

A study of extraction and stripping behaviors of U-Np-Tc ternary system to TBP

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Abstract

In order to remove U, Tc, Np, which are a positioning material or target nuclides for transmutation, from the high-level radioactive waste, conditions of co-extraction and sequential stripping of the nuclides were studied by using 30vol.% TBP. On the basis of experiments of the extraction and stripping on each element of U, Tc, and Np, a combination of co-extraction of U, Tc, Np → Tc stripping → Np stripping → U stripping was suggested. The electrolytic oxidation of Np(V) existing in Np solution to enhance Np extraction yield was required at the step of co-extraction. For the stripping, 5M HNO₃ for Tc, electrolytic reduction of Np(VI) to Np(V) for Np, and 0.3 M sodium carbonate for U were used, respectively. Phase ratios (O/A or A/O) of the co-extraction and the stripping was recommended to be 2~3.

1. Introduction

The concept of partitioning-transmutation to treat HLLW (high-level radioactive liquid waste) has been being studied in several countries during the last decade, because it could diminish the potential long-toxicity of long-lived minor actinides (Am, Cm, Np, etc.) and it could meet the public's concern and encourage the further development of nuclear power for peaceful uses.[1,2] The nuclides in HLLW before the transmutation should be first chemically separated into a few groups according to their characteristics including the minor actinide group, the Cs-Sr group of major heat-generating nuclides, platinum group of Pd, Ru, Rh, and other fission product group. The minor actinides of long-lived nuclides are to be transmuted into short-lived nuclides in an actinide-burning reactor.[1]

Residual U in low content (less than 2 g/l) existing in HLLW should be first removed from the

HLLW, because it is a positioning material against the transmutation of the long-lived nuclides. U has been known to be easily separated from nitric acid by using TBP (Tri-butyl phosphate).[3] Among the long-lived nuclides, Np is considered to be a target element to be first of all separated from the HLLW with respect to the ICRP(International Commission on Radiation Protection) 30 taking into accounting the ANL(Annual Limit of Intake)[4], because Np is a very mobile species in the environment. The chemical behavior of Np is different from those of Am and Cm so that Np is hard to be separated together with Am and Cm. Therefore Np has been considered to be separated from the HLLW with a method different from those for the Am and Cm.[3,5] Moreover, Np is liable to spread over different streams in the partitioning process due to its complicated chemical behavior in nitric acid.[3,5,6] Np exists simultaneously in three stable states: Np(IV) (Np^{4+}), Np(V) (NpO_2^+), Np(VI) (NpO_2^{2+}). The Np oxidation states exhibit different extraction behaviors to TBP. In nitric acid, Np(VI) is easily extractable, Np(IV) is less extractable, and Np(V) is nearly unextractable.⁵ Accordingly, with adjusting the Np valences to Np(VI), Np can be easily separated from the HLLW by TBP together with U. Tc is known to exist in a form of TcO_4^- [Tc(VII)] in nitric acid. Tc is generally suggested to be separated from the HLLW with adsorption/elution or precipitation methods because its behavior is different from those of other metal cations in the solution.[7] If Tc is separated from the HLLW together with U and Np with TBP in one step, the whole partitioning process could be simplified and the amount of waste generated in the process could be much relieved. Once Np, U, and Tc are taken out of the HLLW, U, a positioning material, is necessary to be removed from the Np and Tc to be transmuted.

In this work, the extraction and stripping behaviors of each U, Np, and Tc were studied with several variables such as the valance of each element, nitric acid concentration, phase ratio, etc in order to set up optimal conditions of co-extraction and stripping of U, Np, and Tc with 30 vol.% TBP

2. Experimental

All reagents used in this work were chemical reagent grade and used as received. Np and Tc obtained from AEA Technology in England as Np-237 and Tc-99 dissolved in 2 M HNO_3 were used without further purification. U was used as a form of UO_2^{+2} resulting from dissolving $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich Co.) in nitric acid. The element concentrations of initial stock solution for the co-extraction and the sequential stripping are shown in Table 1. Nd of 5g/l was added in the stock solution as a representative rare earth element together. The concentration of nitric acid in the stock solution was fixed at 2 M.[8]

Table1. Concentrations of elements in initial stock solution

Element	Concentration (M)
HNO ₃	2.0
U	8.4x10 ⁻³
Np	1.0x10 ⁻³
Tc	1.0x10 ⁻⁴
Nd	3.4x10 ⁻²

Batch extraction or batch stripping of U and Tc were carried out by mixing vigorously 30vol.% TBP/n-dodecane and aqueous solution at 25±0.5°C for 10 minutes with a change of phase ratio [O/A (Organic volume/Aqueous volume) or A/O] from 0.5 to 4. In the case of Np, electrolytic extraction [or electrolytic stripping], where adjustment of Np oxidation state and extraction (or stripping) occurred at the same time in the same space, was done by using a GC fiber column system. The GC fiber acts as a working electrode with a large electrode area and it also acts simultaneously as an effective liquid-liquid contactor. Details and principle of the GC fiber column system were described in our previous works.[6,9-16] All the TBP organic phase used in this work was pre-saturated with nitric acid in order to keep the nitric acid concentration in the aqueous phase as constant as possible during the extraction.

