

PARTITIONING OF NEODYMIUM AND AMERICIUM IN THE LIQUID RADIOACTIVE WASTE BY OXALATE PRECIPITATION

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Abstract—The partitioning of americium and neodymium by precipitation with oxalic acid was investigated in the simulated radwaste, which was composed of 10 elements of alkali, alkaline earth, and transition metals in nitric acid solution. The effect of concentrations of oxalic acid and nitric acid in the simulated waste on the precipitation yield and purity of Nd and Am was examined in this study. As a result, the precipitated fraction of each element was increased with increasing concentration of oxalic acid and decreasing concentration of nitric acid. At an initial concentration of 0.5 M nitric acid and 0.5 M oxalic acid, both Am^{3+} and Nd^{3+} were precipitated over 99% and other elements almost remained in the simulated solution. It was also found that Am was completely coprecipitated with Nd-oxalate precipitates, and Zr^{4+} caused the coprecipitation of Cs^+ , Sr^{2+} , and Pd^{2+} .

Key words: Oxalate Precipitation, Liquid Radwaste, Americium, Lanthanide, Partitioning

INTRODUCTION

In order to decrease the toxicity of radwaste containing long-lived radionuclides and enhance their handling flexibility in waste treatment and disposal, partitioning and transmutation of the long-lived radionuclides have been studied in several countries in previous decades [Skalberg and Liljenzin, 1990]. Especially, Miyashio and Kubota [1986] conceptually introduced the partitioning process of high level liquid waste (HLLW), so called four group-separations such as transuranium (TRU) elements, technetium-nobel metals, strontium-caesium and the other elements. Among them, TRU elements as a long-lived nuclide, are the most important nuclides to be separated from high level waste.

Oxalate precipitation process provides the simultaneous precipitation of the transuranium elements and lanthanides from HLLW, and the TRU elements should be separated from the lanthanides either by ion exchange chromatography or by solvent extraction method [IAEA Technical Reports Series No. 214, 1982]. The oxalate precipitation process has been examined at the Joint Research Centre, Ispra and Karlsruhe [IAEA Technical Reports Series No. 214, 1982; IAEA Technical Reports Series No. 137, 1992], at Oak Ridge National Laboratory, and so on [Posey, 1980; Tedder and Blomeke, 1977; Rankin et al., 1977]. Recently, Japan Atomic Energy Research Institute has been running an intensive program for research and development on nuclide partitioning [Miyashiro and Kubota, 1986; Kobayashi et al., 1988; Kobayashi et al., 1989].

The present study aims at confirming the applicability of precipitation to the partitioning process and establishing its optimum operating condition to maximize the recovery yield and the decontamination factor of TRU elements. Experiment was extensively performed with the several sets of simulated liquid wastes containing Am and Nd. They are considered as representative elements

of TRU and lanthanides. Since the precipitation characteristics of lanthanides by oxalic acid are similar to those of trivalent TRU elements [Kobayashi et al., 1989; Forsberg, 1980] such as Am^{3+} and Cm^{3+} , and furthermore, Nd is a dominant element in the HLLW [Kubota and Fukase, 1980], the optimum condition for the concentration of oxalic acid and nitric acid was estimated by an inactive test with Nd^{3+} replaced by Am and finally confirmed in the system with Am^{3+} .

EXPERIMENTAL

1. Simulated Liquid Radwaste and Reagents

A simulated radwaste consisted of 10 components which were selected as representative elements in this study and their concentrations are given in Table 1, based on the estimated HLLW from the first cycle of Purex process for spent fuel of the pressurized-water reactor with 28,000 MWd/MT and 5 year cooling time [Kubota and Fukase, 1980]. Such elements as Cr, Al and so on, were not added in the simulated radwaste because the concentrations might be low and the presence of these elements did not affect the precipitation behavior of Nd^{3+} in the solution. Cesium and Strontium were selected as a representative element for alkali and alkaline earth metals, respectively. Iron, Nickel, Ruthenium, Zirconium, and Molybdenum as representative elements of the transition metals were also selected in the experiment. Most chemical reagents for the simulated HLLW were used as nitrate salt forms except Mo and Pd which are composed of ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ and palladium chloride (PdCl_2). Carrier-free ^{241}Am was obtained from Isotope Products Laboratories (California, U.S.A.) with a total radioactivity of 1 mCi in 1M HCl solution.

