Technetium Separation for Future Reprocessing

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Tc extraction and separation experiments were performed basing on PUREX technique with using spent UO_2 fuel with burn-up of 44 GWd t^{-1}. The experimental results were examined with performing calculations by a simulation code ESSCAR (Extraction System Simulation Code for Advanced Reprocessing). It was demonstrated that Tc can be extracted almost quantitatively from a dissolver solution and that extracted Tc also can be recovered almost quantitatively by scrubbing. Further, it is clearly presented with the calculation results of ESSCAR that Tc extraction mechanism is dominated by the synergistic effect of Zr and U.

1. Introduction

In JAERI (Japan Atomic Energy Research Institute), PARC (Partitioning Conundrum-key) process,[1] a PUREX technique based separation process concept has been proposed and studied as the basis for future development in reprocessing, as a part of safety research to improve safety by simplifying PUREX process. The separation scheme of nuclides in the process concept is illustrated in Figure 1. In the solvent extractive separation scheme, U and Pu are recovered as products with sufficient decontamination factor within a single extraction cycle for recycle use, with controlling the extractive behavior of long-lived nuclides such as Np and Tc. It is significantly important to sufficiently restrict the transfer of Tc into U products and Pu products to obtain high decontamination factor, because Tc easily contaminates the products. Further, restriction of Tc-99 transfer into highly active wastes and recovery of it for transmutation into non-radioactive nuclide, Ru-100 for example, reduces long-term radiation toxicity of the waste.

In the literature,[2] Tc was extracted almost quantitatively from a dissolver solution at U-Pu co-extraction (co-decontamination) part, passed through scrub part and reached at U/Pu partition part. In this report, Tc behavior in the co-decontamination part is mainly explained by the effect of synergistic extraction with Zr, and Tc passes through the scrubbing part, where Zr is back-extracted into scrubbing solution, by the effect of synergistic extraction with U. As for Tc back-extrac-

tion from the extractive solvent, the authors have already shown that it can be possible by utilizing a high-acid scrubbing method.[1]

Under these backgrounds, the authors have conducted extractive separation experiments using actual spent UO_2 fuel solutions, and examined the feasibility of Tc separation and recovery with utilizing PUREX techniques. We also tried to explain the mechanism, which dominates Tc behaviors in extraction process, with utilizing a simulation code.

2. Experimental

The spent fuel used for experiments were UO_2 fuels which were burnt in a commercial light water reactor up to 44 GWd t^{-1}. The spent fuels were treated inside of an alpha-gamma (air-tight, sufficiently shielded) cell in NUCEF (Nuclear Fuel Cycle Safety Engineering Facility) of JAERI, and a test line composed of a dissolver, extractors etc. in the cell[3] was used for experiments.

For respective extraction run, 1.5 to 2 liters of dissolver solutions were used to perform a chemical engineering test on counter-current contact with miniature mixer-settler type liquid-liquid extractors. Three extractive runs, Run No. 1, 2 and 3, were performed. In Table 1, the composition of a dissolver solution for respective extraction run was summarized. The flow-sheet composed from mixer-settler contactors for experimental Run No. 1 and No. 2 is shown in Figure 2. U-Pu co-extraction (co-decontamination) part was composed of 8 stages of extraction banks (banks No. 1–8). A dissolver solution (A1) was supplied at the bank No. 8 and a main extraction solvent (30 vol% TBP in dodecane) was supplied at the bank No. 1. At the bank No. 16, a scrubbing solution was supplied and a scrubbing part of 8 stages (banks No. 9–16) was composed. As already reported in the literature,[2] Tc is expected to pass through this scrubbing part. Thus, Tc separation part of 7
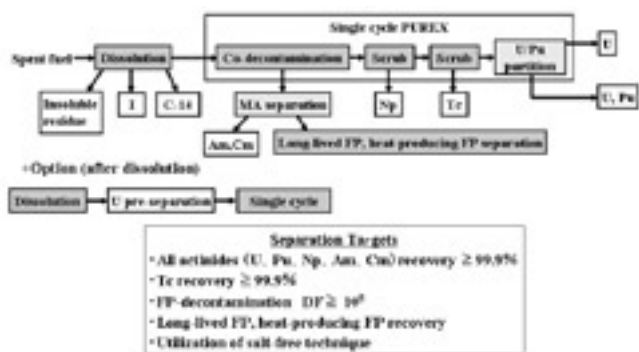

Figure 1. Separation process concept "PARC (Partitioning Conundrum-key)".

