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Application of the Flotation Method for the Treatment of the Waste Solution in the Chemical Processing of Used Nuclear Fuel

—Selective Removal of Mixed Fission Products—

By

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As a part of the fundamental study on the treating of the liquid wastes in the chemical processing of used nuclear fuel, the preferential flotation was investigated for the selective removal of the long-lived fission products such as [137] Cs, ^{90}Sr, [106]Ru, [144]Ce and [95]Zr from the low or intermediate level radioactive solutions.

By three stage preferential flotation using sodium oleate or octadecylamine acetate as the collector and cupric ferrocyanide or ferric hydroxide as the coprecipitant, 95% of ^{137}Cs, 87 % of ^{90}Sr, and above 98 % of the mixture of [144]Ce, [106]Ru and [95]Zr were removed respectively from the radioactive solution.

The whole amount of the resulting radioactive sludge per 1000 ml of the original radioactive solution was 130~190 mg.

1. Introduction

In most cases the present methods of reprocessing the spent nuclear fuels are characterized by producing a large volume of low or intermediate level radioactive waste solution. The waste solution contains many kinds of hazardous radioactive nuclides, and it is particularly required to remove the long-lived fission products such as ^{137}Cs, ^{90}Sr, [144]Ce, [106]Ru and [95]Zr[1] from the waste solution.

As the typical methods of removing the fission products from the radioactive waste solution, there are the evaporation method, the ion exchange method and the chemical flocculation-precipitation method. In recent years, the foam separation method has been studied. However these present methods are not sufficiently economical for treating the large volume of the radioactive waste solution and therefore the development of a more economical and secure method is expected[2].

The study on the removal of the long-lived fission products from the waste solutions by the flotation method has not been made yet. However, in previous

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papers[3]~[7], one of the authors has reported that the flotation method has the following excellent characteristics:

1) The treatment capacity is very large.

2) The amount of the resulting radioactive sludge is small.

3) The effective removal of the long-lived fission products is successful by the selection of the pertinent collector and the coprecipitant.

4) The required amounts of the collector and the coprecipitant are small.

5) The special surface active agents are not necessary.

In the present paper, the selective removal of the long-lived fission products such as ^{137}Cs, ^{90}Sr, ^{144}Ce, ^{106}Ru and ^{95}Zr from solutions simulated a low or intermediate level radioactive waste liquid by the preferential flotation was studied.

2. Classification of the Mixed Fission Products Based upon their Flotability

On the basis of the flotabilities obtained in the previous papers[4]~[7], the long-lived fission products are classified into three groups as shown in **Table 1**. ^{137}Cs

Table 1: Classification of the long-lived fission products based upon their flotabilities

CLASS	NUCLIDE	COPRECIPITANT	COLLECTOR	ACTIVATOR	pH
1	^{137}Cs	cupric ferrocyanide	ODAA	————	3.0 ~ 5.5
2	^{144}Ce ^{106}Ru ^{95}Zr	ferric hydroxide	Na Ol	————	6.0 ~ 8.0
		cobalt hydroxide	Na Ol	————	10.5 ~ 11.5
3	^{90}Sr	ferric hydroxide	ODAA	————	9.5 ~ 10.5
			Na Ol	cupric nitrate	9.5 ~ 10.5

belongs to the first group and is removed selectively at pH 4.0/5.5 by using cupric ferrocyanide as the coprecipitant and octadecylamine acetate (ODAA) as the collector.   The second group, the mixture of ^{144}Ce, ^{106}Ru and ^{95}Zr, is removed selectively at pH 6.0/8.0 or pH 10.5/11.5 by using ferric hydroxide or cobalt hydroxide as the coprecipitant and sodium oleate (NaOl) as the collector. ^{90}Sr belongs to the third group and is removed selectively at pH 9.0/10.5 by using ferric hydroxide as the coprecipitant, sodium oleate as the collector and cupric nitrate as the activator. ^{90}Sr is also removed at pH 9.0/10.5 by using octadecylamine acetate as the collector.

3. Efficiencies of Preferential Flotation

When n kind of the radioactive nuclides are removed selectively through the m stage preferential flotation as shown in **Fig. 1**, the effectiveness for the removal
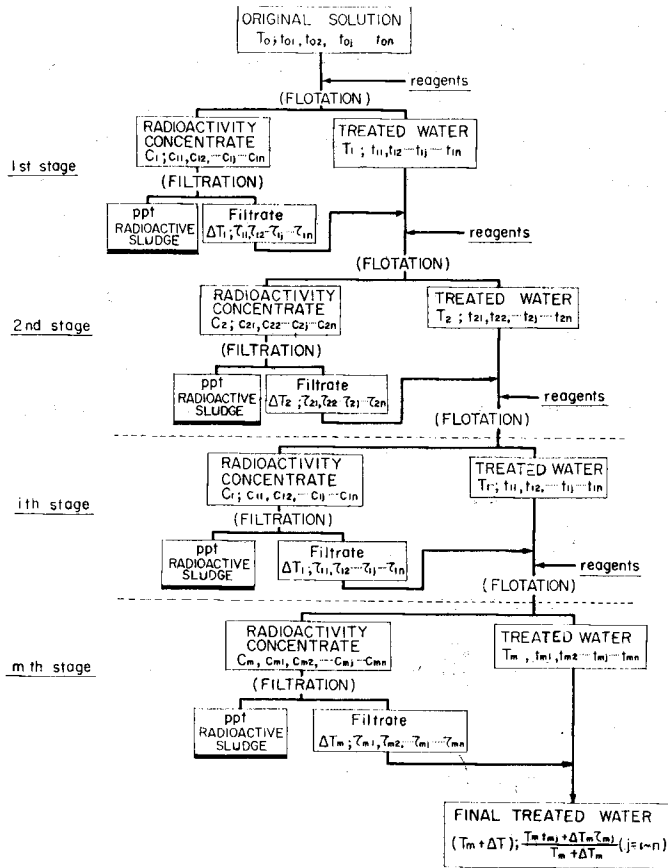

