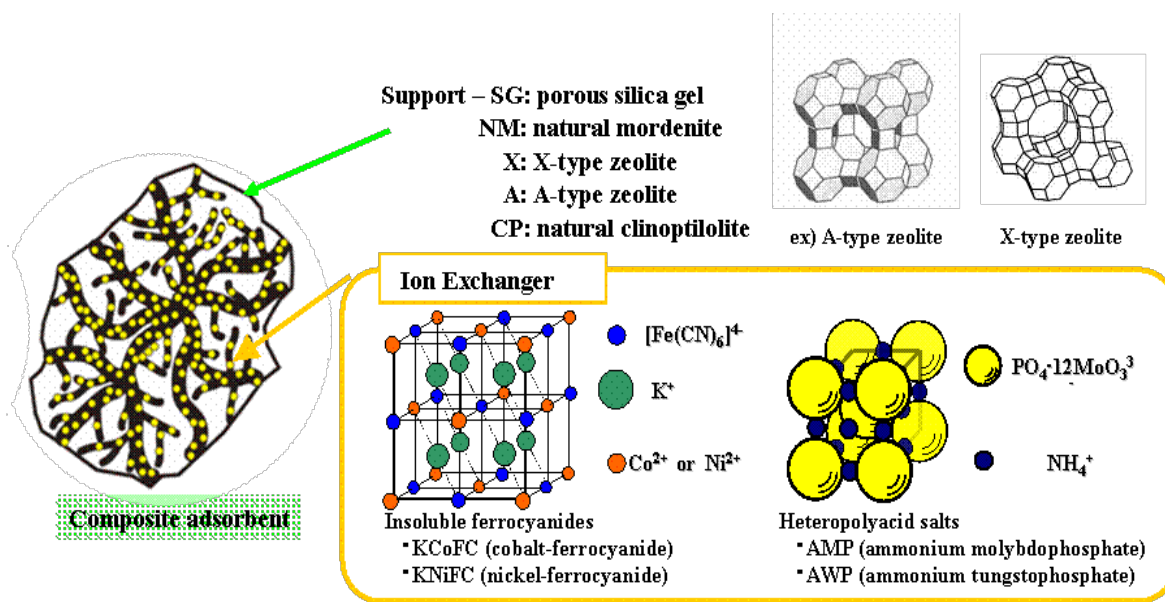
Fig. 2. Schematic view of the structure of composites, zeolite matrices and ion exchangers.
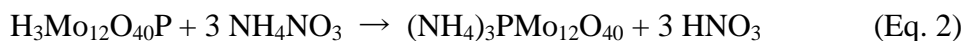
EXPERIMENTAL

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 $Co(NO_3)_2$ 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 $K_4[Fe(CN)_6]$ 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;

$$K_4[Fe(CN)_6] + Co(NO_3)_2 = K_2[CoFe(CN)_6] + 2\ KNO_3 \qquad \text{(Eq. 1)}$$

Synthetic reaction formula for AMP is as follows.

$$H_3Mo_{12}O_{40}P + 3\ NH_4NO_3 \ \rightarrow \ (NH_4)_3PMo_{12}O_{40} + 3\ HNO_3 \qquad \text{(Eq. 2)}$$

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┌ ─ ─ ─ ─ ┌────────────────────┐ ─ ─ ─ ─ ┐      ┌ ─ ─ ─ ─ ┌────────────────────┐ ─ ─ ─ ─ ┐
          │ KCoFC-loaded supports │                          │ AMP-loaded supports │
  ┌──────────────────────────┐                        ┌──────────────────────┐
  │ Supports, 2 g ex) NM, SG │                        │   Supports, 2 g      │
  └──────────────────────────┘                        └──────────────────────┘
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KCoFC-loaded supports

Supports, 2 g ex) NM, SG

Drying (zeolites at 200°C, SG at 110°C)

1 M Co(NO₃)₂ solution, 20 ml

Impregnation (under reduced pressure)

Drying (at 90°C for 3 h)

0.5 M K₄[Fe(CN)₆] solution, 20ml

Impregnation (under reduced pressure)

Drying (at 90°C for 3 h)

KCoFC-loaded supports

AMP-loaded supports

Supports, 2 g

Drying (at 110°C)