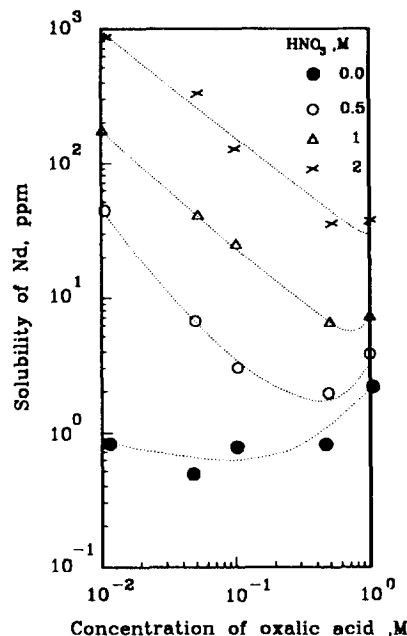
2. Analytical Methods

Concentrations of Nd, Fe, Ni, Zr, and Mo and those of Ru and Pd in a sample solution were determined by inductively coupled plasma atomic emission spectrometer (ISA Jobin-Yvon JY 50P

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Table 1. Chemical composition of estimated HLLW and simulated radwaste

Element	Estimated HLLW (mol/l)	Simulated radwaste (mol/l)	Element	Estimated HLLW (mol/l)	Simulated radwaste (mol/l)
Fe	0.038	0.038	La	0.0147	-
Cr	0.0091	-	Ce	0.033	-
Ni	0.006	0.006	Pr	0.0137	-
Al	0.00076	-	Nd	0.0434	0.04
Na	0.076	-	Pm	0.0012	-
Mo	0.069	0.0069	Sm	0.0086	-
Tc	0.015	-	Eu	0.0019	-
Sr	0.0165	0.0165	Gd	0.0010	-
Ba	0.0207	-	Y	0.0084	-
Cs	0.0371	0.0371	Am	0.0012	2.28×10^{-9}
Rb	0.0074	-	Cm	0.00025	-
Zr	0.069	0.0034	U	0.0076	-
Ru	0.034	0.0034	Pu	0.00095	-
Rh	0.0080	-	PO ₄	0.0023	-
Pd	0.018	0.018	SiO ₃	0.0076	-
Ag	0.00085	-	Cd	0.00085	-
Te	0.0068	-			

**Fig. 1. Solubility of Nd as a function of concentration of oxalic acid.**

and ISA Jobin-Yvon JY 38 PLUS). Concentrations of Cs and Sr were determined by an atomic absorption spectrophotometer. The concentration of ²⁴¹Am was determined by α counting with liquid scintillation counter (Packard-2500 TR/AB, USA).

3. Precipitation Scheme

3-1. Inactive Element Precipitation

To investigate the precipitation behavior of each element and the effect by adding another element on Nd precipitation in a multi-component system, 4 sets of simulated radwaste solution were prepared as follows and the concentrations of each element in the solution were shown in Table 1.

1 component solution : Nd-HNO₃

5 components solution : Nd-Cs, Sr, Fe, Ni-HNO₃

7 components solution : Nd-Cs, Sr, Fe, Ni, Pd, Ru-HNO₃

9 components solution : Nd-Cs, Sr, Fe, Ni, Pd, Ru, Mo, Zr-HNO₃

A precipitation reaction was carried out at room temperature by adding the weighed solid granule of oxalic acid into the simulated solution with a total volume of 20 ml. The working solution was manually shaken, and aged overnight to reach an equilibrium between solid and liquid phase, and then, filtered for liquid-solid separation. The filtrate was analyzed for concentration determination. The added concentration range of oxalic acid was varied as 0.1-1.5 M, and nitric acid as 0-2 M.