Fig. 1:   Process of the preferential flotation

of radionuclides are represented by the following four efficiencies;

$$R_j = \frac{\text{the sum of the radioactivity of the } j \text{ th nuclide removed at each stage } (\mu\text{Ci}/\text{m}l)}{\text{the radioactivity of the } j \text{ th nuclide in the original waste solution } (\mu\text{Ci}/\text{m}l)}$$

$$\times 100\%. \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

$$R_{ij} = \frac{\text{the radioactivity of the } j \text{ th nuclide removed at the } i \text{ th stage } (\mu\text{Ci}/\text{m}l)}{\text{the radioactivity of the } j \text{ th nuclide in the original waste solution } (\mu\text{Ci}/\text{m}l)}$$

$$\times 100\%. \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (2)$$

$$R_i = \frac{\text{the sum of radioactivity removed at the } i \text{ th stage } (\mu\text{Ci}/\text{m}l)}{\text{the total radioactivity in the original waste solution } (\mu\text{Ci}/\text{m}l)} \times 100\%. \quad\cdots (3)$$

$$R = \frac{\text{the sum of radioactivity removed at each stage } (\mu\text{Ci}/\text{m}l)}{\text{the total radioactivity in the original waste solution } (\mu\text{Ci}/\text{m}l)} \times 100\%. \quad \cdots (4)$$

However, since there are various difficulties in the measurement of the radio-activity of the materials collected with the bubbles, in the present study, Eqs. (1)/(4) were transformed as follows;

As shown in **Fig. 1**, T_0 stands for the volume of the original solution and t_{0j} ($j=1, 2, \cdots, n$) for the radioactivity concentration of the j th nuclide in the original solution. C_i and ΔT_i ($i=1, 2, \cdots, m$) represent the volume of radioactivity concentrate and its filtrate at i th stage respectively. T_i ($i=1, 2, \cdots, m$) stands for the volume of the treated water at the i th stage, c_{ij} ($i=1, 2, \cdots, m; j=1, 2, \cdots, n$) for the radioactivity concentration of the j th nuclide in the radioactivity concentrate at the i th stage, τ_{ij} ($i=1, 2, \cdots, m; j=1, 2, \cdots, n$) for the radioactivity concentration of the j th nuclide in the filtrate of the radioactivity concentrate at the i th stage and t_{ij} ($i=1, 2, \cdots, m; j=1, 2, \cdots, n$) for the radioactivity concentration of the j th nuclide in the treated water at the i th stage. Then, R_j, R_{ij}, R_i and R are given as follows;

$$R_j = \frac{\sum_{i=1}^{m} (C_i \cdot c_{ij} - T_i \cdot \tau_{ij})}{T_0 \cdot t_{0j}} \times 100 \ (\%) . \quad (5)$$

From the balance of radioactivity.

$$T_0 \cdot t_{0j} = \sum_{i=1}^{m} (C_i \cdot c_{ij} - T_i \cdot \tau_{ij}) + T_m \cdot t_{mj} . \quad (6)$$

From Eqs. (5) and (6),

$$R_j = \left(1 - \frac{T_m \cdot t_{mj}}{T_0 \cdot t_{0j}}\right) \times 100 \ (\%) . \quad (7)$$

From Eq. (2), R_{ij} is given by

$$R_{ij} = \frac{C_i \cdot c_{ij} - T_i \cdot \tau_{ij}}{T_0 \cdot t_{0j}} \times 100 \ (\%) . \quad (8)$$

From the balance of radioactivity at the i th stage,

$$T_{i-1} \cdot t_{i-1,j} + T_{i-1} \cdot \tau_{i-1,j} = C_i \cdot c_{ij} + T_i \cdot t_{ij} . \quad (9)$$

From Eqs. (8) and (9),

$$R_{ij} = \frac{(T_{i-1} \cdot t_{i-1,j} + \Delta T_{i-1} \cdot \tau_{i-1,j}) - (T_i \cdot t_{ij} + T_i \cdot \tau_{ij})}{T_0 \cdot t_{0j}} \times 100 \ (\%) . \quad (10)$$