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TABLE 1: Composition of Dissolver Solution Used for Experimental Run No. 1, 2, and 3

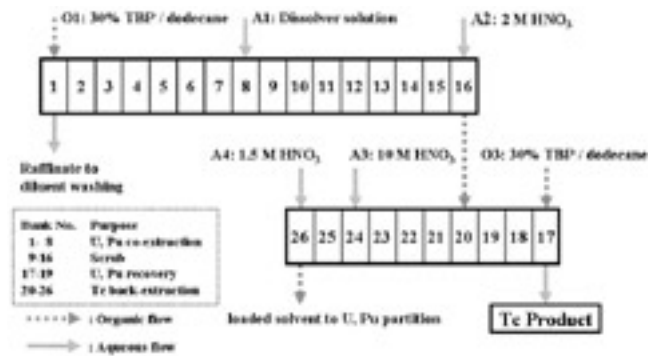| Run No.	Concentration in dissolver solution				
	$[HNO_3]$ /mol l^{-1}	[U] /g l^{-1}	[Pu] /g l^{-1}	[Zr] /g l^{-1}	[Tc] /g l^{-1}
1	3.2	200	2.25	0.682	0.368
2	3.0	196	1.86	0.639	0.188
3	3.1	214	2.03	0.700	0.206

Figure 2. Experimental flow-sheet for Run No. 1 and No. 2.

stages of extraction banks (banks No. 20–26) was composed. To recover U and Pu, which are expected to leak into a Tc product solution, three stages of extraction banks (banks No. 17–19) were used. In Table 2, the flow rates of the solutions, A1–A4, O1, O2, for Run No. 1 and No. 2, respectively, were summarized.

TABLE 2: Flow Rate of Respective Solution in Each Experimental Run

| | Flow rate / ml h^{-1} | | | | | |
	A1	A2	A3	A4	O1	O2
Run 1	193	94	40	82	480	120
Run 2	201	91	42	83	487	121

In Figure 3, the flow-sheet for the experiment Run No. 3 is shown. The number of extraction banks for the U-Pu co-extraction part or the scrub part was the same as Run No. 1 or 2. Organic to aqueous flow rate ratio was increased, and the HNO$_3$ concentration of the scrubbing solution was altered to 4 mol l^{-1} (M). The aim of these alterations was to accelerate Np extraction from a dissolver solution. In this flow-sheet for Run No. 3, 7 stages of a Np separation part (banks No. 20–26) was also composed. Tc separation part was composed of 10 stages of the banks (No. 27–36), and Tc scrubbing solution (A4) was simplified as single solution of 6 M HNO$_3$.

After 10 hours operation with active feed, those extractors were shut down and analytical samples of an organic solution and an aqueous solution were collected from every extraction banks to analyze Tc concentrations. If Tc-95m, which was added to the dissolver solution as a RI tracer, was detected, Tc concentration was determined by the concentration of gamma radioactivity of the tracer. The detection limit for the measurement was 9×10^{-3} g l^{-1} in the case of Run No. 1 and 2, or 9×10^{-4} g l^{-1} in the case of Run No. 3, respectively. If it was not possible to determine the Tc concentration with this method with interferences by other radio-nuclides, the value was deter-
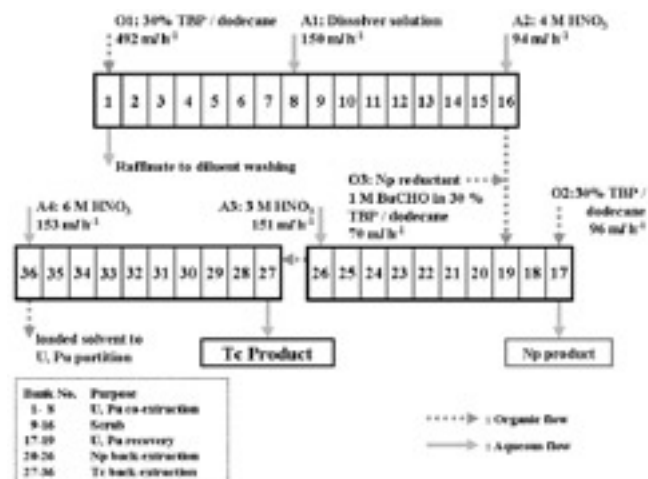

Figure 3. Experimental flow-sheet for Run No. 3.

mined by the emission strength of Tc in ICP-AES (Induction-Coupled Plasma Atomic Emission Spectroscopy) compared to a calibration line for concentration standards. The detection limit for this method was 2×10^{-3} g l^{-1}.

