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Study on valence of Pu, Np and Tc in nitric acid after electrolytic reduction

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Abstract

The adjustment of valence of actinides, e.g. U(VI) to U(IV), is one of the most important subject to increase its affinity onto anion exchanger for quantitative recovery of U, Pu and Np in ERIX Process for advanced FBR reprocessing system. For this purpose, nitric acid concentration of spent fuel solution is adjusted to 6 M and then reduced at −300 mV (versus Ag/AgCl) through a novel flow-type electrolysis cell. In this work, valence of Pu, Np and Tc in concentrated nitric acid solution after the electroreduction was studied.

Electroreduction of 6 M HNO_3 solution containing Pu, Np and Tc through flow-type electrolysis cell was examined. According to the UV–vis spectra, Pu and Np were reduced to Pu(III) and Np(IV), respectively. With existence of hydrazine, Pu stably existed as Pu(III) in 6 M HNO_3 solution after electroreduction. However, Pu(III) was liable to be oxidized to Pu(IV) in case of coexisting with Tc or Ru by their catalytic reaction. Especially, oxidation ratio of Pu(III) to Pu(IV) with Ru was faster than that with Tc. Anion exchanger column separation of the reduced solution was also performed. Tc was reduced and separated from Pu and Np which were quantitatively recovered from the column by dilute nitric acid solution. Since Pu was eluted together with the Np(IV), it is presumed that the Pu(III) was oxidized to Pu(IV) inside the anion exchanger column. U, Pu and Np were well separated from fission product elements and this is a promising result for recovering these elements together in FBR reprocessing system.

Keywords: Electrolysis; Reduction; Pu; Np; Ru; Hydrazine

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1. Introduction

Although the Purex process has been applied to commercial reprocessing plants for about 50 years, there are some significant drawbacks such as the generation of a large amount of waste. For the development of the Fast Breeder Reactor (FBR) cycle system for the future, it is strongly desirable to develop a new reprocessing process which uses more compact equipments and produces less radioactive wastes compared to the present PUREX process [1]. For this purpose, we have proposed a novel aqueous reprocessing system named ERIX Process (The Electrolytic Reduction and Ion Exchange Process for Reprocessing Spent FBR-MOX Fuel) [2]. As shown in Fig. 1, this process consists of (1) Pd removal by selective adsorption using a specific anion exchanger; (2) electrolytic reduction for the valence adjustment of the major actinides including U, Pu, Np and some fission products (FP) such as Tc and Ru [3]; (3) anion exchange separation for the recovery of U, Pu and Np using a new type of anion exchanger, AR-01 [4]; (4) selective separation of long-lived minor actinides (MA = Am and Cm) by extraction chromatography [5,6].

In the ERIX Process, valence adjustment of actinides, e.g. U(VI) to U(IV), is one of the most important subject to increase their affinity towards anion exchanger for quantitative recovery of U, Pu and Np. Because tetravalent actinides such as U(IV), Pu(IV) and Np(IV) exhibit distinct adsorption on an anion exchanger as they form anionic nitrato complexes. Moreover, Tc(VII) is the most stable oxidation sate of Tc in spent fuel solution and it is strongly adsorbed onto an anion exchange resin in nitric acid as the form of pertechnetate anion (TcO_4^-). The elution of the adsorbed Tc(VII) from the resin is difficult because of its strong affinity with the resin [7]. It was reported