3-2. Americium Precipitation

A stock solution of ²⁴¹Am tracer with a total radioactivity of 4.44×10^5 dpm was prepared in 0.5 M HNO₃ medium. In all experiments for Am-oxalate precipitation, the concentration of oxalic acid and nitric acid were fixed to 0.5 M, that is based on the result of section 3-1. The number of components for Am precipitation was 8 including Am. A small volume (20 μ l) of ²⁴¹Am tracer solution was added to a working solution that is simulated solution with oxalic acid and nitric acid. The total volume of a working solution was 2 ml in the experiment. A working solution was shaken for equilibrium, and then, centrifuged for the precipitate to be settled down. An aliquot of 10 μ l was taken from the supernatant and mixed with 5 ml cocktail solution (Scient-AXF, Pac-

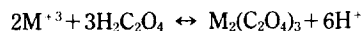
kard). The residual amount of ²⁴¹Am tracer in solution was measured by liquid scintillation counter (Packard 2500 TR/AB, U.S.A.).

RESULTS AND DISCUSSION

1. Precipitation Equilibrium of Simulated Radwaste in Various Oxalic and Nitric Acid Contents

1-1. One Component Solution (Neodymium Nitrate)

Equilibrium concentrations of Nd in the filtrates are shown in Fig. 1, varying oxalic acid concentration from 0.01 M to 1.0 M and nitric acid concentration from 0 to 2.0 M, respectively. The solubility of Nd in the solution decreased as the oxalic acid concentration increased and increased as the hydrogen ion concentration increased. This can be easily understood in a sense of chemical equilibrium, expressed by [Posey, 1980]



However, Nd has a minimum solubility with nitric acid in high H₂C₂O₄ concentration as shown in Fig. 1. These minimum points can be also explained from the fact that metal ion forms more soluble complex compound with oxalate [Crouthamel and Martin, 1950; Crouthamel and Martin, 1951] as $\text{M}(\text{C}_2\text{O}_4)_n^{3-2n}$ [M = rare-earth fission product and tri-valent actinides]. Burney and Porter [1967] have also reported that Am³⁺ and Cm³⁺ oxalates have minimum solubility at high oxalic acid contents. At 0 to 2 M HNO₃ content, therefore, the optimum concentration of oxalic acid is found to be 0.5 M for maximum Nd precipitation.

1-2. Five, Seven and Nine Component Solution

The precipitation fraction of each element in the simulated waste of 5, 7, and 9 components with a variation of oxalic acid and nitric acid concentrations are shown in Fig. 2, 3, and 4. As shown in Fig. 2, 3, and 4, the precipitation behaviors of simulated wastes of 5, 7, and 9 components with increase of oxalic acid concentration show that when adding more than 0.3 M of oxalic acid Nd was precipitated over 99% and precipitation fraction of other elements such as Cs, Sr, ... etc., gradually increased. The precipita-

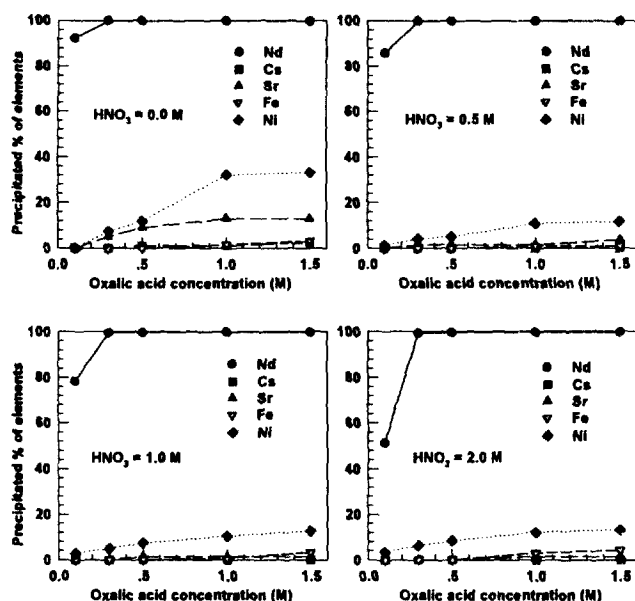


Fig. 2. Effect of oxalic acid concentration on the precipitation of each element in the simulated solution of 5 component at $[HNO_3] = 0-2.0$ M.