3. Simulation Code

For simulation calculation of extraction experiments, ESSCAR (extraction system simulation code for advanced reprocessing)[4] was used. This code can treat TBP-HNO$_3$ extraction system composed of a desired number of pulsed-column type extractors and mixer-settler type extractors. A pulsed-column type extractor is imaginarily divided into desired number of calculation units (meshes) with arbitrary heights. In the case of mixer-settler type extractor, respective extraction bank is the calculation unit. The code numerically solves differential equations, which express material balance of chemical species (HNO$_3$, metal ions etc.) in respective calculation unit, by Newton's method. To describe material balance, mass transfer between organic solution and aqueous solution phase basing on distribution coefficient, and rates of chemical reactions, reduction-oxidation reaction, for example, in respective phase. The code gives us the numeric solutions for steady-state or transient-state.

Tc distribution coefficient is mathematically expressed as empirical equations proposed by Kolarik et al.[5] with slight modification to enable to treat Pu effect on Tc distribution as follows,

$$D_{\text{Tc}} = D_{\text{Tc, 0}} + D_{\text{Tc, Zr}} + D_{\text{Tc, U}} + D_{\text{Tc, Pu}} \tag{1}$$

$$D_{\text{Tc, 0}} = 0.845 C_{\text{free-TBP, org}}^{1.92\exp(3300\tau)}$$
$$\frac{2.324 C_{\text{NO}_3^-, \text{aq}}^{0.848\exp(230\tau)} \exp(8070\tau)}{1+0.157 C_{\text{NO}_3^-, \text{aq}}^{4.69\exp(410\tau)}\exp(324\tau)+01.72 C_{\text{NO}_3^-, \text{aq}}^{1.95\exp(160\tau)}\exp(3150\tau)} \exp(-350\tau) \tag{2}$$

$$D_{\text{Tc, U}} = 0.331 \frac{C_{\text{UO}_2^{2+}, \text{org}}^{2}}{C_{\text{UO}_2^{2+}, \text{org}} + C_{\text{Pu}^{4+}, \text{org}}} \{1+4.87 C_{\text{NO}_3^-, \text{aq}}^{-1.343}\exp(980\tau)\}\exp(-1060\tau) \tag{3}$$

$$D_{\text{Tc, Zr}} = 1670 C_{\text{Zr, org}} C_{\text{NO}_3^-, \text{aq}}^{-0.707} \exp(2810\tau) \tag{4}$$

$$D_{\text{Tc, Pu}} = 3.31 C_{\text{NO}_3^-, \text{aq}}^{-0.707} \frac{C_{\text{Pu}^{4+}, \text{org}}^{2}}{C_{\text{UO}_2^{2+}, \text{org}} + C_{\text{Pu}^{4+}, \text{org}}} \exp(-1060\tau) \tag{5}$$

$$\tau = \frac{1}{298} - \frac{1}{T} \tag{6}$$

Here, D_{Tc}: overall distribution ratio of Tc; $D_{\text{Tc, 0}}$: distribution coefficient of HTcO$_4$ itself; $D_{\text{Tc, U}}$, $D_{\text{Tc, Zr}}$ or $D_{\text{Tc, Pu}}$: contribution of synergistic effect of U, Zr or Pu to the distribution of TcO$_4^-$, respectively; $C_{\text{free-TBP, org}}$, $C_{\text{UO}_2^{2+}, \text{org}}$, $C_{\text{Zr, org}}$ or $C_{\text{Pu}^{4+}, \text{org}}$: concentration (M) of free-TBP, UO$_2^{2+}$, Zr or Pu^{4+}, respectively, in the organic phase; $C_{\text{NO}_3^-, \text{ap}}$: concentration (M) of NO$_3^-$ in the aqueous phase; T: temperature (K).

In the current cases, however, the contribution of Pu effect to Tc distribution is almost negligible because of its small concentration.