From Eqs. (5) and (8), the relation between R_j and R_{ij} is given by

$$R_j = \sum_{i=1}^{m} R_{ij} . \quad (11)$$

Further, from Eqs. (3) and (4), R_i and R are given by

$$R_i = \frac{\sum_{j=1}^{n} (T_0 \cdot t_{0j} \cdot R_{ij})}{\sum_{j=1}^{n} T_0 \cdot t_{0j}} . \tag{12}$$

$$R = \sum_{i=1}^{m} R_i . \tag{13}$$

The volume of the original solution T_0, and its radioactivity concentration t_{0j}, the volumes of the filtrate of radioactivity concentrate ΔT_{i-1} and ΔT_i and their radioactivity concentration $\tau_{i-1,j}$ and τ_{ij} were measured. Efficiencies R_j, R_{ij}, R_i and R were thus calculated from Eqs. (7), (10), (12) and (13) respectively.

4. Materials and Reagents

The solution of radioisotopes, ^{137}Cs, ^{90}Sr, ^{144}Ce, ^{106}Ru and ^{95}Zr dissolved in dilute nitric acid was used instead of the actual waste solution, in the present experiments. The radioactivity concentration of each nuclide was made up to be as strong as 10^{-2} $\mu Ci/ml$. The radioisotopes were obtained commercially from ORNL of America and RCC of England.

For the coprecipitant, 1000 ppm Cu^{2+}, Fe^{3+} and $K_4[Fe(CN)_6]$ aqueous solutions were prepared by dissolving analytical grade cupric nitrate, ferric chloride and potassium ferrocyanide in demineralized water respectively. A 100 ppm solution of cupric nitrate was used as the activator of ferric hydroxide precipitate at the high pH region. Further 1000 ppm sodium oleate solution and 5000 ppm octadecylamine acetate ethyl alcohol solution as the collector and 1000 ppm glycol polypropyleneoxide solution as the frother were prepared. A 0.1 N solution of potassium hydroxide was used as the pH regulator.

5. Apparatus

In the experiments, a test flotation apparatus as shown in Photo. 1 was used. The apparatus is composed of an air compressor (A), an air tank (B), a cock (C), three air washing bottles (D_1, D_2, D_3) and a flotation cell (E). The flotation cell is shown in Fig. 2, where (a) corresponds to a foam chamber, (b) a foam canal, (c, d) sampling cocks and (e) a glass filter.
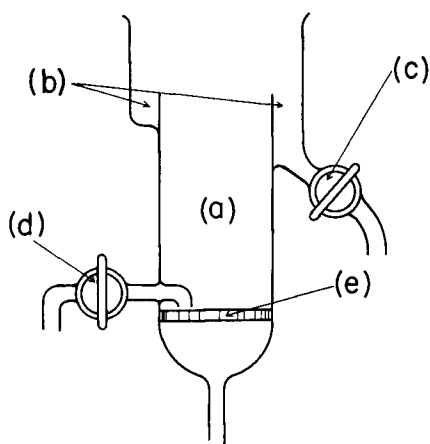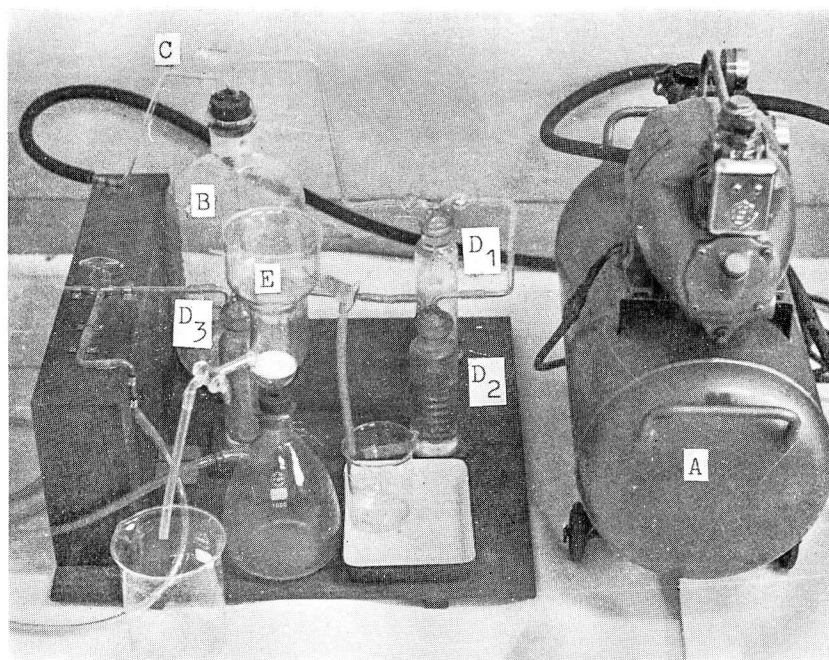

Fig. 2: Flotation cell

Photo. 1: Apparatus of flotation

6. Method of Experiment

(1) Procedure

The procedure of flotation at each stage is essentially the same as that previously reported[4],[7] for ^{144}Ce and ^{137}Cs by one of the authors. One hundred ml of the original waste solution is put in a 300 ml beaker, and to it the coprecipitant and the pH regulating agent are added. After the mixture was stirred rapidly for 10 min the collector is added and the mixture is further stirred for 5 min. The frother is added and the pH is measured with a glass electrode pH meter.

