Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Kwang-Wook Kim[a]; Eil-Hee Lee[a]; Young-Joon Shin[a]; Jae-Hyung Yoo[a]; Hyun-Soo Park[a]
[a] NUCLEAR ENVIRONMENT MANAGEMENT CENTER KOREA ATOMIC ENERGY RESEARCH INSTITUTE YUSONG, TAEJEON, KOREA

To cite this Article Kim, Kwang-Wook , Lee, Eil-Hee , Shin, Young-Joon , Yoo, Jae-Hyung and Park, Hyun-Soo(1995) 'Removal of Residual Uranium in Simulated Radwaste Solution by TBP Extraction', Separation Science and Technology, 30: 17, 3351 — 3362

To link to this Article: DOI: 10.1080/01496399508013150

URL: http://dx.doi.org/10.1080/01496399508013150

SEPARATION SCIENCE AND TECHNOLOGY, **30**(17), pp. 3351–3362, 1995

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KWANG-WOOK KIM, EIL-HEE LEE, YOUNG-JOON SHIN,
JAE-HYUNG YOO, and HYUN-SOO PARK
NUCLEAR ENVIRONMENT MANAGEMENT CENTER
KOREA ATOMIC ENERGY RESEARCH INSTITUTE
YUSONG P.O. BOX 105, TAEJEON, KOREA

ABSTRACT

The extraction behavior of uranium in a multicomponent system simulated on the basis of high-level liquid waste was examined in order to find effective conditions for the removal of residual uranium in a simulated radwaste solution by the TBP solvent extraction method. While the conventional semiempirical equation for the distribution coefficient of uranium could be used in a system composed of only uranium and nitric acid, it was found to be unsuitable for a multicomponent system where the concentration of uranium is not dominant. Uranium extractability by TBP was found to be limited in multicomponents systems regardless of high TBP concentration, phase ratio, and extraction times because of the presence of neodymium and iron together with uranium in the systems.

INTRODUCTION

Introduction of the concept of partitioning and transmutation of long-lived radionuclides to manage high-level liquid waste (HLLW) will be beneficial in achieving public acceptance and will become essential technology to future radioactive waste management (1–6). It could also become a leading future technology while boosting other nuclear industries (7–9). If longed-lived radionuclides are to be transmuted in a special reactor or an accelerator, they should first be separated chemically into several groups according to their characteristics including the minor actinide group, the Cs-Sr group of major heat-generating nuclides of HLLW, the platinum group, and the other fission products groups (9–16). This is called group separation. For this, a combination of several unit chemical separation methods, including solvent extraction, ion exchange, crystallization–precipitation, and adsorption should be used to meet a given criteria of hazard assessment based on maximum permissible concentration (MPC) (5, 13, 17) with satisfactory separation efficiency (1–16).

Residual U (or Pu) existing in low content in HLLW must usually be removed from the solution as the first step because it could affect the separation efficiency of the succeeding steps of the group separation process. An effective conventional method for removing U (or Pu) is by solvent extraction using the extractant tributyl phosphate (TBP). The relationship of U and Pu with TBP is well known (18–21), but data collected to date are for U (or Pu) as a single system or for cases where the concentration of U (or Pu) is dominant compared with other elements in such multicomponent systems as spent nuclear fuel. It is expected that the relationship between U and TBP in a HLLW containing multicomponents will be different from that of U in the single component state or in the dominant state. However, there are few reports about the degree of extraction of U by TBP in multicomponent systems where the concentration of U is low compared with the other elements.

For this work the extraction behavior of residual U in simulated radwaste solutions by TBP was analyzed in order to determine the effective conditions for the removal of U. The effects of other elements existing with U on the extraction of U were examined.

EXPERIMENTAL

The simulated solution was prepared with a few major elements representing the HLLW on the basis of material from the PNC (Power Reactor and Nuclear Fuel Development Corporation in Japan) (1–5). The concentration of nitric acid was fixed at 2.0 N. The selected elements, their chemical formulas, and their concentrations are listed in Table 1. All chemicals were of reagent grade.

For the extraction experiments, a simulated solution of 3 mL was mixed at 25 ± 0.5°C for 15 minutes with the organic phase of TBP/*n*-dodecane presaturated with 2.0 N nitric acid. Then 250 μL of the raffinate solution after extraction was sampled for analysis. The experimental parameters and their ranges are shown in Table 2. The concentrations of all elements were measured by induced coupled plasma spectroscopy (Model: Jobinyvon JY38 plus).