0.2 M PMA solution, 20 ml

Impregnation (under reduced pressure)

Freezed Drying

0.5 M NH₄NO₆ solution, 20ml

Impregnation (under reduced pressure)

Freezed Drying

AMP-SG

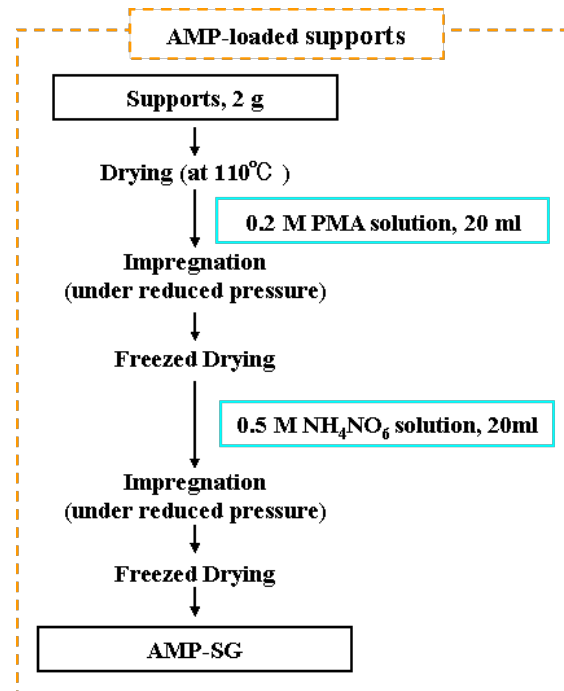Fig. 3. Preparation procedure of KCoFC-loaded adsorbents.

Fig. 4. Preparation procedure of AMP-loaded adsorbents.

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_2SO_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 :

$$R = (C_i - C_f) / C_i \times 100 \quad (\%), \quad\quad\quad (\text{Eq. 3})$$

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

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_{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.

$$Q_{max} = C_f/C_i \times C_s \times V/m \times 1000 \quad (mmol/g), \qquad (Eq.\ 5)$$

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_2SO_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
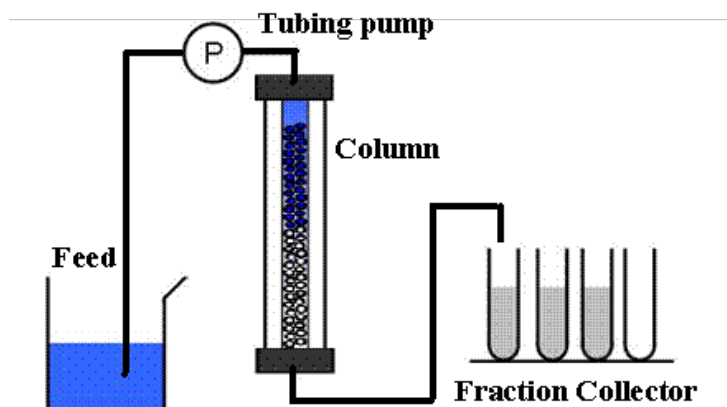

Fig. 5. Apparatus for the column experiments.

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 ~ 1,300 μm. **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.
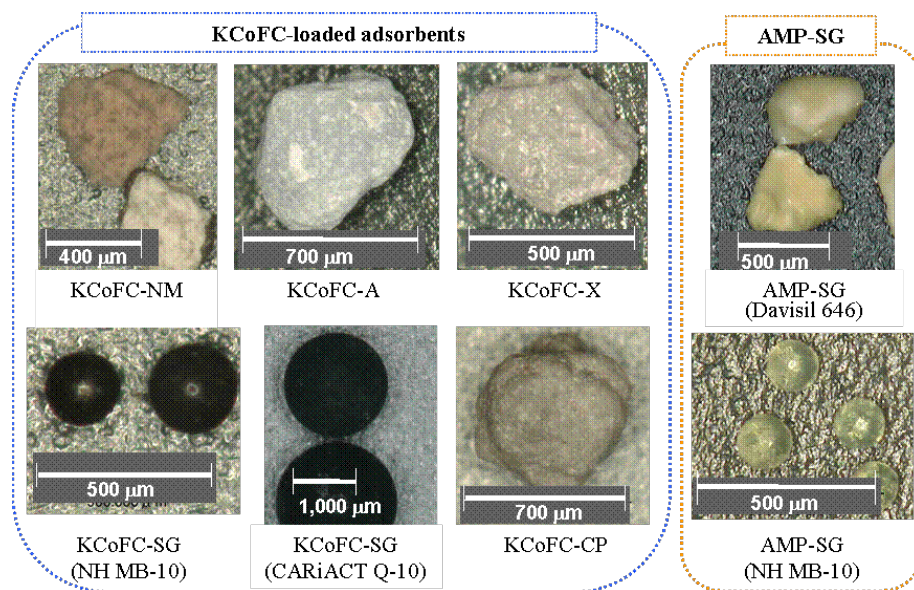