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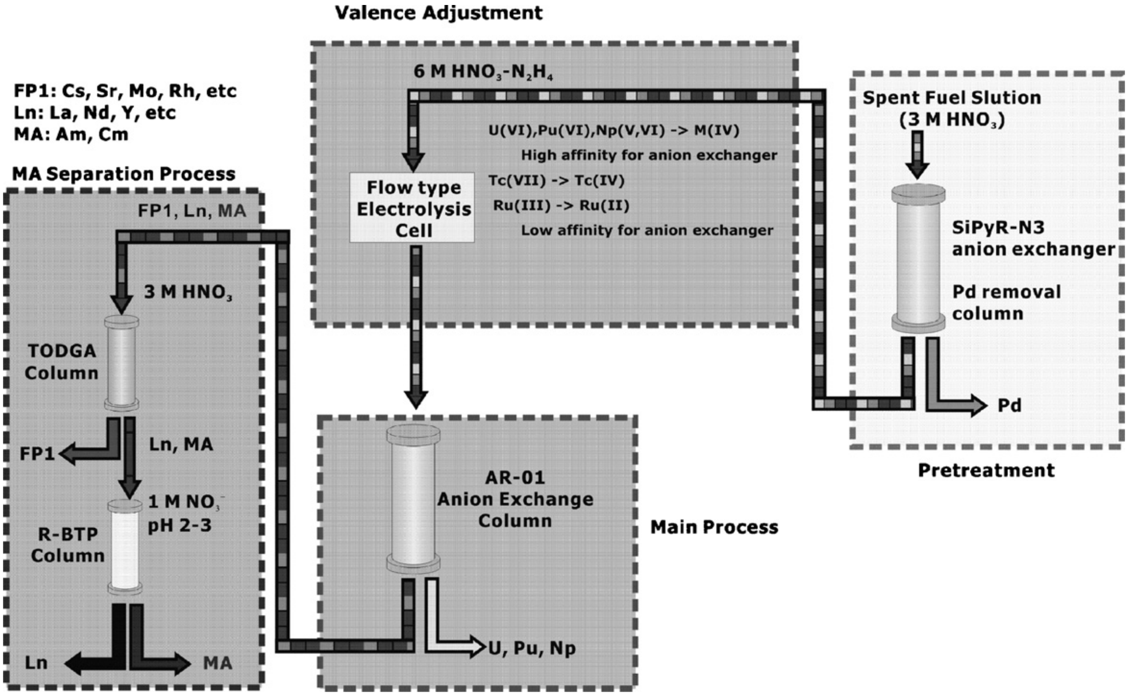

Fig. 1. ERIX Process.

that reduction method was effective for the elution of TcO_4^- from anion resin [8]. In this work, valence of Pu, Np and Tc in concentrated nitric acid solution after the electroreduction was studied.

2. Experimental

2.1. Materials

A stock solution of Pu was prepared by dissolving of PuO_2 into nitric acid solution. It contained ^{241}Am as daughter nuclide, but since Am has no effects on electrolysis, it was used without further purification. ^{99}Tc solution was prepared from NH_4TcO_4 powder (DuPont Co.). A standard solution of ^{237}Np (CERCA) was used. This standard solution contained daughter nuclide ^{233}Pa, but it was used without further purification. Ru was purchased from STREAM CHEMICAL as $Ru(NO)(NO_3)_3$. Hydrazine was used for a scavenger of HNO_2 which occurred during electroreduction.

2.2. Electrolytic reduction

Feed solution was prepared by dilution of definite amount of nuclides into 6 M nitric acid solution. Electroreduction system was composed of a flow-type electrolysis cell (HX-201; Hokuto Co.) as shown in Fig. 2, potentio/galvanostat, and PC for data collection. Counter compartment of electrolysis cell was filled with nitric acid solution of the same concentration as feed solution. The feed solution (20 cm^3) was introduced to the electrolysis cell by a peristaltic pump at 1 cm^3/min. At room temperature, electroreduction was performed at −300 mV (versus Ag/AgCl) constantly. The reduced solution was analyzed by UV–vis spectrophotometry.

2.3. Column separation experiment

Separation experiments for electroreduced solutions were carried out by using a Pyrex®-glass column with 10 mm diameter and 200 mm in length. An anion exchanger resin was transferred to the column in slurry state under 0.2–0.3 MPa of N_2 gas pressure. Head space was adjusted to near zero with a mobile plug. The bed volume (BV) of the resin was 15.7 cm^3. Prior to the separation experiment, dead volume (DV) was measured and the resin was conditioned by passing an excess amount of 6 M HNO_3. All the mobile phases (Table 1) were pumped at 1 cm^3/min by a peristaltic pump and the effluents were collected in 1 cm^3 aliquots. The activity and metal concentration in the effluents were determined by gamma spectrometry (GMX-20190-P; ORTEC), 10 channel low-level counter (LB770; BERTHOLD) and ICP-AES (ICPS-1000; Shimadzu) in glove box, respectively.