Np in aqueous and organic phases was analyzed by a γ -spectrometer with a HP-Ge detector (Oxford Inc., Model 5000 Radiation Analyzer). Tc was analyzed by beta counting using a liquid scintillation spectrometer (A Canberra Co. Packard 2500 TR/AB). U and Nd were measured by an inductive couple plasma spectrophotometer (Jobiny von JY38 plus) Nitric acid concentrations in the solution were measured by an auto-titrator (Kyoto Electronics, Model AT-400).

3. Results and discussion

To establish a process for the co-extraction of U, Np, and Tc from nitric acid with 30 vol.% TBP and stripping them in series, it is necessary to study first the behaviors of extraction and stripping of each element. On the basis of the results, the conditions of extraction and each stripping step and an arrangement of each step can be established.

Figure.1 shows the distribution coefficients of U(VI) and U(IV) with a change of nitric acid concentration. U(IV) was prepared with using a GC fiber column at -0.5 V[vs. SSE(saturated KCl-Ag/AgCl)] where U (VI) solution of 2g/l was fed into at 0.5ml/min. Experimental distribution coefficients of U(VI) relatively agree with published data¹⁷ and those calculated by SEPHIS code of a report ORNL-TM-5123.[18] As 0.01 M nitric acid is known to be used as a solution for stripping

U(VI) from 30vol.% TBP, the distribution of U(VI) at 0.01 M HNO₃ is about 0.05 which is low enough to back-extract U(VI) effectively. The distribution coefficient of U(IV) at 2 M HNO₃ is about 1. It means that only a change of oxidation state of U(VI) to U(IV) without using a low nitric acid of stripping solution is not an effective way to strip U from the TBP organic phase. Figure 2 shows the extraction yield of U(VI) with nitric acid and phase ratio (O/A). The extraction yield is over 95% at phase ratio of 2 and at 2 M HNO₃.

Figure 3 shows the U stripping yields from 30 vol.% TBP containing 1.95g/l U(VI) by 0.01 M HNO₃ and those by electrolytic stripping with reduction of U(VI) to U(IV) at -0.5 V (vs SSE)[15] with a change of phase ratio (A/O). The batch stripping yield of U by 0.01 M HNO₃ increases with the phase ratio and comes to about 90% at phase ratio of 3. In the case of using GC fiber column without applying any potential (the GC fiber column act simply as a liquid-liquid contactor) where 30 vol.% TBP containing U(VI) and 0.01 M HNO₃ are fed into at flow ratio of 1 (at superficial velocity of organic phase : 1.15 cm/min), the stripping yield gets to 90% of that in batch at phase ratio of 1. It means the GC fiber column generates an effective liquid-liquid contact area for the stripping. These results mean the GC fiber column system can be effectively used as an electrolytic extraction (or an electrolytic stripping) system where an adjustment of oxidation state and an extraction (or a stripping) occurs at the same time. Figure 3 shows also electrolytic stripping yields with reduction of U(VI) to U(IV) using a GC rod electrode in batch at 2 M HNO₃ and those by a GC fiber column, -0.5 V (vs SSE) being applied to those electrolytic systems. As predicted above, U stripping yield is low because the distribution coefficient of U(IV) is not low enough at 2 M HNO₃ as *ca.* 1, and the diffusion of U ion in the organic phase to aqueous phase during the stripping is not fast enough.[15]

Figure 4 shows the distribution coefficient of Np at 2M HNO₃. It has been confirmed in our previous work⁶ that the Np solution used in this work consisted of Np(V) and Np(VI) without Np(IV) and the ratio of Np(V) to Np(VI) in the solution depended on the nitric acid concentration. The ratio of Np(VI) to Np(V) at 2M HNO₃ was 7:3. The changes of distribution coefficients of Np(V) and Np(VI) with nitric acid and the voltammograms of redox of Np(VI) between Np(V) has been also elucidated already.[6] The distribution coefficient of Np solution without the adjustment of Np(V) to Np(VI) at 2M HNO₃ is about 1.8. However, after an adjustment of Np solution to Np(VI) by a GC fiber column with +1.0 V (vs SSE) being applied, its distribution coefficient increases to 6.5. With an adjustment of Np solution to Np(V) at +0.5 V (vs SSE) of a potential to reduce Np(VI) to Np(V), the distribution coefficient gets down to 0.07. The distribution coefficients of pure Np(VI) and Np(V) in the literature,[3,5,6,19] where they were prepared by a chemical oxidant in excess, are about 10 and 0.15, respectively. The differences between published value and ours are attributable to a partially re-reduction or re-oxidation of Np(VI) or Np(V) prepared in the GC fiber column system due to the disproportionation reaction of Np.[5,6] Figure 5 shows the extraction yield of Np solution without the

adjustment of oxidation state and with adjustments to Np(VI) or to Np(V) using the GC fiber column with a change of phase ratio (O/A). The extraction yield changes from 69% to 91% at phase ratio of after the adjustment of Np solution to Np(VI).