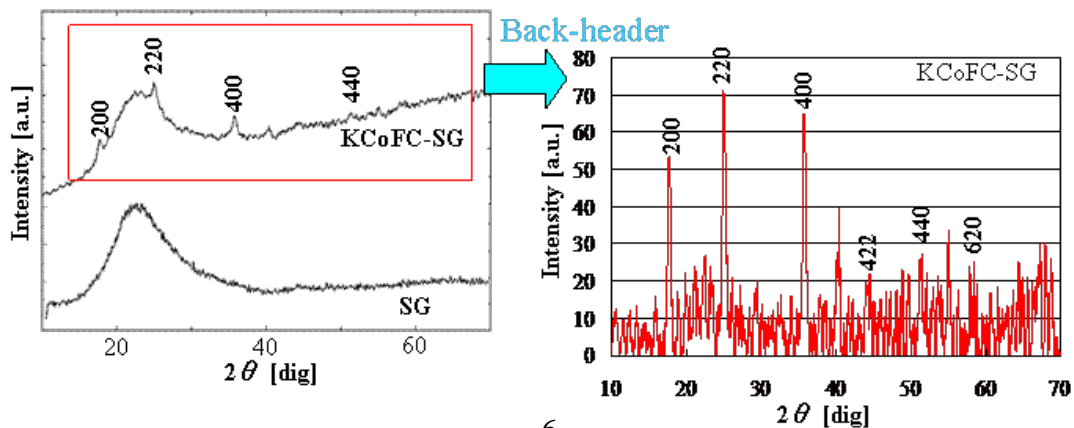Fig. 6. Digital microscope images of composite adsorbents.

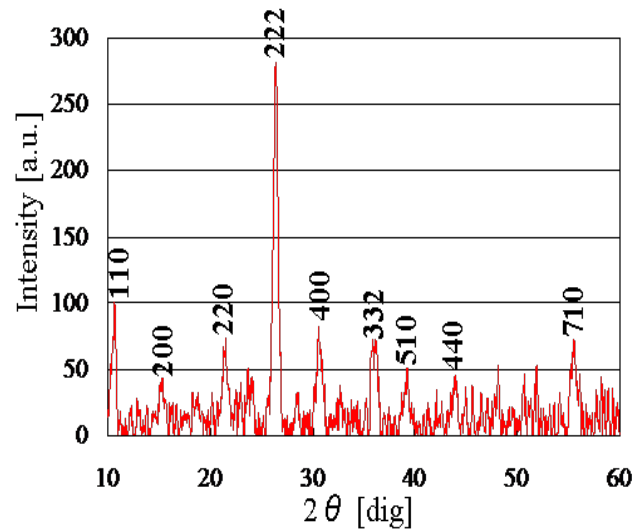Fig. 7. X-ray diffraction patterns of KCoFC-SG (Q-10).