The pre-treated waste solution is fed into the flotation cell. The froth is collected for 1 min. The collected froth (radioactivity concentrate) and the treated water are taken from the cock (c) and (d) respectively.

(2) Order of Collection

According to the classification of the fission products (Table 1), the following three typical cases are considered;

(a) At the first stage, as shown in Fig. 3, the mixture of ^{144}Ce, ^{106}Ru and ^{95}Zr is removed selectively at pH 6.0–8.0 by using 30 ppm of ferric hydroxide as the coprecipitant and 20 ppm of sodium oleate as the collector.

At the second stage, ^{90}Sr is removed selectively at pH 9.5–10.5 by using 60 ppm
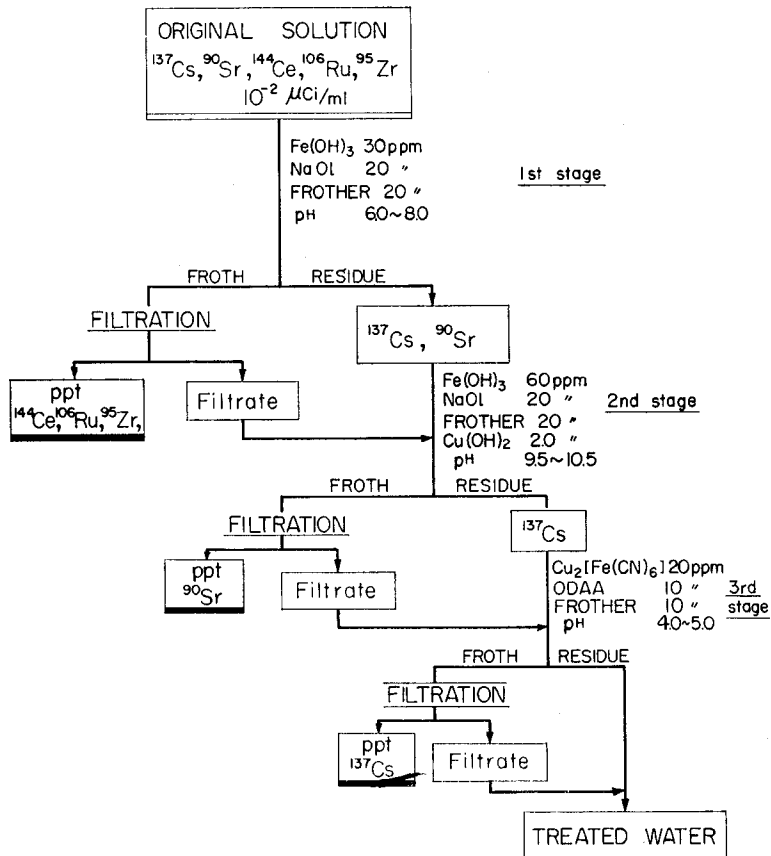
Fig. 3: Procedure of the preferential flotation of the long-lived fission products (a)

of ferric hydroxide as the coprecipitant, 20 ppm of cupric hydroxide as the activator and 20 ppm of sodium oleate as the collector.

At the third stage, ^{137}Cs is removed selectively at pH 5.0–6.0 by using 20 ppm cupric ferrocyanide as the coprecipitant and 10 ppm of octadecylamine acetate as the collector.

(b) As shown in Fig. 4, the long-lived fission products are removed selectively in the order of ^{137}Cs, the mixture of ^{144}Ce, ^{106}Ru and ^{95}Zr, and ^{90}Sr.

(c) At the first stage, as shown in Fig. 5, the mixture of ^{144}Ce, ^{106}Ru and ^{95}Zr is removed selectively. At the second and third stage, ^{90}Sr is removed selectively. In this case, ^{137}Cs is not removed.

(3) Representation of Efficiency of Preferential Flotation

In the present experiment, the number of nuclide to be removed $n=5$, and the

ORIGINAL SOLUTION
^{137}Cs, ^{90}Sr, ^{144}Ce, ^{106}Ru, ^{95}Zr
10^{-2} μCi/ml

Cu$_2$(Fe(CN)$_6$)   20 ppm
ODAA   10 "   1st stage
FROTHER   10 "
pH   4.0~5.0

FROTH   RESIDUE

FILTRATION

ppt   Filtrate ^{144}Ce, ^{106}Ru, ^{95}Zr, ^{90}Sr
^{137}Cs

Fe(OH)$_3$ 30ppm
NaOl   20 "   2nd stage
FROTHER 20 "
pH   6.0~8.0

FROTH   RESIDUE

FILTRATION

ppt   Filtrate ^{90}Sr
^{144}Ce, ^{106}Ru, ^{95}Zr

Fe(OH)$_3$ 60ppm
NaOl   20 "   3rd stage
FROTHER 20 "
Cu(OH) 20 "
pH   9.5~10.5
FROTH   RESIDUE