Figure 6 shows the stripping yield of Np from 30 vol.% TBP to 2 M nitric acid with applying +0.5 V (vs SSE) in the GC fiber column with a change of phase ratio (A/O). The stripping yield increases with the phase ratio and it is about 62% at a phase ratio of 2. This value with respect to Fig.4 should have been about more than 90% at a phase ratio of 2. The reason is considered to be because the diffusion of Np ions from organic phase to aqueous phase is not fast enough during a time for two phases to pass through the GC fiber column, as mentioned in the case of electrolytic stripping of U above. In such circumstance, in order to increase the residence time necessary for the stripping reaction to reach to equilibrium enough, a decrease of organic flow rate or a longer GC fiber column are considered to be required.

Figure 7 shows the distribution coefficient of Tc with a change of nitric acid concentration. The results agree with published data well.[20] It has a peak of 0.93 at 0.6~0.8 M HNO₃ and gets down to about 0.03 at 5M HNO₃. From these results, it is considered that 5 M HNO₃ can be used as a stripping solution of Tc from TBP organic phase. In order to check a change of distribution coefficient resulting from a change of Tc oxidation status at a potential to oxidize Np(V) to Np(VI) due to a possibility of coexistence of non-pertechnetate(non-TcO₄⁻)[21] in the initial Tc solution, the electrolytic extraction of Tc to 30 vol.% TBP was carried out with applying the potential of +1.0 V(vs SSE). The results are the same to those without the applying the potential. This means that only pertechnetate exists in the initial Tc solution used in our work without other oxidation state Tc species. Figure 8 shows the Tc extraction yields in batch and those by using GC fiber column with a change of phase ratio(O/A). The extraction yield of Tc is about 50% at phase ratio of 2. As observed in Fig.3, the extraction yield by the GC fiber column is about 90% of that in batch.

Figure 9 shows the stripping yields of Tc from 30 vol.% TBP by 5 M HNO₃ in the GC fiber column and in batch with a change of phase ratio (A/O). The stripping yield easily reaches high as much as 97% at phase ratio of 2 using the GC fiber column because the distribution coefficient of Tc is very low at 5 M HNO₃ as shown in Fig.7. It means 5 M HNO₃ is effective for the stripping of Tc.

With the results of Fig1 to Fig.9, an optimal condition and an order of co-extraction and sequential stripping of U, Np, Tc can be established. At the co-extraction step, to enhance the extraction yield of Np, an oxidation of Np(V) existing in the solution to Np(VI) at +1.0 V (vs SSE) is required. As for the sequential stripping, an arrangement of Np→U→Tc or Np→Tc→U could be first considered. In the case of that of the Np stripping step being placed ahead of U or Tc stripping step, if the nitric acidity of stripping solution is equal to or less than that at the co-extraction step, a big portion of Tc and some portion of U in the organic phase can be co-stripped together with Np at the

Np stripping step of 2 M HNO₃, because the distribution coefficient of Tc is not high (less than 1) and because a change of distribution coefficient of U due to the change of acidity in the organic phase occurs. During the electrolytic Np stripping with 2 M HNO₃, about 80% of Tc in organic phase was experimentally observed to be back-extracted together with Np. On the other hand, if the nitric acidity of stripping solution is more than that at the co-extraction step, the stripping yield of Np could decrease, because the distribution coefficient of Np increases with nitric acid.[5,6] If the Tc stripping step using 5M HNO₃ is placed just ahead of U stripping with 0.01 M HNO₃, most of the nitric acid extracted into organic phase during Tc stripping can be stripped into 0.01M HNO₃ solution again, which results in the increase of nitric acid concentration in the U stripping solution. This may cause a decrease of the stripping yield of U. In fact, when the U stripping was done by 0.01 M HNO₃ at phase ratio (A/O) of 2 after Tc stripping with 5M HNO₃, the nitric acid concentration in the stripping solution was observed to change from 0.01 M to about 0.3 and as much as 20% of the stripping yield decreased, compared with that without contacting the organic phase with 5 M HNO₃ ahead. In this case, Na₂CO₃ had better be used as a stripping solution of U. As shown in Fig. 10, the Na₂CO₃ of more than 0.3 M with phase ratio of more than 1 strip almost 100% of U from 30% vol.% TBP.