TABLE 1
Elements and Their Concentrations in Simulated Solution

Element	Concentration	Chemical formula
U	0.0084 M (2.0 g/L)	$UO_2(NO_3)_2 \cdot 6H_2O$
Nd	0.043 M (6.2496 g/L)	$Nd(NO_3)_3 \cdot 6H_2O$
Eu	0.0019 M (0.2888 g/L)	$Eu(NO_3)_3 \cdot 5H_2O$
Zr	0.0690 M (6.279 g/L)	$ZrO(NO_3)_2$
Cs	0.0371 M (4.934 g/L)	$CsNO_3$
Sr	0.0165 M (1.452 g/L)	$Sr(NO_3)_2$
Fe	0.0380 M (2.128 g/L)	$Fe(NO_3)_3 \cdot 9H_2O$
Ru	0.0340 M (3.434 g/L)	$RuNO(NO_3)_3$
Mo	0.0690 M (6.624 g/L)	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$
La	0.0147 M (2.042 g/L)	$La(NO_3)_3 \cdot 5H_2O$
Y	0.0084 M (0.747 g/L)	$Y(NO_3)_3 \cdot 5H_2O$

TABLE 2
Experimental Parameters and Their Ranges

TBP vol%	Phase ratio (org/aq)	Extraction times
5–30	0.5–4	1–4

RESULTS AND DISCUSSION

Extraction Behavior of Elements toward TBP

The distribution coefficients of the individual elements in a single component system by our experiment and in previous papers, and the experimental values of the same elements in a multicomponents system with 30 vol% TBP and a phase ratio of 1 are shown in Table 3. The distribution coefficients of all elements except U in the case of the multicomponent system are similar to those reported in the single component system (18–25) It is peculiar that the experimental value of U in the multicomponents system differs so much from the experimental value and the value reported for the single component state. The concentrations of several elements in the aqueous phase after extraction, i.e., remaining degrees of the elements in the aqueous phase after extraction $[(C_{\text{aq, raffinate}}/C_{\text{aq, initial}}) \times 100]$, are shown in Fig. 1 with changes of the TBP vol% and the phase ratio at a nitric acid concentration of 2.0 N. There is hardly any change in the concentration of U for a TBP concentration of more than 15 vol% and a phase ratio above 2. The extractabilities of Ru and Zr become signifi-

TABLE 3
Distribution Coefficients of Several Elements with TBP (30 vol%) at 2 N HNO_3

Element	Distribution coefficient In reference	In single component system by experiment	In multicomponent system by experiment	Extractability
U	~15.9 (25)	15.6	2.1	
Zr	~0.1 (18)	0.34	0.33	
Ru	~0.15 (18)	0.19	0.15	
Eu	~0.02 (21)	0.03	0.07 ± 0.03	
Nd	~0.02 (21)	0.01	0.04	
Fe	<~0.001 (19)	<0.01	<0.01	None
Mo	<~0.001 (19)	<0.01	<0.01	None
Cs	<~0.001 (19)	<0.01	<0.01	None
Sr	<~0.001 (19)	<0.01	<0.01	None

cant above 20 vol% TBP and increase more drastically with an increase of the phase ratio. The concentrations of Fe, Cs, Sr, and Mo are almost the same as they were in the initial solution before extraction under any conditions. In other words, they could be said to have almost no extractability.

Extraction Behavior of U in the Multicomponent System

The concentrations of U in the aqueous phase in the single component and multicomponent states after extraction are shown in Fig. 2 with changes of TBP vol% and phase ratio with 2.0 N nitric acid. The concentration in the single component system with only U decreases distinctly with increases of TBP vol% and the phase ratio. The remaining degree of U in the aqueous phase could easily be less than 10% of the initial concentration under the proper conditions, i.e., with TBP of more than 15 vol% and the phase ratio above 2. However, the concentration of U in the multicomponent system is more than that of the single component system by about 20%, and the remaining degree is less than 30% in spite of the high TBP vol% and phase ratio.