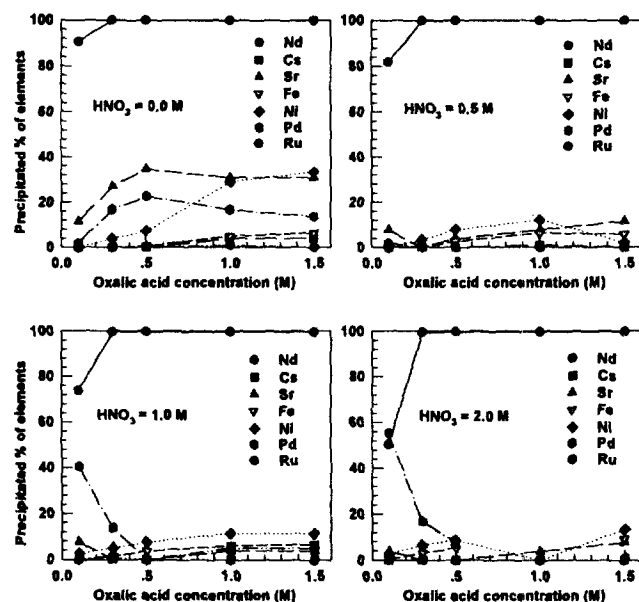


Fig. 3. Effect of oxalic acid concentration on the precipitation of each element in the simulated solution of 7 component at $[HNO_3] = 0-2.0$ M.

tion behaviors of simulated wastes with respect to HNO_3 concentration commonly show that the precipitation of all elements except Nd is suppressed with increase of nitric acid. Especially all elements except Nd remained nearly constant in nitric acid over 0.5 M in cases of 5 and 7 component simulated wastes and in the case of 9 component also comparatively constant. It suggests that an optimal concentration of HNO_3 is desirable to be 0.5 M.

When the concentrations of oxalic acid and nitric acid are selected as 0.5M, therefore precipitation condition of various simulated wastes shows optimum: Nd was almost precipitated over 99%

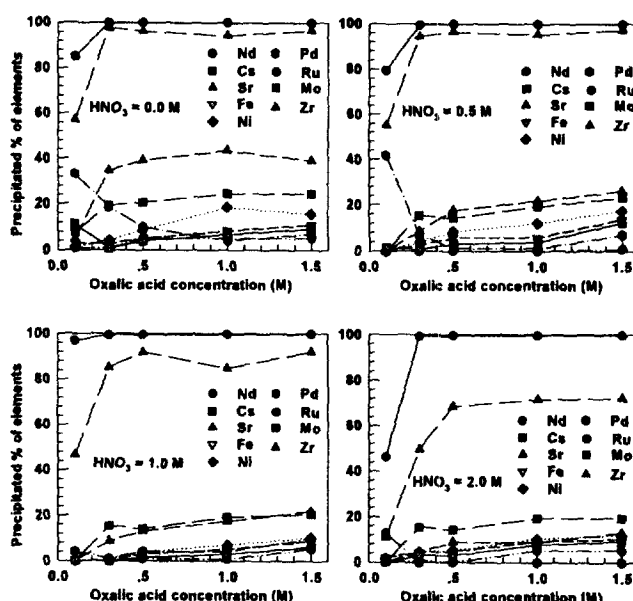


Fig. 4. Effect of oxalic acid concentration on the precipitation of each element in the simulated solution of 9 component at $[HNO_3] = 0-2.0$ M.

and most of other elements remained in the simulated waste. The precipitation of each element, however, increases with increasing the number of components in the simulated waste. Particularly, the precipitation fraction of elements in 9 components including Mo and Zr increased more rapidly, compared to those of 5 and 7 components. Even at 2 M HNO_3 , each precipitation fraction of Zr, Cs and Sr increased to much higher values, 70%, 20% and 10%, respectively. This means that Mo and/or Zr may affect the precipitation of other elements.

2. Comparison of Precipitation Behaviors of Each Element

Precipitation behaviors of each element in the simulated radwastes are shown in Fig. 5, 6, 7, 8, 9, 10, 11, and 12, respectively. Neodymium precipitation of Fig. 5 behaves like one described in sections 1-1 and 1-2. In Fig. 5, the precipitation fraction of Nd are decreased only at 0.1 M oxalic acid. It seems to be in short of oxalate that had been used up in the oxalate precipitation or in the complex formation with other elements. Fig. 8 shows that Fe precipitation is affected by Pd and/or Ru rather than by Mo and/or Zr, and Fig. 9 shows that Ni precipitation depends only upon the contents of oxalic acid regardless of kinds of simulated wastes. As mentioned previously, precipitations of Cs, Sr and Pd increased in the 9 component solution containing Mo and Zr which was shown in Fig. 6, 7, and 11 respectively. Since Mo relative to Zr does not nearly precipitate, it seems that Zr plays an important role in precipitation.