From these results, it is considered that the Tc stripping step by 5 M HNO₃ has to be placed ahead of Np and U stripping steps in order to prevent the co-stripping of other elements at a minimum and Np stripping has to be ahead of U stripping step. Figure 11 shows a flow diagram of the co-extraction and sequential stripping of U, Np, and Tc with their experimental conditions and with phase ratios (O/A or A/O) of 2 at all steps. All the steps of Fig.11 were done in one stage operation. The experimental results were shown in Table 2. All results are almost the same to those of the batch experiments of each element. The ratios of concentration of each element at each stripping step to that in feeding solution are 49.1% for Tc, 52.4% for Np, 84.9% for U, respectively. If a cascade multi-stage operation at each step is carried out, the extraction yield and stripping yields can be increased. Our simple calculation in cascade based on SEPHIS code[3,18] with using the results of Fig.1 to Fig.9 and Table 2 showed that the extraction yield and stripping yield got to 99% in 9~10 stages with phase ratio of 2 to 3. The phase ratio at the co-extraction of U, Np, and Tc from the HLLW has to be less than 3 because a co-extraction of some rare earth elements such as Nd, which are desired to remain in the raffinate solution still, could happen together[22,23] when the phase ratio is over 3.

From these results above, the process suggested in Fig.11 is considered to be a process for the purpose of extraction of U, Np, and Tc from the HLLW and then separation of Np and Tc to be transmuted from U to be removed. However, a study on the selection of a new extractant to enhance the extraction yield of Tc, which could result in a decrease of the number of stages necessary to meet a desired extraction yield, will be required furthermore. Also, when Zr exists with Tc in the solution, the extraction behavior of Tc with nitric acid concentration is known to become quite different.[3,20] In

that case, a step to remove Zr has to be taken into consideration to be added before the process of Fig.11. A denitration where Zr and Mo can be removed from the HLLW through precipitation could be used.[5]

Table 2. Co-extraction yields and sequential stripping yields of Tc, Np, and U.

Element \ Step	Co-extraction yield at 1.1 Volt O/A=2	Stripping step \ Stripping yield	Tc stripping with 5M HNO ₃ A/O=2	Np stripping at 1.1 Volt A/O=2	U stripping with 0.3M Na ₂ CO ₃ A/O=2
Np	90.6%	Stripping yield	6.8%	62.1%	100%
		$C_{aq.}/C_{aq.feed}$	6.2%	52.4%	32.0%
Tc	51.1%	Stripping yield	96.1%	86.9%	100%
		$C_{aq.}/C_{aq.feed}$	49.1%	1.7%	0.3%
U	95.5%	Stripping yield	2%	9.2%	100%
		$C_{aq.}/C_{aq.feed}$	1.9%	8.7%	84.9%

4. Conclusions

An conceptual process for the co-extraction and sequential stripping of U, Np, and Tc in the HLLW was suggested as an order of co-extraction of U, Np and Tc → Tc stripping → Np stripping → U stripping. The electrolytic oxidation of Np(V) existing in Np solution to Np(VI) was required at the co-extraction step to enhance Np extraction yield. For the strippings, 5M HNO₃ for Tc, electrolytic reduction of Np(VI) to Np(V) for Np, and 0.3 M sodium carbonate for U were suitable. In one stage operation, the ratio of concentration of each sequentially-stripped element to that in the feeding solution was 49.1% for Tc, 52.4% for Np, and 84.9% for U, respectively. Phase ratios (O/A or A/O) of the co-extraction and the stripping was recommended to be 2~3.

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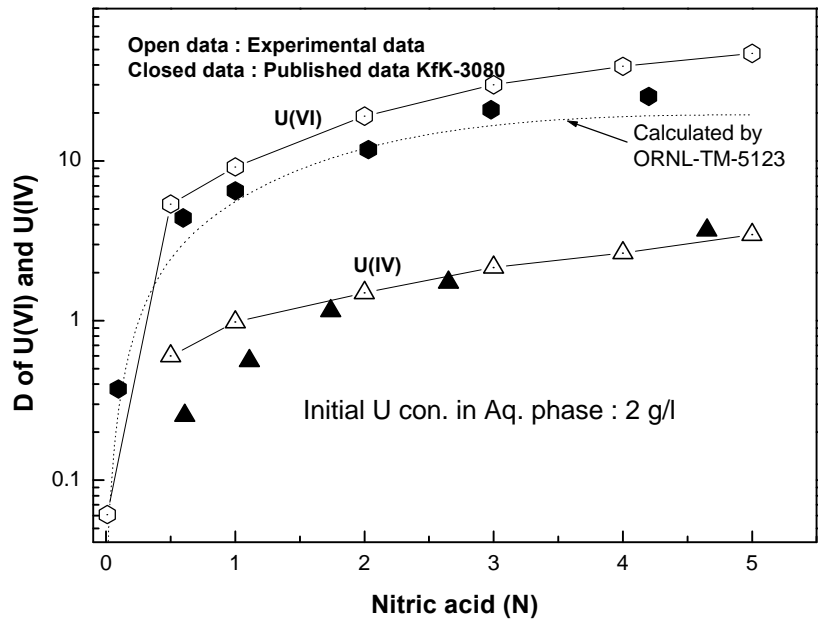


Fig.1 Distribution coefficients of U(VI) and U(IV) to 30 vol.% TBP with a change of nitric acid.