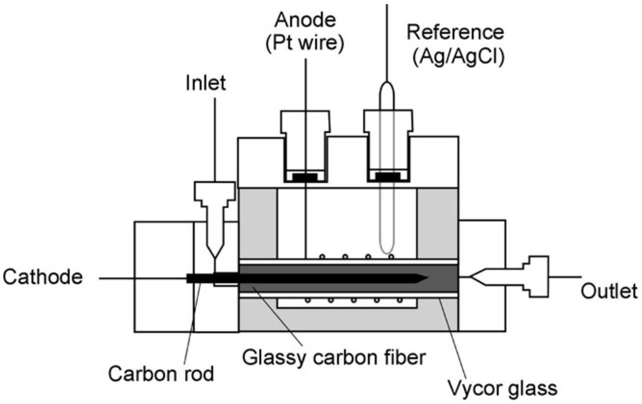

Fig. 2. Flow-type electrolysis cell.

Table 1
Mobile phases of column separation

Eluent	Volume (cm^3)	Time (min)
Feed	2.5	2.5 (0–2.5)
6 M HNO_3	5.5	5.5 (2.5–8.0)
0.5 M HNO_3	17	17 (8.0–25)

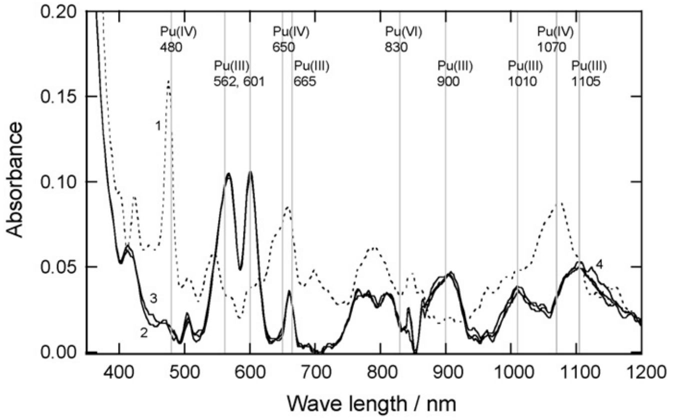

Fig. 3. UV–vis spectra of Pu solution; 1 mM Pu + 1 M N_2H_4 in 6 M HNO_3. (1) Before electrolysis, (2) 16 min, (3) 32 min, and (4) 54 min after electrolysis.

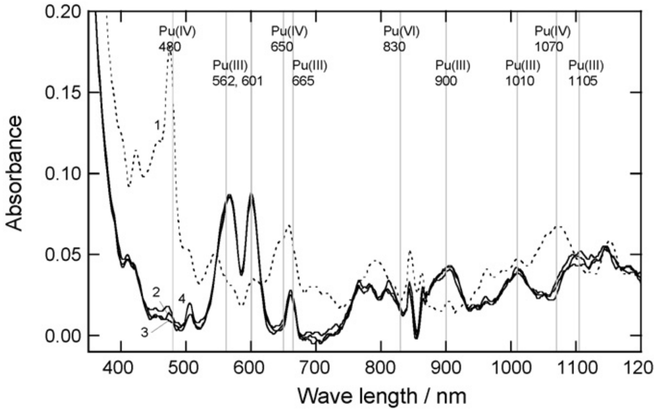

Fig. 5. UV–vis spectra of Pu–Ru solution; 1 mM Pu + 1 mM Ru + 1 M N_2H_4 in 6 M HNO_3. (1) Before electrolysis, (2) 4 min, (3) 8 min, and (4) 12 min after electrolysis.

3. Results and discussion

3.1. Electrolytic reduction

UV–vis spectra of Pu solution before and after the electrolysis are shown in Fig. 3. No Pu(III) was detected before electrolysis by its typical absorption peaks, i.e. 480 and 1070 nm. Pu solution was quantitatively reduced to Pu(III) after passing through the flow-type electrolysis cell. Pu(III) was not oxidized within about an hour.

UV–vis spectra of Pu–Tc solution before and after electrolysis are shown in Fig. 4. Some air bubbles were observed not only during electrolysis but also after the electrolysis owing to decomposition of HNO_3. It was difficult to estimate Pu(IV) concentration from the absorption peak at 480 nm, because a large absorption peak of reduced Tc was observed in short wavelength range. However, no absorption peak of Pu(IV) at 1070 nm indicates that Pu(IV) was completely reduced to Pu(III).