Fig. 8. X-ray diffraction pattern of AMP-SG (NH)

Distribution and Uptake Rate of Cs^{+}

As for the distribution properties, the largest $K_{d,Cs}$ value of 3.8×10^4 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 1.0×10^4 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
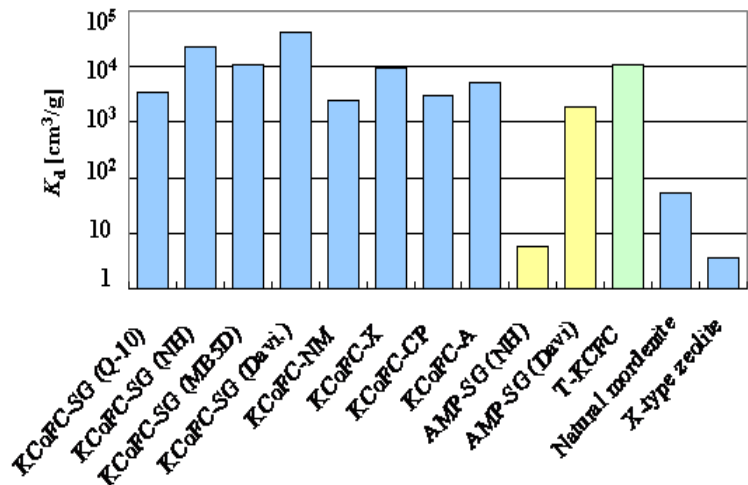

Fig. 9. Distribution property of Cs.
[Cs^{+}]: 0.1 ppm; [Sr^{2+}]: 0.1 ppm; [NaNO$_3$]: 400 g/L; [Na$_2$SO$_4$]: 4.3 g/L; V/m: 100 cm^3/g; shaking time: 1 d; 25°C.

follows.

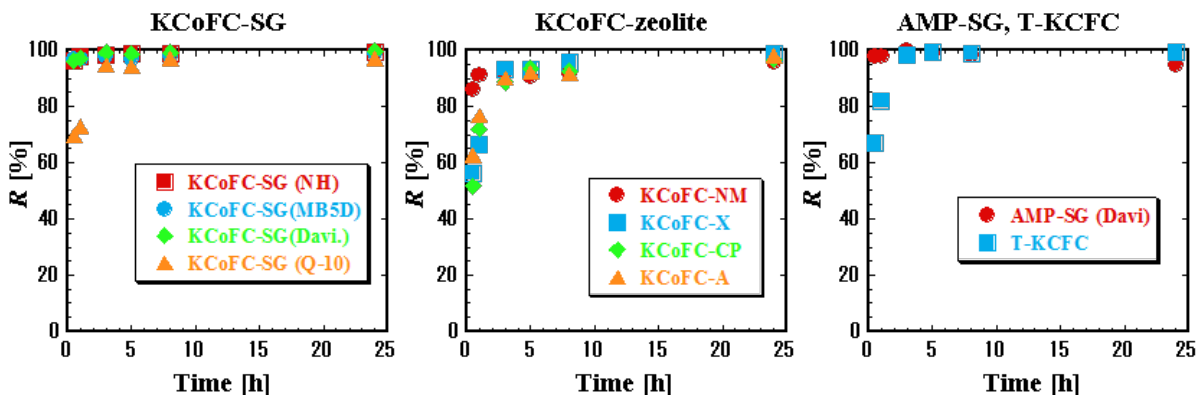KCoFC-SG(NH, MB5D), AMP-SG(Davi) > KCoFC-NM > T-KCFC > KCoFC-A, KCoFC-X, KCoFC-CP.

Fig. 10. Uptake rate of Cs.
$[Cs^+]$: 0.1 ppm; $[Sr^{2+}]$: 0.1 ppm; $[NaNO_3]$: 400 g/L; $[Na_2SO_4]$:
4.3 g/L; V/m: 100 cm^3/g; shaking time: 1 ~ 24 h ; 25°C.

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
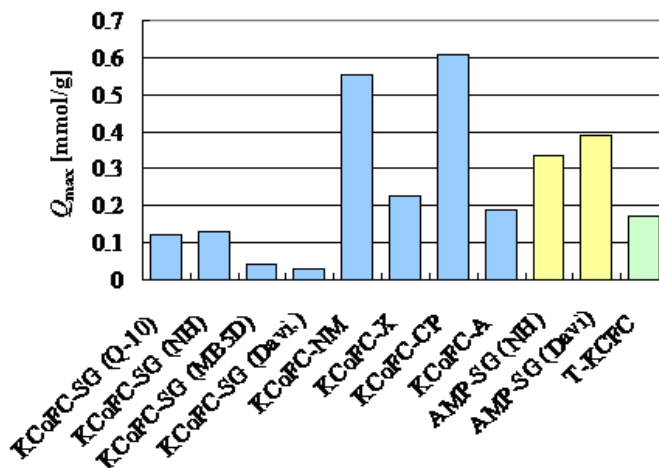