FILTRATION

ppt   Filtrate
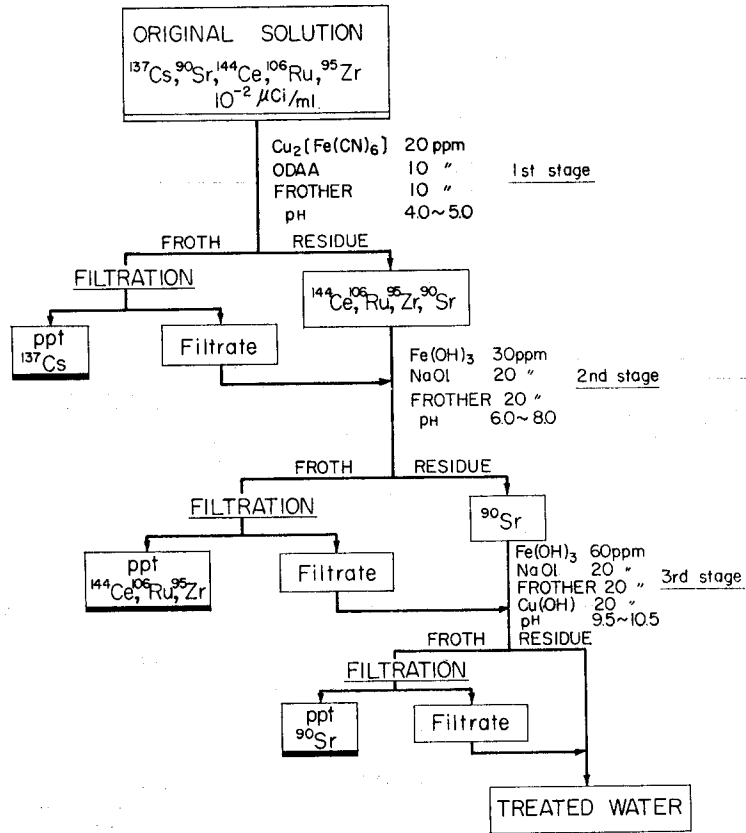^{90}Sr

TREATED WATER

Fig. 4: Procedure of the preferential flotation of the long-lived fission
         products (b)

Table 2: Representation of preferential flotation
          efficiencies

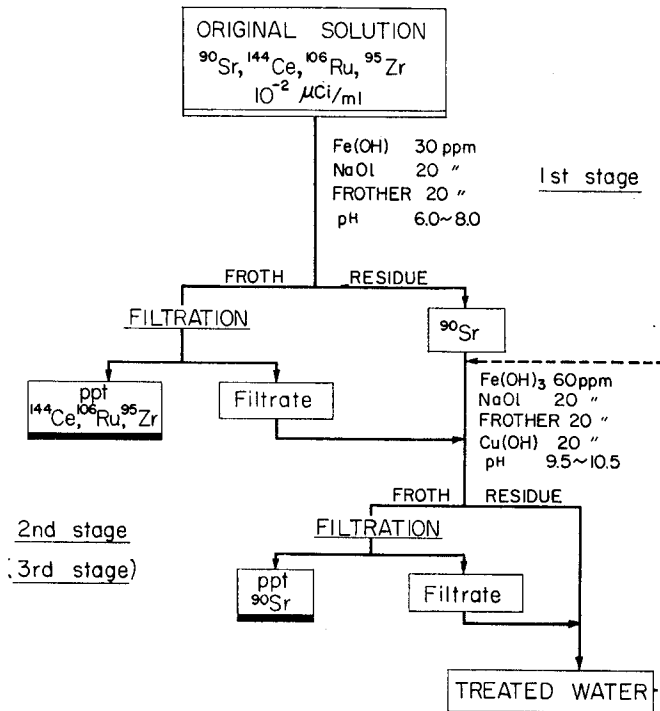| NUCLIDE / STAGE	1 ^{137}Cs	2 ^{144}Ce	3 ^{106}Ru	4 ^{95}Zr	5 ^{90}Sr	
1st Stage	R_{11}	R_{12}	R_{13}	R_{14}	R_{15}	$\mathbb{R}_1$
2nd Stage	R_{21}	R_{22}	R_{23}	R_{24}	R_{25}	$\mathbb{R}_2$
3rd Stage	R_{31}	R_{32}	R_{33}	R_{34}	R_{35}	$\mathbb{R}_3$
	R_1	R_2	R_3	R_4	R_5	$\mathbb{R}$

Fig. 5: Procedure of the preferential flotation of the long-lived
fission products (c)

number of stage $m=3$. Therefore the efficiencies of the preferential flotation are given by $R_j (j=1\sim5)$, $R_{ij} (i=1\sim3; j=1\sim5)$, $R_i (i=1\sim3)$ and R. These flotation efficiencies are represented by a matrix as shown in Table 2.