Since the oxalate precipitation mechanism of each element in the simulated radwaste with multicomponents is very complex as mentioned above, it is important to know whether the precipitation is due to interactions (e.g., adsorption and coprecipitation) with other elements or due to sole heterogeneous equilibrium with bulk liquid phase. This can be answered by preparing single-component solutions and eye-observing the oxalate precipitation behavior. The observation of the precipitation of each element, being followed the concentrations of Table 1, is represented in Table 2. As expected, oxalate precipitation of Nd always occurred.

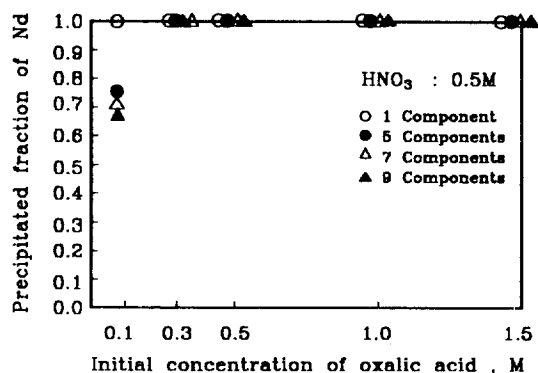


Fig. 5. Effect of oxalic acid concentration on the precipitation of Nd from a simulated solution.

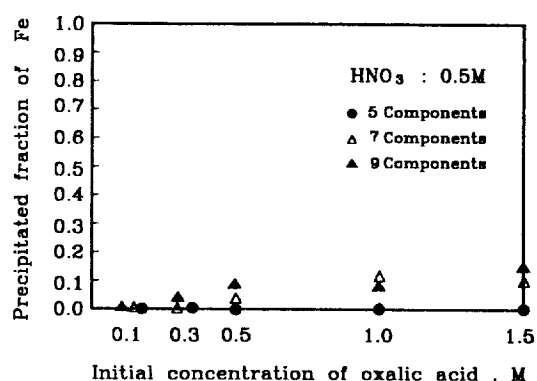


Fig. 8. Effect of oxalic acid concentration on the precipitation of Fe from a simulated solution.

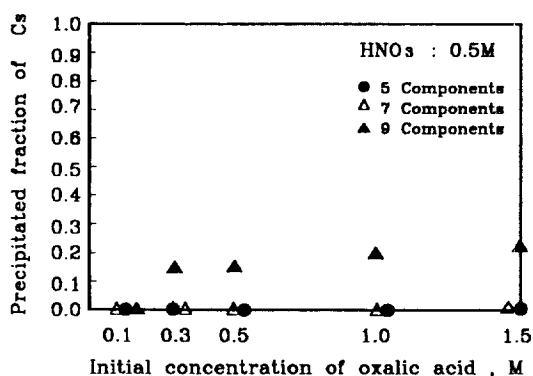


Fig. 6. Effect of oxalic acid concentration on the precipitation of Cs from a simulated solution.

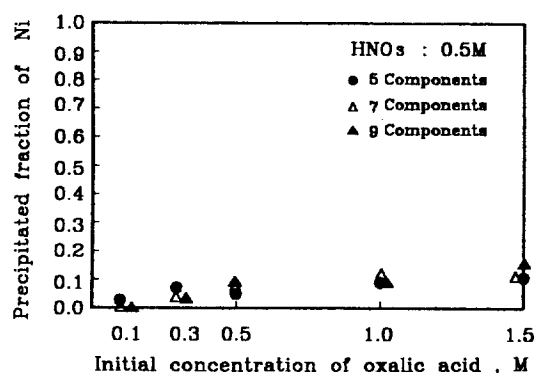


Fig. 9. Effect of oxalic acid concentration on the precipitation of Ni from a simulated solution.