Fig. 11. Maximum uptake capacity of Cs.
$[Cs^+]$: 0.1 mol/L; $[NaNO_3]$: 400 g/L; $[Na_2SO_4]$:
4.3 g/L; V/m: 100cm^3/g; shaking time: 1 d; 25°C

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 $NaNO_3$ and 4.3 g/L Na_2SO_4. Irradiation conditions were summarized in **Table I**. Relatively large $K_{d,Cs}$ values above 10^3 cm^3/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 I. Irradiation condition

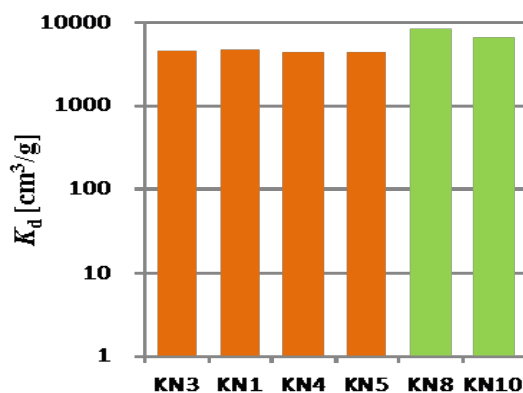|	KCoFC-NM composite					
	KN3	KN1	KN4	KN5	KN8	KN10
Adsorbed Dose [MGy]	0.32	0.82	1.55	2.72	-	-
Immersion（Irradiation）Time [h]	104	268	506	887	268	887

Fig. 12. Distribution properties of Cs for irradiated specimens. [Cs^+]: 0.1 ppm; [Sr^{2+}]: 0.1 ppm; [$NaNO_3$]: 400 g/L; [Na_2SO_4]: 4.3 g/L; *V/m*: 100cm^3/g; shaking time: 1 d; 25°C.
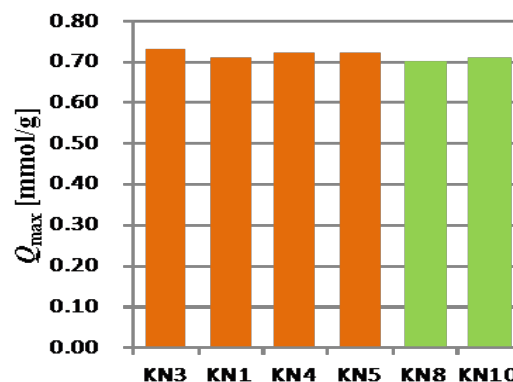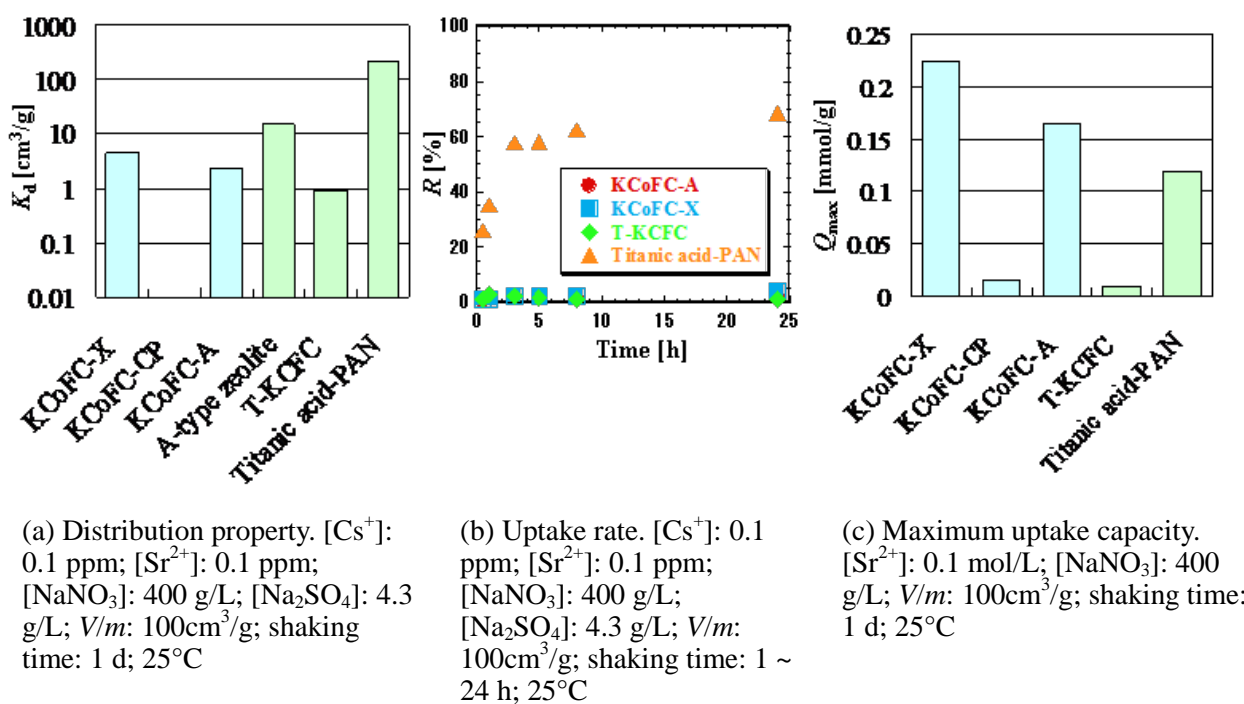