(4) Analyses of Long-Lived Fission Products

One ml of the original solution and the treated water were evaporated to dryness and γ-ray spectra were measured by using the 100 channel γ-ray spectrometer. From these γ-ray spectra, the removal efficiencies for ^{137}Cs, ^{144}Ce, ^{106}Ru and ^{95}Zr were estimated qualitatively.

Further, ^{137}Cs, ^{90}Sr, ^{144}Ce, ^{106}Ru and ^{95}Zr were estimated quantitatively by wet radiochemical analyses[8–12].

7. Results of Experiment

The experimental results of the selective removal of the mixed fission products, according to the order of collection illustrated in Fig. 3 are shown in Fig. 6.

Curve (I) in Fig. 6 is the spectrum of the original solution. From this curve, it is seen that ^{144}Ce, ^{106}Ru-^{106}Rh, ^{137}Cs and ^{95}Zr-^{95}Nb show their photopeaks at
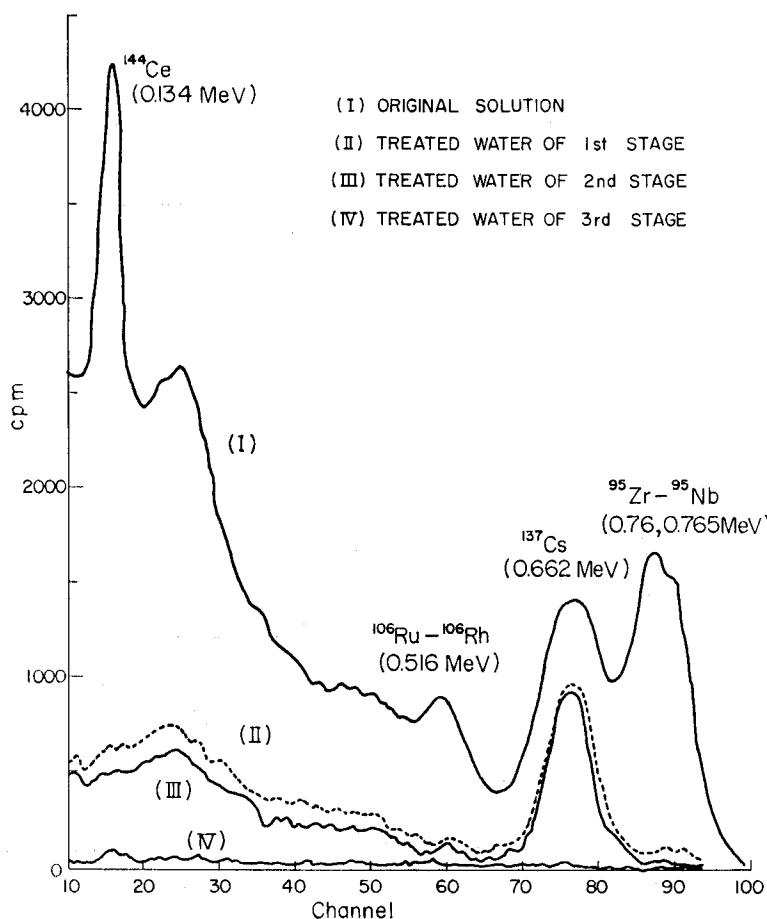
Fig. 6: γ-ray spectra of the original solution and the treated water (a)

channel number 15, 59, 75 and 89 respectively.

Curve (II) gives the γ-ray spectrum of the treated water of the first stage, in which the above original solution was treated by flotation at pH 6.0 by using 30 ppm of ferric hydroxide as the coprecipitant and 20 ppm of sodium oleate as the collector. The photopeaks of ^{144}Ce, ^{106}Ru-^{106}Rh and ^{95}Zr-^{95}Nb considerably disappear. From these results, it is recognized that the mixture of ^{144}Ce, ^{106}Ru-^{106}Rh and ^{95}Zr-^{95}Nb was removed efficiently.

The photopeak of ^{137}Cs moves downward to some degree because of the disappearance of Compton continuous band of ^{95}Zr-^{95}Nb, but its height remains almost unchanged. Consequently, it is clear that ^{137}Cs can not be removed at the first stage flotation.

By the wet quantitative analyses of the long-lived fission products, it was

confirmed that 98% of ^{144}Ce, 98% of ^{106}Ru and 99% of ^{95}Zr were removed selectively at the first stage flotation, while 98% of ^{137}Cs and ^{90}Sr remained in the treated water.

Curve (III) gives the γ-ray spectrum of the treated water of the second stage in which the treated water of the first stage flotation was further treated for the selective removal of ^{90}Sr at pH 9.5 by using 60 ppm of ferric hydroxide as the coprecipitant, 20 ppm of cupric hydroxide as the activator and 20 ppm of sodium oleate as the collector. In comparison with the above curve (II), the height of all photopeaks decrease slightly. From the results of the wet quantitative analyses, it was recognized that 2% of ^{137}Cs and 1% of ^{144}Ce and ^{106}Ru were removed and 87% of ^{90}Sr were selectively removed by this second stage flotation.