Ru is a complicated fission product elements in reprocessing system [9] and its nitrosyl nitrato complexes include numerous monocular, neutral, anionic and cationic species [10]. The presence of Ru(III) in nitric acid solutions accelerate the oxidation of Pu [11]. The standard redox potential of Ru^{3+}/Ru^{2+} is 0.249 V [12]. Thus, Ru(III) is reduced to Ru(II) in this process and adsorption behavior of Ru onto anion exchanger resin is changed. UV–vis spectra of Pu–Ru solution before and after electrolysis are shown in Fig. 5. As the result, majority of Pu(IV) was reduced to Pu(III).

As described above, Pu was quantitatively reduced to Pu(III) immediately after the electrolysis even when a catalytic element, such as Tc or Ru, existed in the solution. Subsequently, long term stability of Pu(III) was examined. UV–vis spectra of reduced Pu solution after 1, 2, 3, 4, and 7 days after the electrolysis are shown in Fig. 6. The shape of spectra remained unaltered until 1 week, indicating Pu(III) was stable. Pu(III) is usually unstable in acidic medium, but it was indicated that hydrazine worked effectively as an stabilizing reagent.

UV–vis spectra of the reduced Pu–Tc solution after 1, 2, 3, 4, and 7 days after the electrolysis are shown in Fig. 7. The absorption peak of Pu(III) remained unchanged until 3 days after the electrolysis. But, the peak height decreased after 4 days and it finally disappeared after 1 week. A peak which appeared around 1070 nm after 1 week shows that Pu(III) was oxidized to Pu(IV). Thus, oxidation from Pu(III) to Pu(IV) was promoted by Tc.

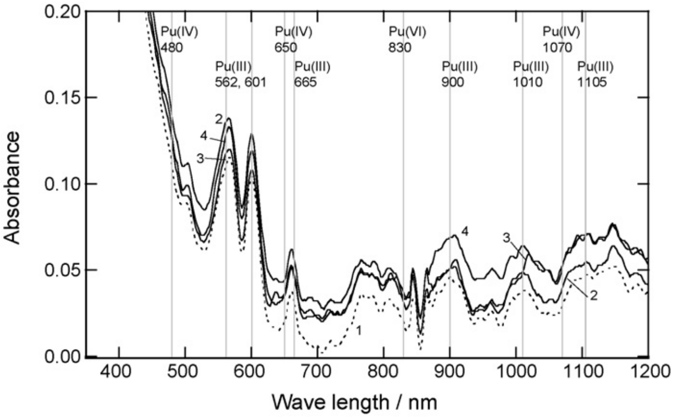

Fig. 4. UV–vis spectra of Pu–Tc solution; 1 mM Pu + 1 mM Tc + 1 M N_2H_4 in 6 M HNO_3. (1) Before electrolysis, (2) 4 min, (3) 8 min, and (4) 13 min after electrolysis.

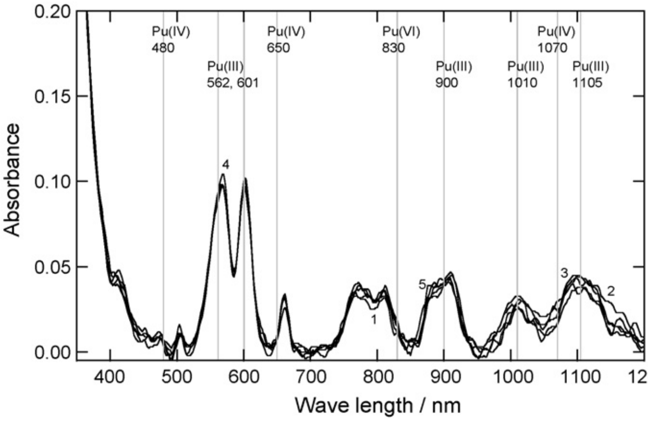

Fig. 6. UV–vis spectra of Pu solution; 1 mM Pu + 1 M N_2H_4 in 6 M HNO_3. (1) 1 day, (2) 2 days, (3) 3 days, (4) 4 days, and (5) 7 days after electrolysis.