The concentrations of U, Ru, and Zr in the aqueous phase after extraction are shown in Fig. 3 with changes of extraction times and the phase ratio for TBP of 15 vol%, where the extraction time indicates the contact number of the aqueous phase with a fresh TBP phase. The concentration of Zr does not change perceptibly because Zr is hardly extracted with 15

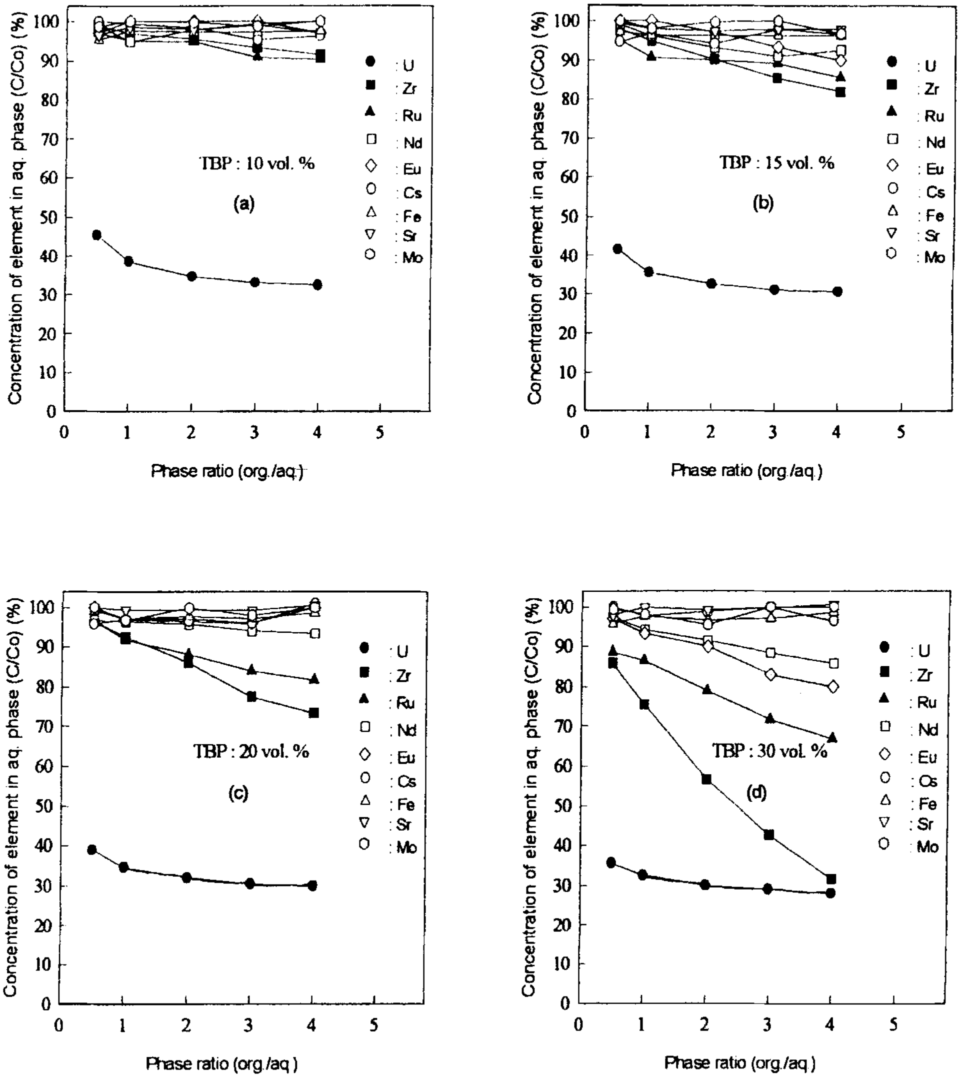

FIG. 1 Concentrations of several elements in aqueous phase after extraction with changes of TBP vol% and phase ratio (HNO_3, 2 N).