Curve (IV) shows the γ-ray spectrum of the treated water of the third stage in which the flotation was carried out at pH 5.0 for the removal of ^{137}Cs using 20 ppm of cupric ferrocyanide as the coprecipitant and 10 ppm of octadecylamine acetate as the collector. From the result, it is seen that the photopeak of ^{137}Cs disappears. It was confirmed by the wet quantitative analyses that 95% of ^{137}Cs and 7% of ^{90}Sr were removed in the third stage flotation.

By the calculations of the over-all flotation efficiencies R_j $(j=1\sim5)$ according to Eq. (11), it was seen that R_1 for ^{137}Cs, R_2 for ^{144}Ce, R_3 for ^{106}Ru and R_4 for ^{95}Zr were all above 99% and R_5 for ^{90}Sr was 96%. The radioactive removal efficiencies of each stage $\boldsymbol{R}_i$ $(i=1\sim3)$ according to Eq. (12), $\boldsymbol{R}_{1-3}$ were 60%, 18% and 20% respectively. And the over-all radioactivity removal efficiency $\boldsymbol{R}$ was 98%.

In Table 3, the above efficiencies were summarized in terms of the matrix form of Table 2.

By the above preferential flotation, 130 mg of the radioactive sludge per 1000 ml of the original solution was yielded. This yielded amount of sludge is much

Table 3: Flotation efficiencies for each nuclide (a)

NUCLIDE \ STAGE	1 ^{137}Cs	2 ^{144}Ce	3 ^{106}Ru	4 ^{95}Zr	5 ^{90}Sr	
1st Stage	2*	98	98	99	2	60*
2nd Stage	2	1	1	trace	87	18
3rd Stage	95	trace	trace	trace	7	20
	99*	99	99	99	96	98*

less than that in the chemical flocculation method .

Fig. 7 shows the results of the selective removal of the mixed fission products according to the order of collection of Fig. 4.

Curves (I)–(IV) in Fig. 7 are the γ-ray spectra of the original solution and the treated waters at the first, the second and the third stage flotation respectively.

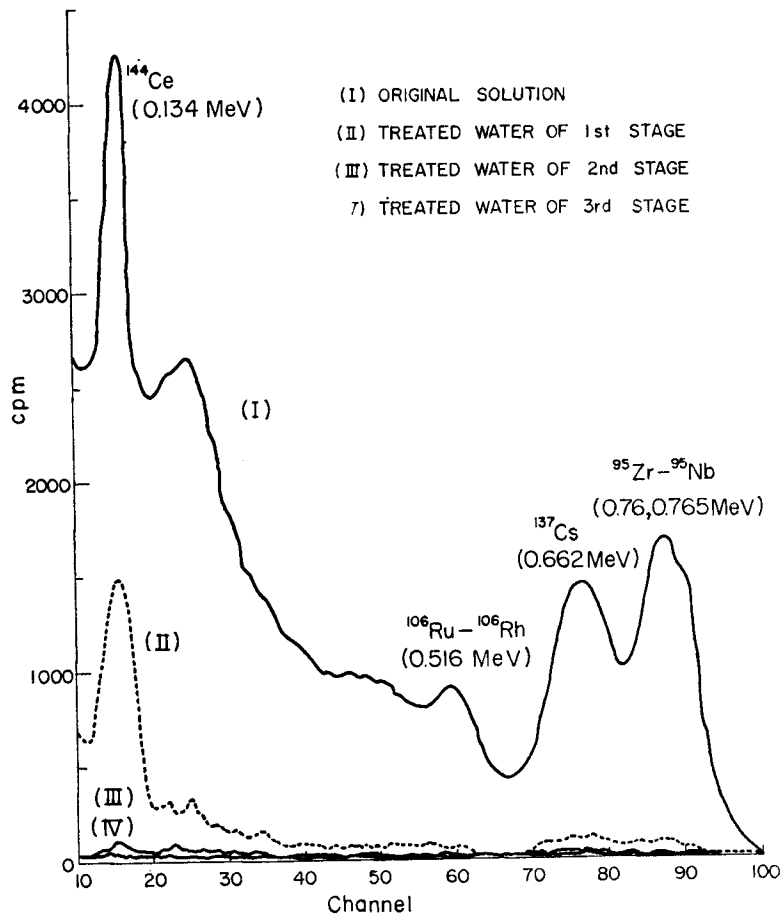Fig. 7: γ-ray spectra of the original solution and the treated water (b)

From the comparison of curve (I) with curve (II), it is seen that the photopeaks of ^{137}Cs, [106]Ru-   [106]Rh and [95]Zr-[95]Nb disappear simultaneously.   Therefore it is clear that the preferential flotation using cupric ferrocyanide as the coprecipitant and octadecylamine acetate at the collector at first stage does not give sufficient selective removal of the mixed fission products.

In Table 4, the efficiencies of the above preferential flotation are summarized.