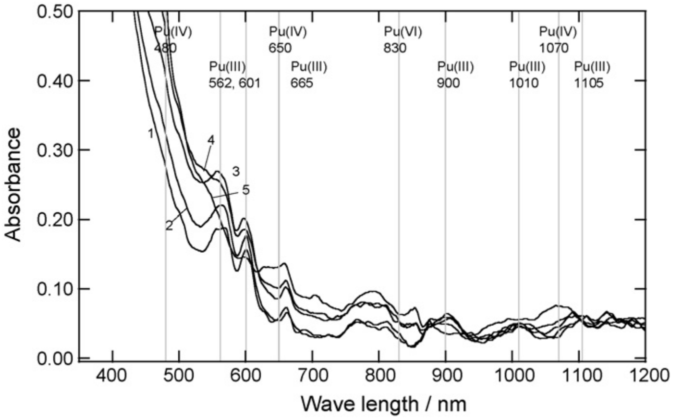

Fig. 7. UV–vis spectra of Pu–Tc solution; 1 mM Pu + 1 mM Tc + 1 M N_2H_4 in 6 M HNO_3. (1) 1 day, (2) 2 days, (3) 3 days, (4) 4 days, and (5) 7 days after electrolysis.

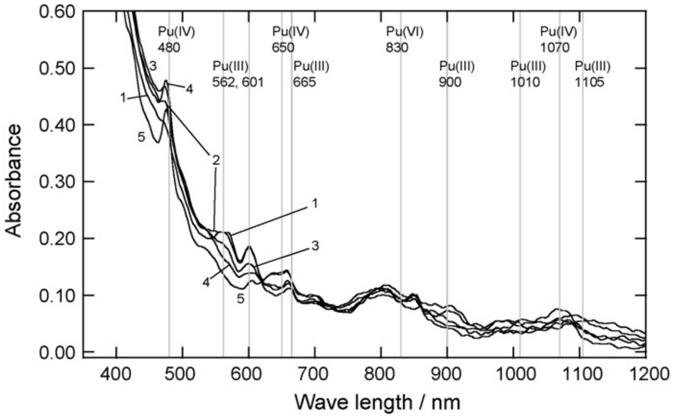

Fig. 9. UV–vis spectra of U–Pu–Np–Tc–Ru solution; 1 mM U + 1 mM Pu + 1 mM Np + 1 mM Tc + 1 mM Ru + 1 M N_2H_4 in 6 M HNO_3. (1) 1 day, (2) 2 days, (3) 3 days, (4) 4 days, and (5) 7 days after electrolysis.

UV–vis spectra of the reduced Pu–Ru solution after 1, 2, 3, 4, and 7 days from the electrolysis are shown in Fig. 8. As shown in Fig. 5, Pu(IV) was reduced to Pu(III) immediately after the electrolysis even when Ru was contained in the nitric acid solution. However, an apparent absorption peak of Pu(IV) was observed a day after the electrolysis while the shape of absorption peak remained unaltered until 1 week. It was different from the results with Pu–Tc solution shown in Fig. 7. Since oxidation of Pu did not proceed completely, Pu(III) was probably oxidized through redox reaction with a small amount oxidant through catalytic action of Tc.

UV–vis spectra of the reduced U–Pu–Np–Tc–Ru solution after 1, 2, 3, 4, and 7 days after the electrolysis are shown in Fig. 9. There was no absorption peak of Pu(IV) 1 day after the electrolysis. But, absorption peak of Pu(IV) was observed 2 days after the electrolysis and the absorption peak of Pu(III) decreased. Though small peak of Pu(III) remained after 7 days, most of Pu was oxidized to Pu(IV). It took 2 or 3 days for Pu(IV) to appear. It was rather longer than in the case of Pu–Ru solution. In this experiment, U(IV) existed in the solution and the oxidized Pu(IV) was reduced again by U(IV) and U(IV) was oxidized faster than Pu(III).

3.2. Separation by anion exchanger column

A chromatogram of electroreduced Pu solution through an anion exchanger column is shown in Fig. 10. Am(III) was not adsorbed onto anion exchanger column and passed thorough it. The recovery ratio of Am was 100%. It was confirmed by UV–vis spectra shown above that Pu was reduced to Pu(III). However, the recovery ratio of eluted Pu together with Am(III) (peak I) was 81.1% of fed amount. Second peak eluted by dilute nitric acid solution contained 2.5% of fed Pu. From this result, it is considered that peak I was Pu(III), peak II was Pu(IV) and some amount of Pu was remained in anion exchanger column as Pu(IV). Once reduced Pu(III) was oxidized during the column separation procedure.