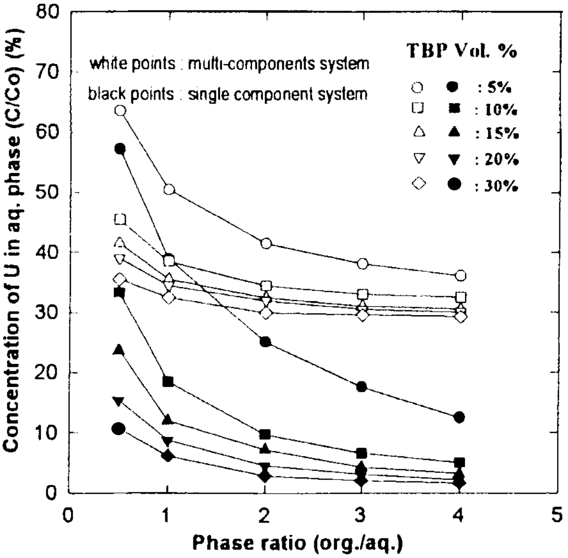

FIG. 2 Concentration of uranium in aqueous phase with single component and multicomponents after extraction with changes of TBP vol% and phase ratio (initial concentration of U, 2 g/L; HNO_3, 2 N).

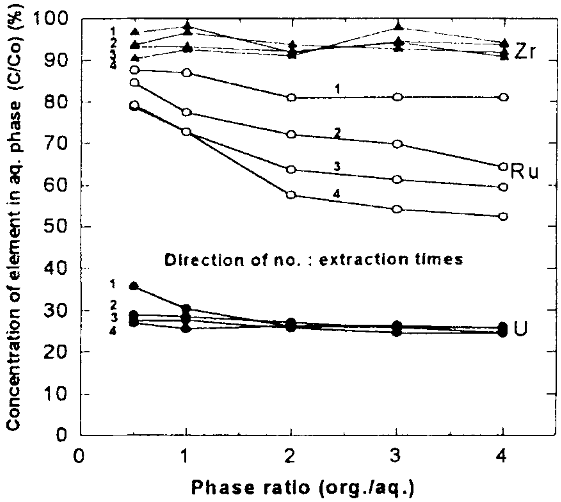

FIG. 3 Concentration of several elements in aqueous phase with multicomponents after extraction with changes of phase ratio and extraction times.

vol% TBP based on the results of Fig. 2. The extraction rate of Ru toward TBP is known to depend on the time of extraction, so that an increase in the time of extraction with the organic phase means an increase in the total time of extraction of Ru by TBP (24). Therefore, as shown in Fig. 2, the concentration of Ru increases with a change of the number of extraction times. In the case of U, however, the concentration is hardly affected by the number of extraction times.

Figure 4 shows the experimental distribution coefficients of U in the single component and multicomponent systems and one calculated by a semiempirical equation (25) with a change of TBP concentration. The experimental results of the single component system agree with the calculated ones, but those of the multicomponent system are much lower than those of the calculated ones. Figure 5 shows the effect of the initial concentration of U in the multicomponent system on the distribution coefficient of U and on the concentration of U in the aqueous phase after extraction. The distribution coefficient of U must theoretically increase with a decrease of the initial concentration of U, in agreement with the results calculated by the two conventional semiempirical equations (25, 26). The experimental results, however, are the reverse to the calculated ones when the initial concentration of U in the aqueous phase is less than 5 g/L. The values approach the calculated ones as the initial concentration increases.

Summarizing the results of Figs. 1 through 5, when U coexists with several different elements and its concentration is comparatively low, the

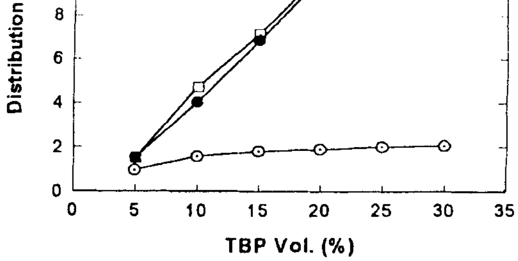

FIG. 4 Distribution coefficients of uranium with a change of TBP vol% by experiment and SEPHIS code (25) (initial concentration of U, 2 g/L; HNO_3, 2 N).