Table 4: Flotation efficiencies for each nuclide (b)

NUCLIDE / STAGE	1 ^{137}Cs	2 ^{144}Ce	3 ^{106}Ru	4 ^{95}Zr	5 ^{90}Sr	
1st Stage	95*	trace	80	80	55	62*
2nd Stage	2	97	17	12	5	28
3rd Stage	trace	2	2	1	27	6
	97*	99	99	99	87	96*

(I) ORIGINAL SOLUTION

(II) TREATED WATER OF 1st STAGE

(III) TREATED WATER OF 2nd STAGE

(IV) TREATED WATER OF 3rd STAGE

^{144}Ce (0.134 MeV)

^{95}Zr –^{95}Nb (0.76, 0.765MeV)

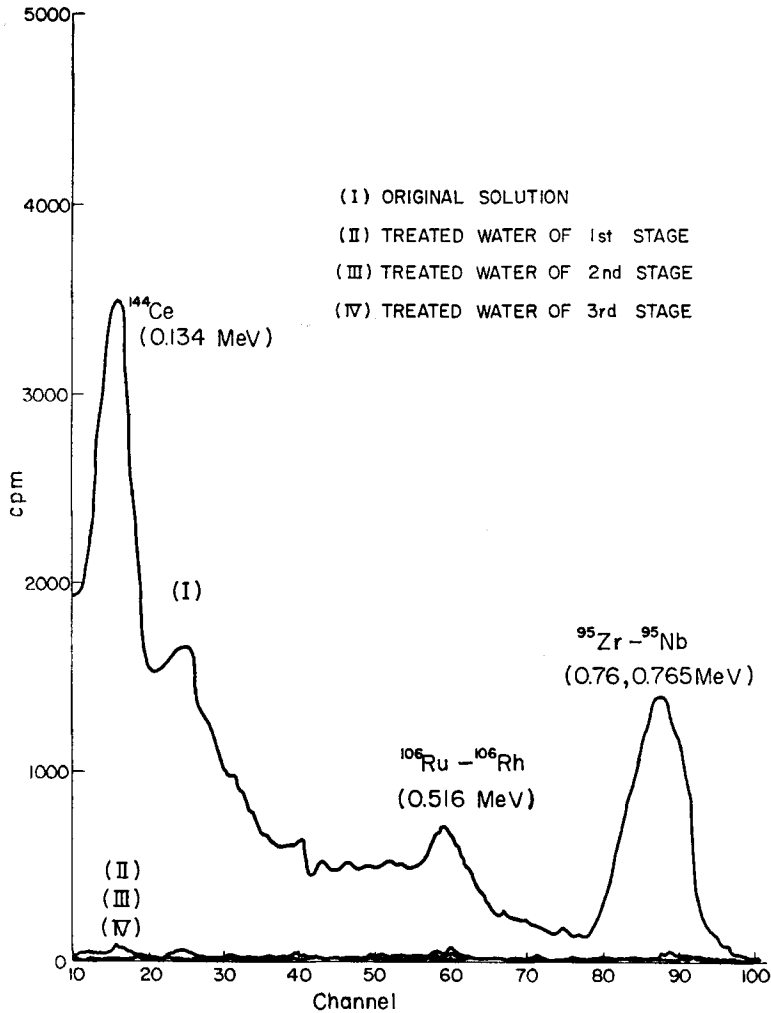^{106}Ru –^{106}Rh (0.516 MeV)

(I)

(II)
(III)
(IV)

cpm

Channel

Fig. 8: γ-ray spectra of the original solution and the treated water (c)

Table 5: Flotation efficiencies for each nuclide (c)

NUCLIDE STAGE	1 ^{144}Ce	2 ^{106}Ru	3 ^{95}Zr	4 ^{90}Sr	
1st Stage	98*	99	99	1	74*
2nd Stage	1	trace	trace	90	23
3rd Stage	trace	trace	trace	7	2
	99*	99	99	98	99*

Fig. 8 and Table 5 show that the results of the selective removal of the mixed fission products according to the order of the collection of Fig. 5. From these results, it is seen that at the first stage flotation, 98% of ^{144}Ce, 99% of ^{106}Ru and 99% of ^{95}Zr were removed selectively and at the second and the third stage flotation, 90% and 7% of ^{90}Sr were removed respectively. The overall flotation efficiencies R_{1-4} are all above 98%. The amount of the resulting sludge was 190 mg per 1000 ml of the original solution.

8. Conclusion

The selective removal of the long-lived fission products from a large volume of the radioactive solution such as the nuclear fuel reprocessing waste solutions by the preferential flotation method was studied by using solutions simulated a radioactive waste liquid.

As the result of this study, it was confirmed that the mixed long-lived fission products could be removed selectively by the preferential flotation of three stages.

For the effective application of such preferential flotation method to the real waste solution in the chemical processing of used nuclear fuel, some practical considerations on the scale-up of flotation cell, the treatment of the resulting radioactive sludge and the effect of the co-existent ions to the flotation efficiencies are necessary. However, from the above experimental results, it is conceivable that the preferential flotation can be a new economical and secure method for the treating of a waste solution in the chemical processing of used nuclear fuel.

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