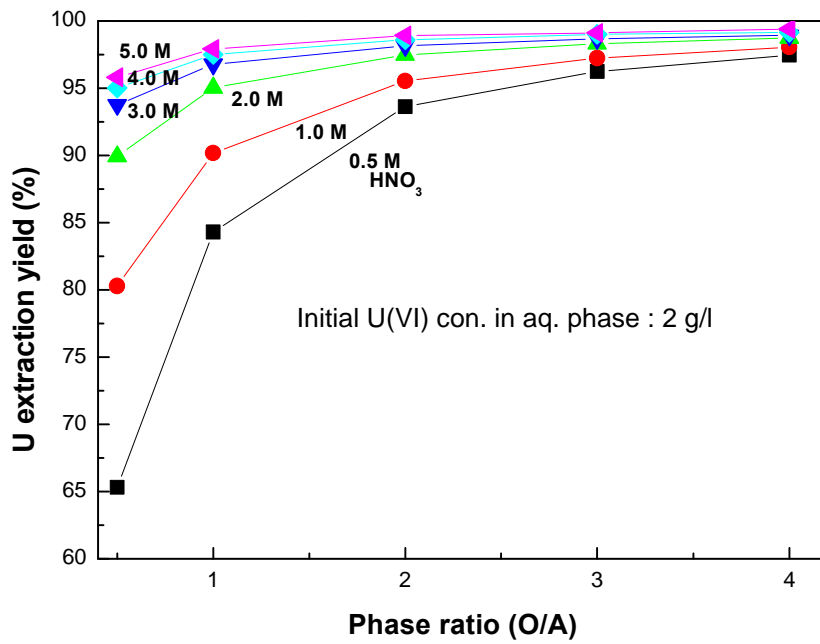


Fig.2 Extraction yield of U(VI) in different nitric acid concentrations by 30 vol.% TBP with a change of phase ratio.

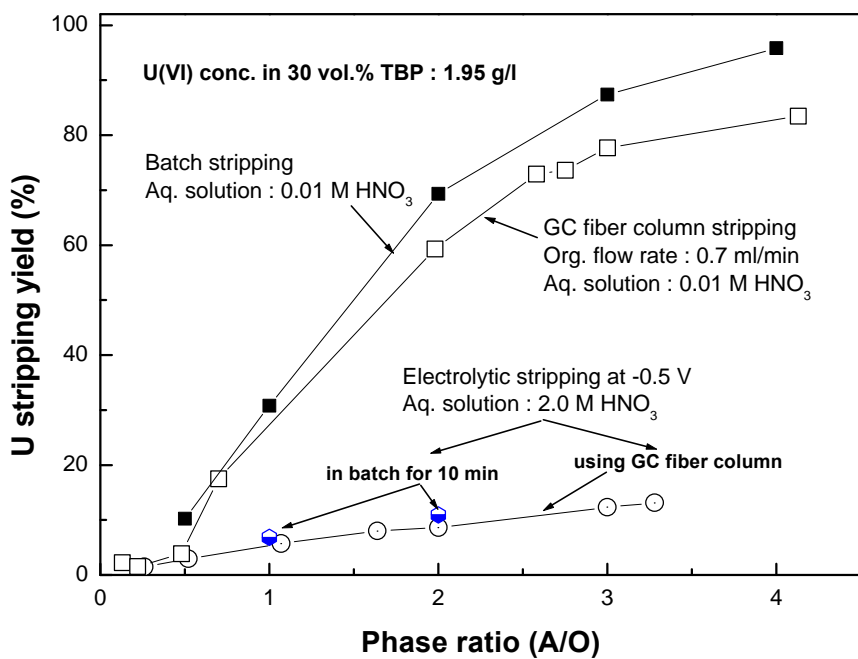


Fig.3 Stripping yield of U(VI) from 30 vol.% TBP with and without electrolytic stripping with a change of phase ratio.