Tc(VII) is the most stable oxidation state of Tc in spent fuel solution and it is strongly adsorbed onto an anion exchange

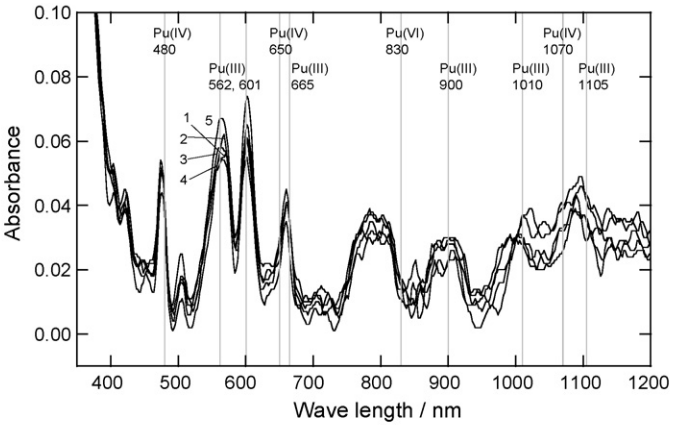

Fig. 8. UV–vis spectra of Pu–Ru solution; 1 mM Pu + 1 mM Ru + 1 M N_2H_4 in 6 M HNO_3. (1) 1 day, (2) 2 days, (3) 3 days, (4) 4 days, and (5) 7 days after electrolysis.

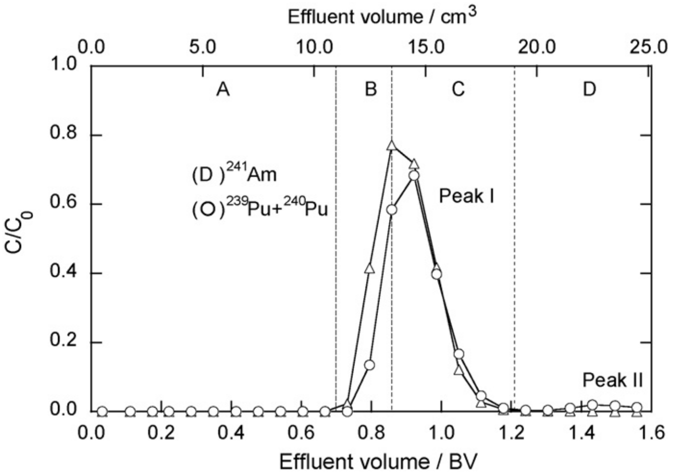

Fig. 10. Chromatogram of reduced Pu solution. Feed: electroreduced 1 mM Pu + 1 M N_2H_4 in 6 M HNO_3. (A) DV, (B) feed, (C) 6 M HNO_3, and (D) 0.5 M HNO_3.

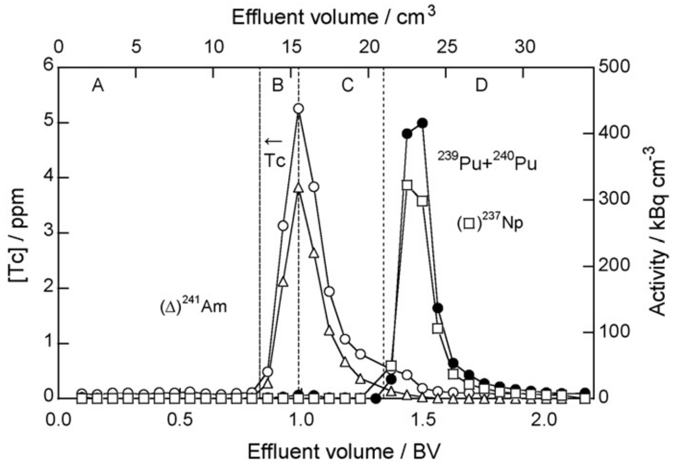

Fig. 11. Chromatogram of reduced Pu, Np, Tc and Ru solution. Feed: electroreduced 1 mM Pu + 1 mM Np + 1 mM Tc + 1 mM Ru + 1 M N_2H_4 in 6 M HNO_3. (A) DV, (B) feed, (C) 6 M HNO_3, and (D) 0.01 M HNO_3.