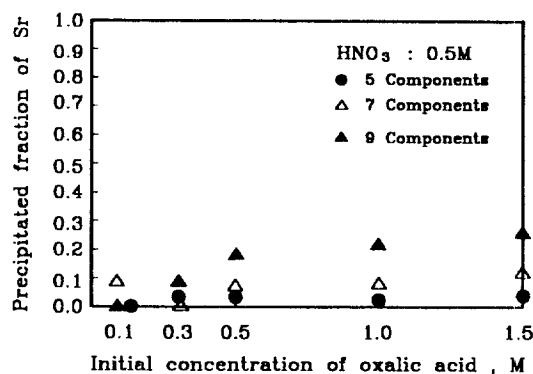


Fig. 7. Effect of oxalic acid concentration on the precipitation of Sr from a simulated solution.

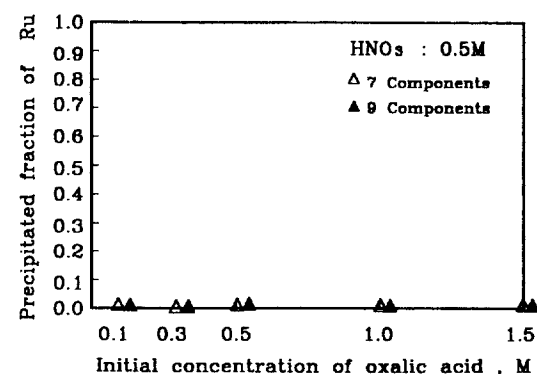


Fig. 10. Effect of oxalic acid concentration on the precipitation of Ru from a simulated solution.

It means that oxalate precipitation of Nd can occur indifferently from other elements composing liquid radwaste. In case of Sr, precipitation was immediately started in a solution without adding HNO_3 , and it was observed with addition of 0.5 M HNO_3 in a day. It indicates that HNO_3 concentration over 0.5 M is desirable to suppress Sr precipitation from the solution. Being similar to the precipitation behavior of Nd, Ni precipitation does not depend on the acidity of HNO_3 . Precipitations of Fe, Ru and Pd did not occur as expected, and Mo and Zr precipitates are not also formed. It agrees with the high solubility for Mo and Zr precipitates due to complex formation of Mo [Shirahashi and Kubota, 1992]

and Zr [Forsberg, 1980] with oxalate. However, Zr precipitation fraction in 9 components solution is 95% in this study, which is in good agreement with the data of the previous report [Kobayashi et al., 1989].

Therefore, it is necessary to examine which element can cause Zr precipitation. Elements, such as Cs, Sr and Pd, expected to be coprecipitated with Zr as described in Sections 1-2 and 2 were introduced to prepare three sets of 2-components solution including Zr. The results of precipitation are represented in Table 3. As shown in Table 3, precipitation in solutions containing Cs, and Sr, respectively, occurred as expected. Especially Zr-Sr pair

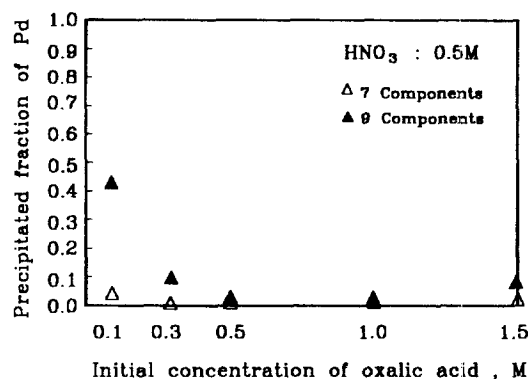


Fig. 11. Effect of oxalic acid concentration on the precipitation of Pd from a simulated solution.

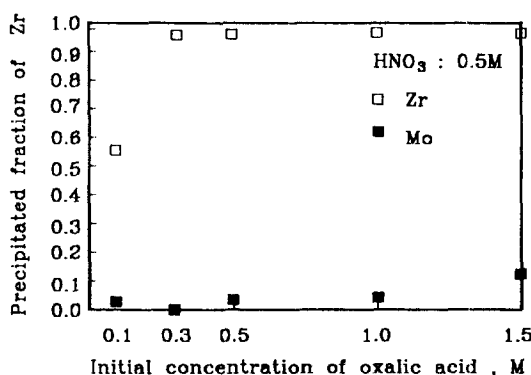


Fig. 12. Effect of oxalic acid concentration on the precipitation of Zr and Mo from the simulated solution of 9 component system.