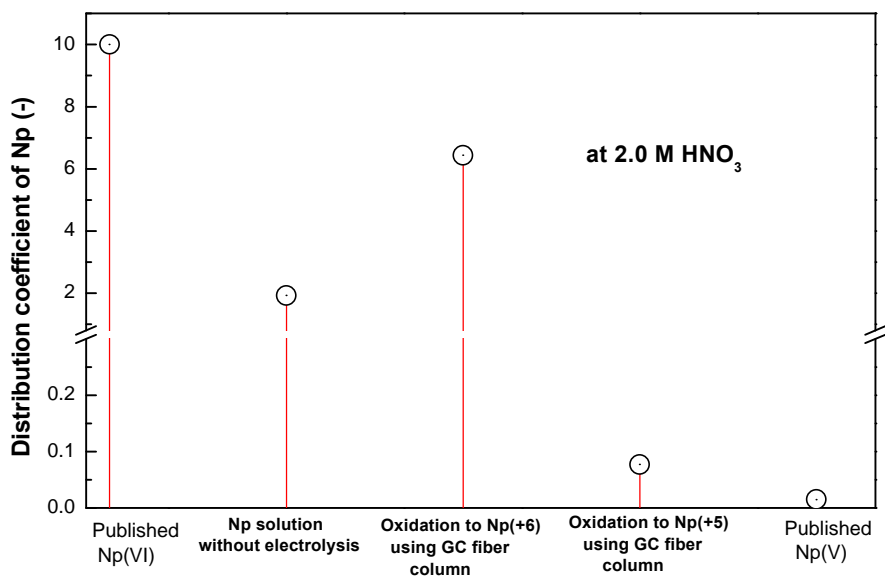


Fig.4 Distribution coefficients of Np(VI) and Np(V) at 2M HNO₃

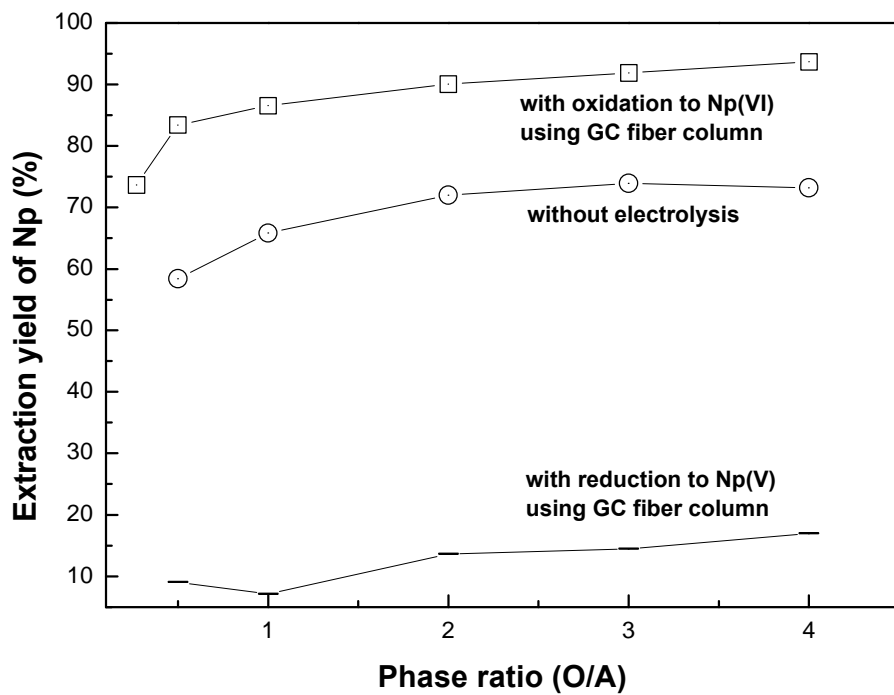


Fig.5 Extraction yield of Np by 30 vol.% TBP with a change of phase ratio.

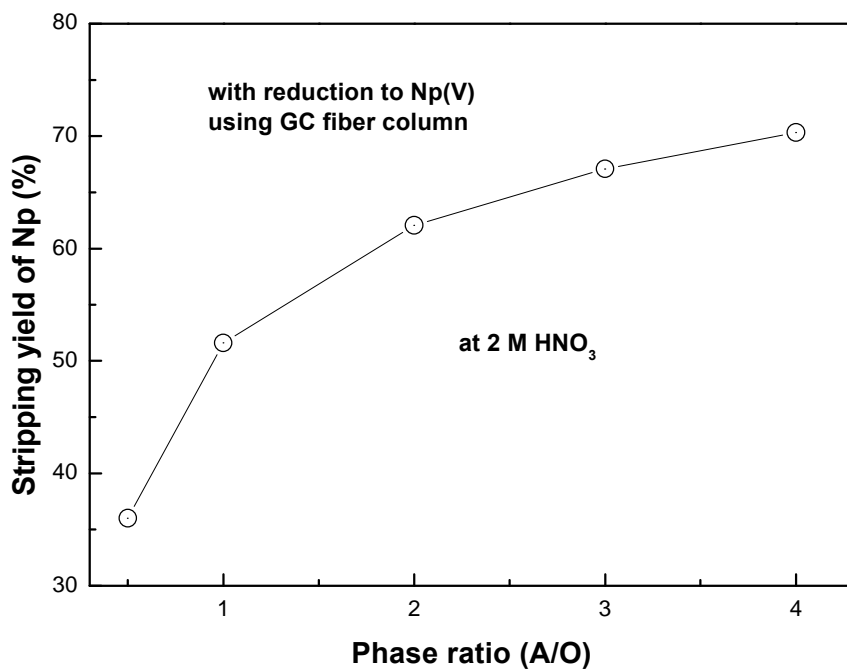


Fig.6 Electrolytic stripping yield of Np with reduction to Np(V) at 2M HNO₃ with a change of phase ratio.