resin in nitric acid in the form of pertechnetate anion (TcO_4^-). Therefore, quantitative recovery of Tc from anion exchanger column is one of the important subjects in this process. A chromatogram of electroreduced mixture solution of Pu, Np, Tc and Ru is shown in Fig. 11. The electroreduced solution was pumped at 1 cm^3/min and passed through the column less than 10 min. Am(III), non adsorptive specie, passed through the column and was eluted first. Because Tc showed no adsorption onto anion exchanger column and was eluted together with Am(III), Tc(VII) was reduced to Tc(IV) or Tc(II) [13]. Tc was separated from actinides, U, Pu, and Np, through anion exchanger column after electro reduction. Np and Pu were eluted together by dilute nitric acid solution as tetravalent species. The ratio of Pu recovered as trivalent was about 1.4% of fed amount. About 80% of Pu was recovered as trivalent species in the above experiment, on the other hand, most of Pu was recovered as tetravalent species in this experiment. As described above, most amount of Pu was oxidized by Tc or Ru.

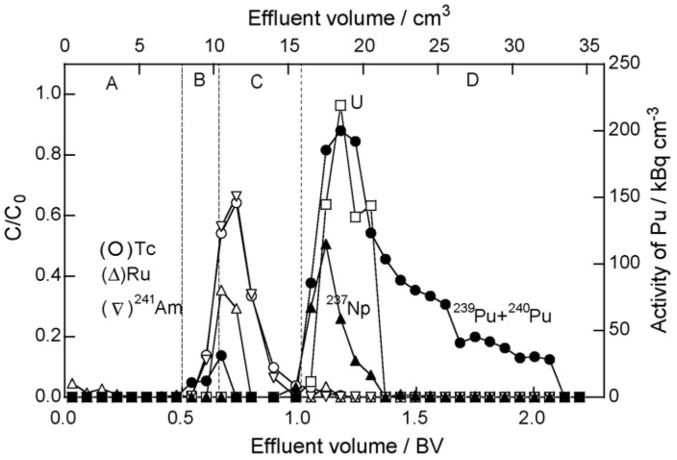

Fig. 12. Chromatogram of reduced U, Pu, Np, Tc and Ru solution. Feed: 1 mM U + 1 mM Pu + 1 mM Np + 1 mM Tc + 1 mM Ru + 1 M N_2H_4 in 6 M HNO_3. (A) DV, (B) feed, (C) 6 M HNO_3, and (D) 0.01 M HNO_3.

A chromatogram of electroreduced mixture solution of U, Pu, Np, Tc and Ru is shown in Fig. 12. Am, Ru and electroreduced Tc were eluted first because of their weak adsorption onto anion exchanger. Finally, U, Pu and Np were recovered by passing dilute HNO_3 solution. U, Pu and Np were well separated from fission product elements and it is a promising result for recovering these elements together in FBR reprocessing system.

4. Conclusions

Pu(IV) was reduced to Pu(III) through a flow-type electrolysis cell. About 20% of Pu was reoxidized during anion exchanger column separation procedure. Tc was reduced from Tc(VII) to Tc(IV) or Tc(II). The reduced Pu(III) was mostly oxidized to Pu(IV) when Tc or Ru exists in solution.

Electroreduction of 6 M HNO_3 solution containing Pu, Np and Tc through the flow-type electrolysis cell was examined. According to the UV–vis spectra, Pu and Np were reduced to Pu(III) and Np(IV), respectively. In presence of hydrazine, Pu stably existed as Pu(III) in 6 M HNO_3 solution after electroreduction. However, Pu(III) was liable to be oxidized to Pu(IV) in case of coexistence with Tc or Ru by their catalytic reaction. Especially, oxidation rate of Pu(III) to Pu(IV) with Ru was faster than that with Tc. Anion exchanger column separation of the reduced solution was also performed. It was confirmed that all the Np was reduced to Np(IV). Np was quantitatively recovered by dilute nitric acid solution. As Pu was eluted together with Np(IV), Pu(III) was oxidized to Pu(IV) within the anion exchanger column. U, Pu and Np were well separated from fission product elements, It is a promising result for recovering these elements together in FBR reprocessing system.

Acknowledgments

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