Table 2. Precipitation characteristics of each element by oxalic acid ($[H_2C_2O_4]$: 0.5 M, initial concentrations of each element; see Table 1)

Element	HNO_3 , M			
	0.0	0.5	1.0	2.0
Nd	P ^{a)}	P	P	P
Sr	P	WP ^{b)}	N ^{c)}	N
Ni	P	P	P	P
Mo	N	N	N	N
Zr	N	N	N	N
Fe	N	N	N	N
Ru	N	N	N	N
Pd	N	N	N	N

a) P: Precipitation, b) Wp: Waiting time of approximately 1 day, c) N: None

was vigorously precipitated in all solutions when 0 to 2 M HNO_3 was added. It is attributed to the possibility in the coprecipitation of Zr-Sr oxalate as described previously. On-going work confirms the compound of Zr-Sr coprecipitate as $SrZrO(C_2O_4)_2 \cdot 6H_2O$ by X-ray analysis [Kim et al.]. In case of Cs-Zr, a very small amount of precipitates was formed approximately in a day. Modeiaios [1966] have reported that gel-like zirconyl oxalate represented by the formula, $ZrO(OH)C_2O_4H$, has an affinity for the alkaline cations such as K^+ or Cs^+ by ionic exchange. In the case of Pd,

Table 3. Coprecipitation characteristics of Zr with each element ($[H_2C_2O_4]$: 0.5 M, initial concentrations of each element; see Table 1)

Element	HNO_3 , M			
	0.0	0.5	1.0	2.0
Cs	P ^{a)}	P ^{a)}	P ^{a)}	P ^{a)}
Sr	P	P	P	P
Pd	None	None	None	None

P: Precipitation.

a): Very small amount of precipitate was formed after 12 hr's aging.

Table 4. Effect of elements in simulated solution on the Am precipitation ($[HNO_3]$: 0.5 M, $[H_2C_2O_4]$: 0.5 M, initial concentrations of each element: see Table 1)

Element	Precipitation	Activity of the solution after precipitation (dpm)	Yield, %
Am	-	4.4×10^3	0
Am-Nd	Precipitation	7	99.998
Am, Nd-Cs, Sr, Fe	Precipitation	4	99.999
Am, Nd-Cs, Sr, Fe-Pd	Precipitation	84	99.979
Am, Nd-Cs, Sr, Fe-Mo, Zr	Precipitation	0	100
Am, Nd-Cs, Sr, Fe-Mo, Zr-Pd	Precipitation	50	99.987

Table 5. Precipitated yield of each element by oxalic precipitation, %

Element	Am	Nd	Cs	Sr	Fe	Ni	Pd	Ru
Yield, %	100	>99	0	<3	<3	<8	0	0

Pd-Zr precipitate was not formed in the present concentration range. This result agrees with that of 9 component as shown in Fig. 11. However, Fig. 11 shows precipitation fraction of Pd increased at oxalic acid below 0.5 M. Although this phenomenon was not clearly examined in this study, it is thought that Pd may be also coprecipitated with Zr at low concentration of oxalic acid.

3. Simulated Radwaste Containing Americium

In the inactive test, the optimum condition was 0.5 M $H_2C_2O_4$ and 0.5 M HNO_3 , at which Nd could be almost recovered as precipitate over 99% and most of other elements remained in the radwaste. At this condition, Am precipitation and effects by other elements on Am precipitations are reported in Table 4. Activity of ^{241}Am used in all experiments was held constant as 4.4×10^3 dpm. This value corresponds to 5×10^{-5} ppm of ^{241}Am concentration at 2 ml of working volume. As shown in Table 4, precipitation did not occur in the solution of ^{241}Am alone. Burney and Porter [1967] have reported that the solubility of Am is 4 ppm at 0.5 M oxalic acid and 0.5 M nitric acid. This satisfies our experimental result which precipitation did not occur at 5×10^{-5} ppm of ^{241}Am concentration.

However, 99.98% recovery of Am as oxalate precipitate were obtained in the binary component solution with 0.04 M Nd. Although the high activity of filtrate was detected in the simulated solution containing Pd, this result does not affect the yields of Am precipitation fractions. It represents that Am^{3+} does not precipitate by itself in oxalic acid solution, but coprecipitates with Nd

as a carrier.

As a final suggestion of optimal condition for oxalate precipitation process, precipitation yields of 8 component radwaste excluding Zr and Mo are listed in Table 5.