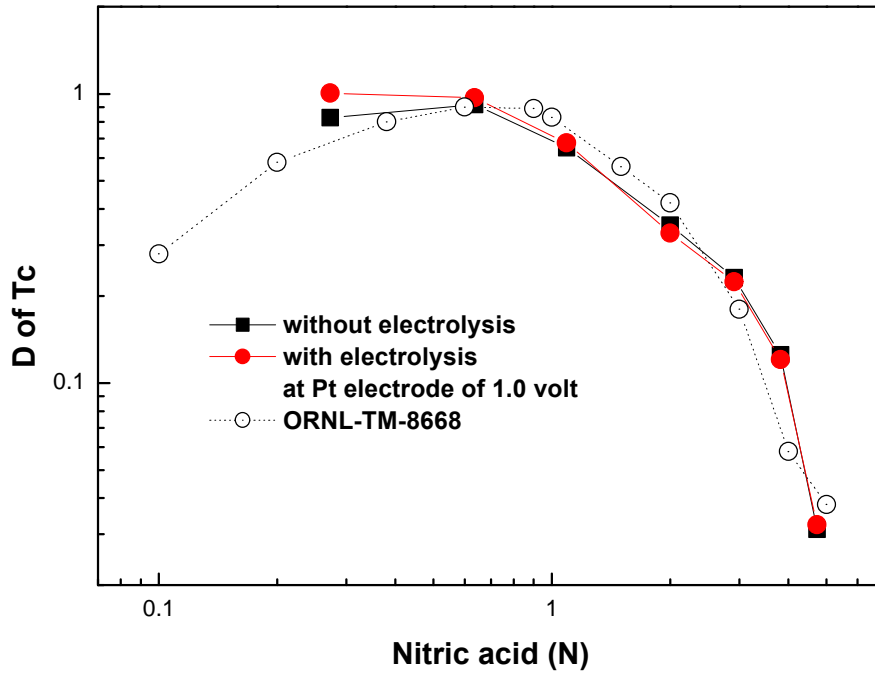


Fig.7 Distribution coefficients of technetium by 30 vol.% TBP with a change of nitric acid.

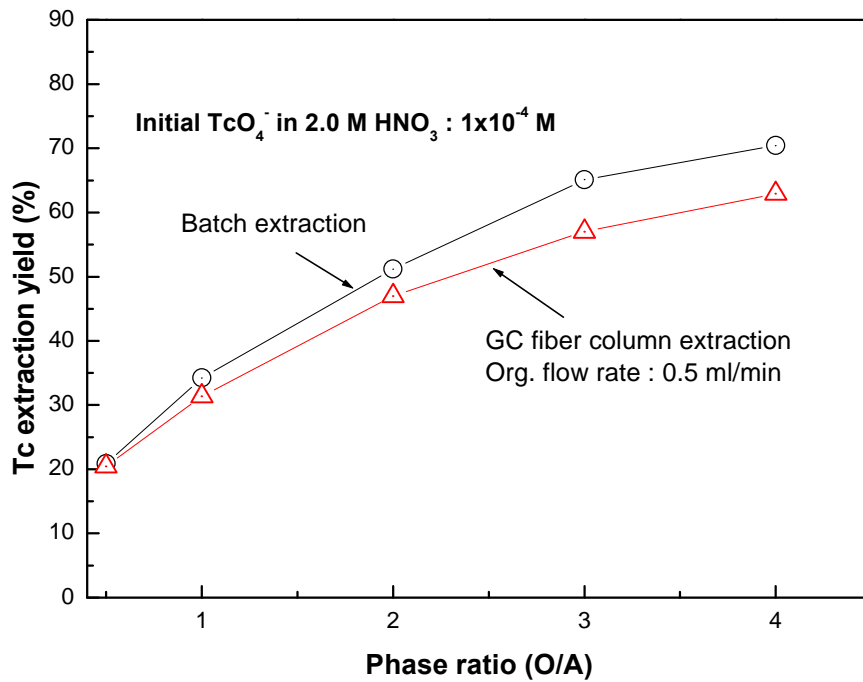


Fig.8 Extraction yield of TcO_4^- by 30 vol.% TBP with a change of phase ratio.