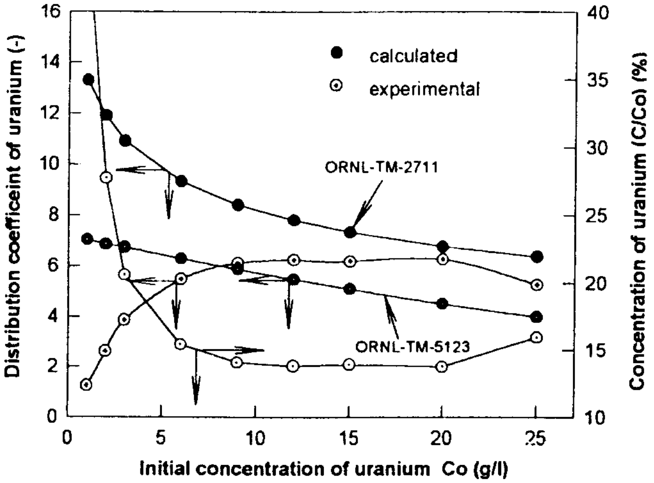

FIG. 5 Distribution coefficient and concentration of uranium in aqueous phase with a change of initial concentration of uranium in aqueous phase.

extractability of U by TBP is suppressed by some causes which might be due to the nonideality of the solution or some complex formation between U and some other elements.

Effect of Several Elements on Extraction of U in the Multicomponent System

In order to find the reason for the poor extractability of U in the multicomponent system, the concentrations of U after extraction in several aqueous solutions prepared by systematically adding all elements one by one into the U single solution were measured and are plotted in Fig. 6. First, a few systems prepared involving Ru, i.e., U + Ru + other element, were examined because Ru has been known to be a troublesome element in the PUREX process. The results of all systems except U + Ru + Nd and U + Ru + Fe are closely similar to those of the U single system. This means that Ru itself and other elements such as Mo, Zr, Sr, Cs, and Eu basically have no effect on the extraction of U in the multicomponent system, but Ru + Nd or Nd itself, and Ru + Fe or Fe itself do. In order to elucidate these results, systems of U, U + Nd, U + Fe, U + Ru + Nd, U + Ru + Fe, and U + Ru + Nd + Fe + other elements, such as Sr, Cs, La, Y, and Eu, were added step by step and checked out. The results are plotted in Fig. 7. The result of U + Nd and U + Fe are similar to ones of U + Ru + Nd and U + Ru + Fe, respectively. The results

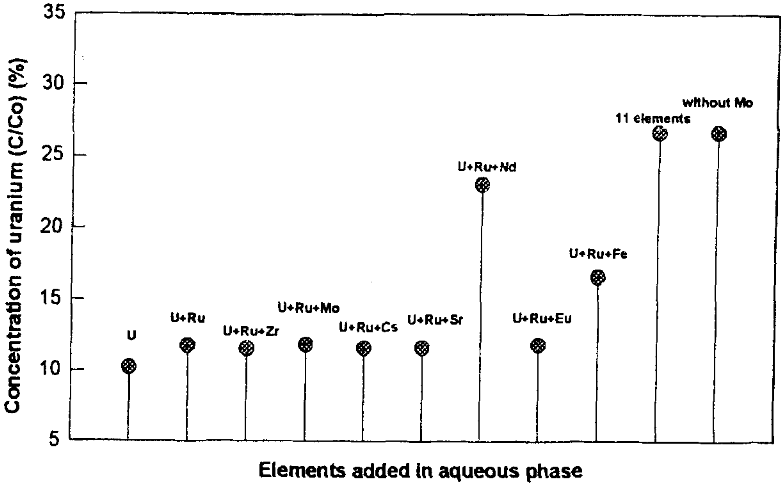

FIG. 6 Effect of elements added in aqueous phase on the concentration of uranium remaining in aqueous phase after extraction (TBP, 15 vol%; phase ratio, 1; HNO_3, 2 N).

of other systems including U + Ru + Nd + Fe agree with those of the multicomponent systems including all elements. The result of the system without Nd and Fe is closely similar to that of the U single system. Figure 8 shows the extraction results of U in a single system and in the multicomponent system of 11 elements by 15 and 30 vol% TBP, respectively. In the case of the U single system, the result of 30 vol% TBP is half that by 15 vol% TBP. However, in the case of multicomponent systems, there is not much difference. It is also thought to result from the effect of Nd and Fe. Figure 9 shows that the concentration of U in aqueous solution after extraction with a change of extraction times in the U single system, in the multicomponent system of 11 elements, and in the multicomponent system without Nd and Fe, respectively. In the cases of the U single system and the multicomponent system without Nd and Fe, the results agree well with each other and the concentration of U approaches to zero after 3 times, as expected. However, in the case of the multicomponent system, the degree of extraction of U is not affected by the extraction times after 1 time, as in the result of Fig. 3. If the poor extractability of U in the multicomponent system is not due to Nd and Fe but to other reasons, such as an error in analyzing for the concentration of U, the concentration of U in the aqueous phase, including the multicomponents in Figs. 8 and 9, should change distinctly according to the changes of TBP concentration or extraction times. Therefore, the results depicted in Fig.