Fig. 13. Maximum uptake capacity of Cs for irradiated specimens. [Cs^+]: 0.1 mol/L; [$NaNO_3$]: 400 g/L; [Na_2SO_4]: 4.3 g/L; *V/m*: 100cm^3/g; shaking time: 1 d; 25°C.

Uptake of Sr

Figures 14(a)~(c) show the adsorption properties of Sr^{2+}. The largest value of $K_{d,Sr}$ was estimated to be 218 cm^3/g for titanic acid-PAN. The $K_{d,Sr}$ value for KCoFC-A (2.3 cm^3/g) was smaller than that for A-type zeolite (15 cm^3/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 Sr^{2+} ions for this composite. Titanic acid-PAN had the largest uptake rate of Sr^{2+} 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

(a) Distribution property. [Cs^+]: 0.1 ppm; [Sr^{2+}]: 0.1 ppm; [$NaNO_3$]: 400 g/L; [Na_2SO_4]: 4.3 g/L; V/m: 100cm^3/g; shaking time: 1 d; 25°C

(b) Uptake rate. [Cs^+]: 0.1 ppm; [Sr^{2+}]: 0.1 ppm; [$NaNO_3$]: 400 g/L; [Na_2SO_4]: 4.3 g/L; V/m: 100cm^3/g; shaking time: 1 ~ 24 h; 25°C

(c) Maximum uptake capacity. [Sr^{2+}]: 0.1 mol/L; [$NaNO_3$]: 400 g/L; V/m: 100cm^3/g; shaking time: 1 d; 25°C

Figs. 14(a)~(c). Adsorption properties of Sr^{2+} ions.

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

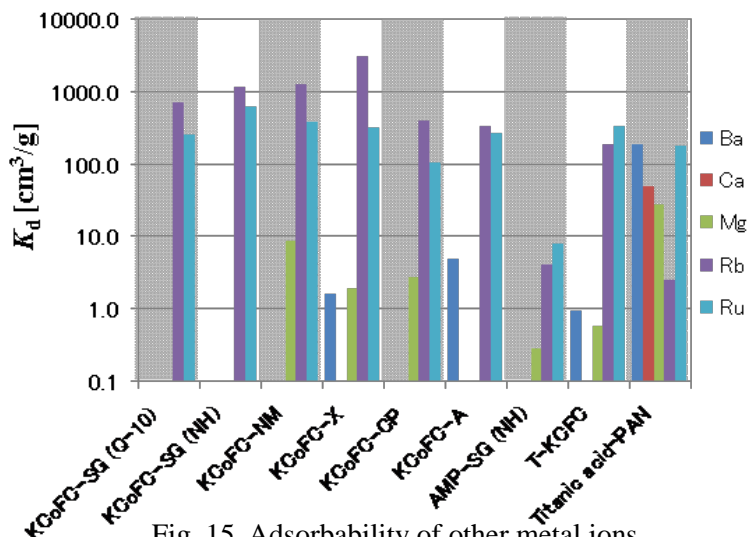Fig. 15. Adsorbability of other metal ions. [Metallic ion]: 10 ppm; [$NaNO_3$]: 400 g/L; [Na_2SO_4]: 4.3 g/L; V/m: 100cm^3/g; shaking time: 1 d; 25°C.