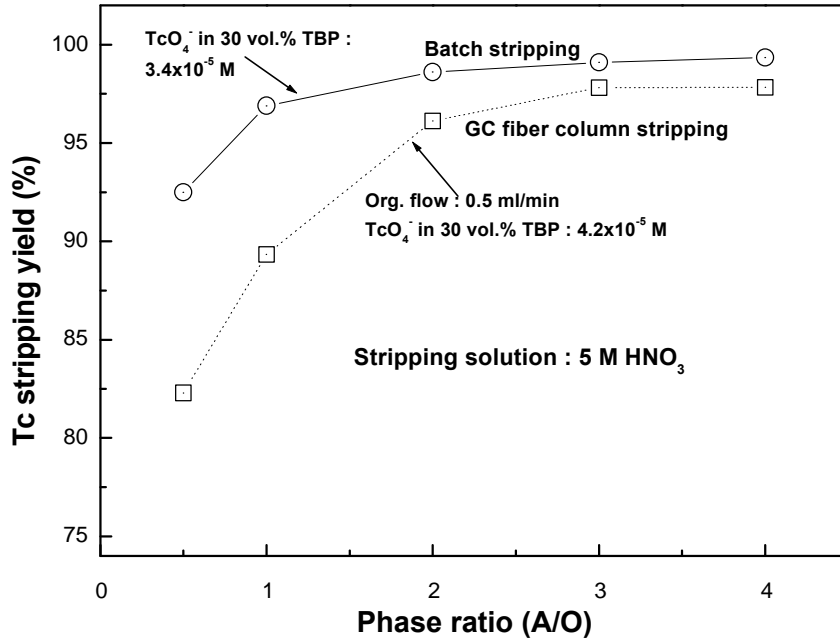


Fig.9 Stripping yield of TcO_4^- by 5M HNO_3 with a change of phase ratio.

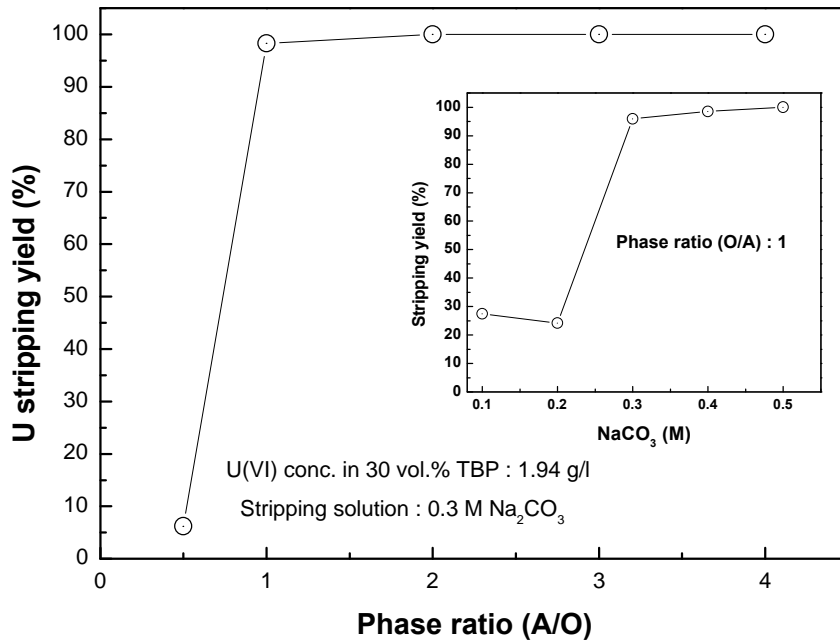


Fig.10 Stripping yield of U(VI) from 30 vol.% TBP by Na_2CO_3 with a change of phase ratio

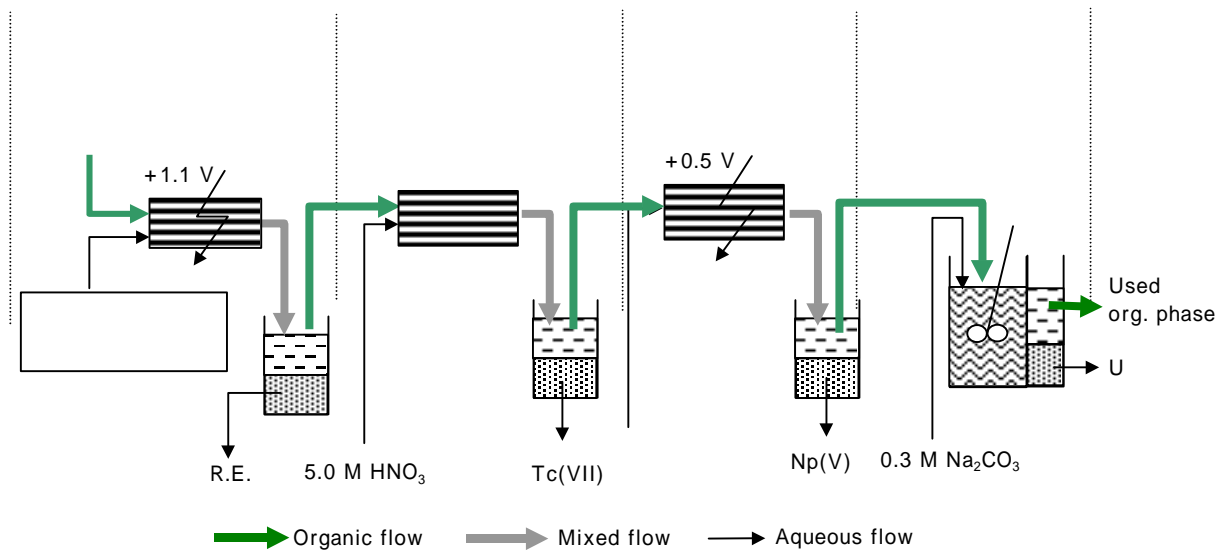


Fig.11 Flow diagram of Co-extraction and sequential stripping of U/Np/Tc