This result makes next process easy because the presence of Fe, Cs and Sr causes the third phase formation and the degradation of solvent due to heat generation.

CONCLUSION

Results of the precipitation partitioning of Nd and Am for the simulated liquid radwaste which composed characteristically of Am, Nd, Cs, Sr, Fe, Ni, Pd, Ru, Mo, and Zr, were obtained as follows.

1. With the concentration of 0.5 M oxalic acid and of 0.5 M nitric acid, Am and Nd are precipitated up to 100% and above 99%, respectively, and other elements almost remained in the solution.

2. Zirconium must be separated from the waste solution prior to the precipitation, because the presence of Zr significantly causes the coprecipitations of Cs, Sr, and Pd in radwaste.

3. The precipitation fractions of each element increased with an increased oxalic acid concentration, and decreased with an increased nitric acid concentration, regardless of their composition in the simulated radwaste.

REFERENCES

- Burney, G. A. and Porter, J. A., "Solubilities of Pu(III), Am(III), and Cm(III) Oxalates", *Inorg. Nucl. Chem. Letters*, **3**, 79 (1967).
- Crouthamel, C. E. and Martin, D. S. Jr., "The Solubility of Ytterbium Oxalate and Complex Ion Formation in Oxalate Solutions", *J. Am. Chem. Soc.*, **72**, 1382 (1950).
- Crouthamel, C. E. and Martin, D. S. Jr., "Solubility of the Rare Earth Oxalates and Complex Ion Formation in Oxalate Solution (II), Neodymium(III) and Cerium(III)", *J. Am. Chem. Soc.*, **73**, 569 (1951).
- Forsberg, C. W., "Separation of Americium, Curium, and Trivalent Lanthanides from High-Level Wastes by Oxalate Precipitation: Experiments with Synthetic Waste Solutions", *Nuclear Technology*, **49**, 243 (1980).
- IAEA Technical Reports Series No. 214, "Evaluation of Actinide Partitioning and Transmutation", IAEA, Vienna (1982).
- IAEA Technical Reports Series No. 137, "Chemical Precipitation Process for the Treatment of Aqueous Radioactive Waste", IAEA, Vienna (1992).
- Kim, E. H., et al., in preparation.
- Kobayashi, T., Morita, Y. and Kubota, M., "Development of Partitioning Method: Method of Precipitation Transuranium Elements with Oxalic acid", JAERI-M88-026 (1988).
- Kobayashi, T., Shirahashi, K. and Kubota, M., "Development of Partitioning Method: Precipitation Behavior of Other Elements in Separating the Transuranic Elements Group with Oxalic Acid", JAERI-M89-168 (1989).
- Kubota, M. and Fukase, T., "Formation of Precipitate in High-Level Liquid Waste from Nuclear Fuel Reprocessing", *J. Nuclear Sci. and Tech.*, **17**(10), 783 (1980).
- Miyashio, H. and Kubota, M., "Development of Partitioning Method: Fundamental Study on Oxalate Precipitation Method", JAERI-M86-0144 (1986).
- Medeiros, L. O., "Cation-Exchange Properties of Zirconyl Oxalate Precipitates", *J. Inorg. Nucl. Chem.*, **28**, 599 (1966).
- Posey, J. C., "Process for the Recovery of Cm-244 from Nuclear Waste", ORNL-5687 (1980).
- Rankin, D. T., Burney, G. A., Smith, P. K. and Sission, R. D. Jr., "Precipitation and Characterization of Oxalate-Based $^{237}\text{NpO}_2$ Powder", *Ceramic Bulletin*, **56**(5), 478 (1977).
- Shirahashi, K. and Kubota, M., "Precipitation Behavior of Transuranium Elements during Denitration of High-Level Radioactive Liquid Waste by Formic Acid", *J. Nuclear Sci. and Tech.*, **29**(6), 61 (1992).
- Skalberg, M. and Liljenzin, J.-O., "Partitioning and Transmutation: the State of the Art", *Nuclear Eng. Int.*, **Feb.**, 30 (1990).
- Tedder, D. W. and Blomeke, J. O., "Actinide Partitioning and Transmutation Program Progress Report for Period April 1 to June 30, 1977", ORNL/TM-6056 (1977).