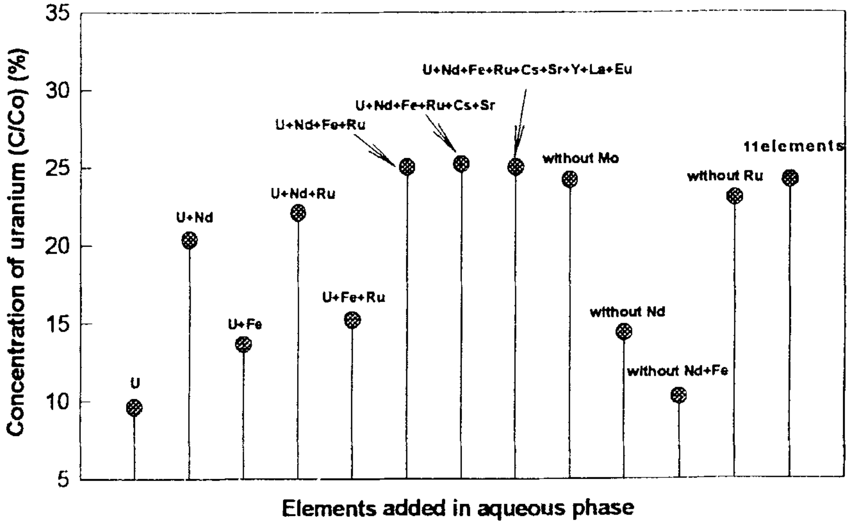

FIG. 7 Effect of elements added in aqueous phase on the concentration of uranium remaining in aqueous phase after extraction (TBP, 15 vol%; phase ratio, 1; HNO_3, 2 N).

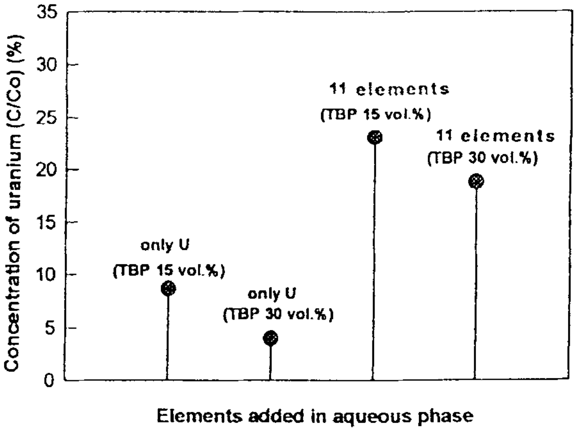

FIG. 8 Concentrations of uranium in aqueous phases of only uranium and 11 elements after extraction with TBP of 15 and 30 vol%, respectively (phase ratio, 1; HNO_3, 2 N).

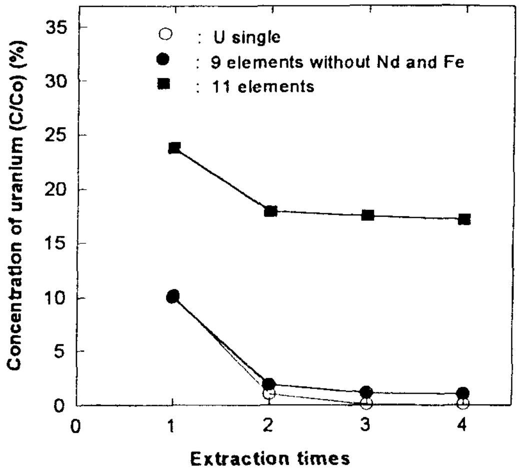

FIG. 9 Concentration of uranium in aqueous phase after extraction in a single uranium system and in multicomponent systems with and without Nd and Fe with a change of extraction times (TBP, 15 vol%; phase ratio, 1; HNO_3, 2 N).