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acid-PAN was about 1, indicating that
the $K_{d,Sr}$ of titanic acid-PAN tends
to decrease in the presence of Ba^{2+}.

Breakthrough Properties

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 (**Figs. 16 and 17**). The order of 5 % breakthrough capacity of Cs^+ is as follows.

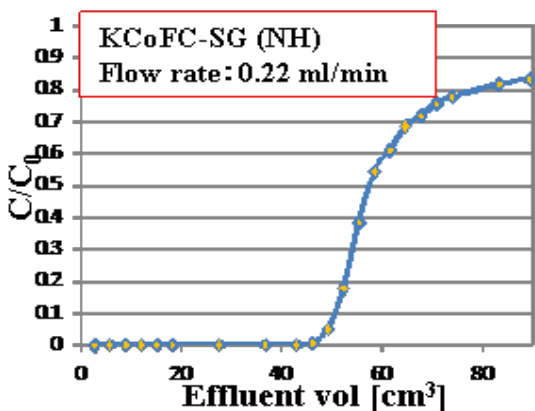KCoFC-SG (NH) > KCoFC-NM > KCoFC-SG(Q-10) > T-KCFC > KCoFC-X > KCoFC-CP.

Fig. 16. Breakthrough cave of Cs^+ ions. KCoFC-SG (NH): 1 g; Flow rate: 0.22 ml/min; Feed: 200 ppm Cs -400 g/L $NaNO_3$ – 4.3 g/L Na_2SO_4.
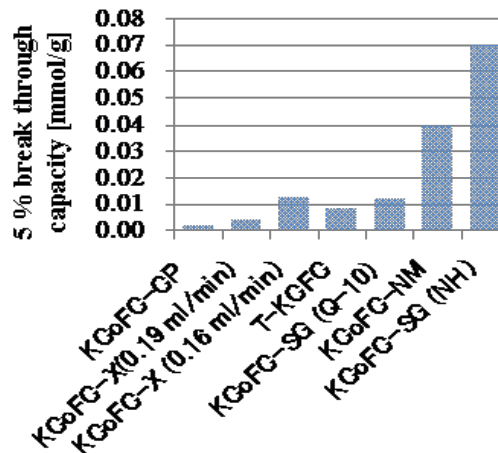
Fig. 17. 5 % Breakthrough capacities of Cs^+ ions

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 (**Table II**).

TABLE II. Performance comparison of adsorbents

		KCoFC-SG (NH)	KCoFC-SG (Q-10)	KCoFC-NM	KCoFC-CP	KCoFC-X	AMP-SG	T-KCFC	Titanic acid -PAN
Cs	Uptake rate	◎	○	○	△	△	◎	△	/
	Q_{max}	△	×	◎	◎	△	○	△	/
	5 % breakthrough capacity	○	△	○	×	×	/	×	/
Sr	K_d	/	/	/	/	△	/	△	○
	Q_{max}	/	/	/	/	△	/	×	△
	Uptake rate	/	/	/	/	×	/	×	△

Uptake rate ◎… 1 h, ○… 3 h, △… 5 h, ×… 24 h
Q_{max} ◎… above 0.5 mmol/g, ○… 0.3~0.5 mmol/g, △… 0.1~0.3 mmol/g, ×…below 0.1 mmol/g
5 % breakthrough capacity ○… above 0.03 mmol/g, △…0.01~0.03 mmol/g, ×… below 0.01 mmol/g
$K_{d,Sr}$ ○… above 10^2 cm^3/g, △…about 10^0 cm^3/g, ×… below 10^{-1} cm^3/g

CONCLUTIONS

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 $K_{d,Cs}$ value of 3.8×10^4 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 1.0×10^4 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.

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