8 were reconsidered to again confirm that the poor extractability is due to some action of Nd and Fe in the solution.

In closing, it could be said that the presence of Nd and Fe among the multicomponents results in the low extractability of U by TBP. However, as the initial concentration of U in the multicomponent system becomes dominant, the effect of Nd and Fe on the extraction is screened and the degree of extraction of U increases. And the behavior of U toward TBP could be predicted by conventional empirical equations for the distribution coefficient of U in the TBP–HNO_3 system. A phenomenon similar to the suppressed extractability by TBP of uranium in our study has been reported by some scientists (27). They observed a considerable decrease in the plutonium distribution coefficient in a high-level radwaste solution as the plutonium concentration became lower in consecutive stages. They did not supply any explanation.

It cannot be explained at the moment how Nd and Fe act on the extraction of U with TBP, but further research will be done to study the relation of Nd and Fe and the extraction.

CONCLUSION

The degree of removal of residual U (2 g/L) in simulated radwaste by TBP did not exceed around 70% of the initial concentration of U.

The extraction behavior of U by TBP in multicomponent systems could not be anticipated by the conventional semiempirical equation, but it could be determined when the concentration of U in the system was more than 5 g/L.

The low extractability of U by TBP in a multicomponent system was due to Nd and Fe coexisting in the solution.

REFERENCES

1. M. Kubota, Y. Morita, O. Tochiyama, and Y. Inoue, JAERI-M 88-002 (1988).
2. Y. Kondo, M. Kubota, T. Abe, and K. Nagato, JAERI-M 91-47 (1991).
3. T. Fujiwara, K. Shirahashi, Y. Morita, and M. Kubota, JAERI-M 90-178 (1990).
4. M. Kubota, I. Yamaguchi, H. Nakamura, S. Tachimori, and K. Sato, JAERI-M 9627 (1981).
5. M. Kubota and H. Nakamura, JAERI-M 85-066 (1985).
6. H. Koyama, *Nucl. Eng. Jpn.*, *35*, 37 (1989).
7. T. Takahashi and A. Yamashita, *Ibid.*, *35*, 26 (1989).
8. K. H. Byun, D. Y. Chung, J. H. Yoo, H. S. Park, and I. S. Suk, *Chem. Ind. Technol.*, *9*, 18 (1991).
9. M. Kubota, JAERI-M 85-030 (1985).
10. IAEA, Technical Report Series No. 214, International Atomic Energy Agency, 1982.
11. G. F. Vandegrift et al., ANL-84-85, Argon National Laboratory, 1984.
12. J. Davis and J. A. Paisner, UCID-20448, Lawrence Livermore National Laboratory, 1985.
13. M. Kubota, *J. At. Energy Soc. Jpn.*, *29*, 775 (1987).
14. M. Bresesti, STI/DOC/10/214, International Atomic Energy Agency, 1982.
15. Z. Kolarik and R. Schuler, *Actinide Processing Methods and Materials*, TMS, 1994, p. 359.
16. M. Skalberg and J. O. Liljenzin, *Nucl. Eng. Int.* (February 30, 1993).
17. M. Kubota, S. Dojiri, I. Yamaguchi, et al., *High Level Radioactive Waste and Spent Fuel Management*, Vol. II, The American Society of Mechanical Engineers, 1989, p. 537.
18. W. W. Schulz et al., *Science and Technology of Tributyl Phosphate*, CRC Press, 1990.
19. T. Ishimori, K. Kimura, E. Nakamura, et al., JAERI 1047 (1963).
20. J. M. McKibben, H. P. Holcomb, D. A. Orth, W. E. Prout, and W. C. Scotten, DP-1361 (1974).
21. M. C. Thompson, DP-1336 (1973).
22. E. R. Irish and W. H. Reas, TID-7534 (1957).
23. J. C. Mailen et al., *Sep. Sci. Technol.*, *15*, 959 (1980).
24. D. J. Pruett, *Radiochim. Acta*, *27*, 115 (1980).
25. S. B. Watson and R. H. Rainey, ORNL-TM-5123 (1975).
26. D. E. Horner, ORNL-TN-2711 (1970).
27. W. D. Bond and R. E. Leuze, CONF-750913-9 (1975).

Received by editor March 20, 1995