4. Results and Discussion

4.1. Tc Extraction. In Figure 4, the Tc concentration profiles at the U, Pu co-extraction part (the extraction banks No. 1 to 8) and the scrub part (the extraction banks No. 9 to 16) obtained from two experimental runs are summarized as Figure 4a for Run No. 1 and Figure 4b for Run No. 2. The Tc concentration values are represented by plot symbols, the squares for
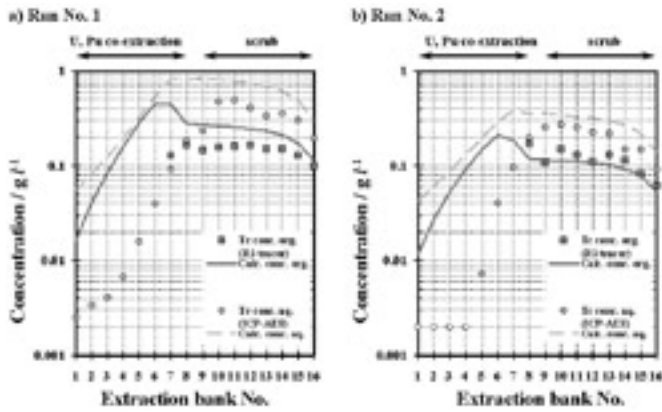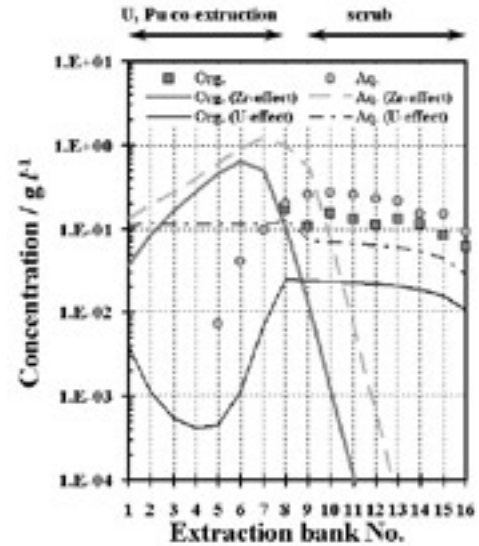
Figure 4. Tc concentration in the extraction banks No. 1–16, U, Pu co-extraction part and scrub part. Experimental values expressed as plot symbols, and calculated values expressed as lines. a) Run No. 1 and b) Run No. 2.

the organic solutions and the circles for the aqueous solutions, in these figures. The open plots represent the values under detection limit. The analytical methods utilized to determine these values are also shown in the figures. As shown in the figures, Tc concentration in the aqueous solution at the respective extraction bank steadily decreased according to the aqueous flow direction in the U-Pu co-extraction part, from the bank No. 8, the feed point of the dissolver solution, toward the bank No. 1 in both runs. These results clearly imply that the majority of Tc was extracted into the solvent. The percentage of Tc remaining in the raffinate is calculated to be 1.0% for Run No. 1 or under 1.5% for Run No. 2, respectively, assuming that the aqueous concentration value at the bank No. 1 obtained in the respective experiment, 2.49×10^{-3} g l^{-1} for Run No. 1 or under the detection limit (2×10^{-3} g l^{-1}) for Run No. 2, is equal to the concentration in raffinate constantly flowing out, and using the flow rate values in Table 1 and the concentration values in the feed in Table 2. It should be noted that the Tc concentration in the raffinate was not directly determined. As described in the experimental section, the analytical samples were collected from all banks after shut down operation of the mixers-settlers extractors and the influence of such operation on the concentration profiles in the extractors was not clarified. In the scrub part, the extraction banks No. 9 to 16, the Tc concentrations in the organic solutions maintained roughly constant values at the banks No. 9 to No. 14. Although the values decrease at the banks No. 15 and No. 16, the differences from the former banks are not substantial. Therefore, it is clear that the extracted Tc passed through the scrub part.

In these figures, the calculation results by ESSCAR are also shown as the lines. Although the calculated values do not completely agree with the experimental values in each figure, but the calculation results successfully represent the essential phenomena, Tc extraction in the co-extraction part and passing through the scrubbing part.

Further, we succeeded to clearly present the extraction mechanism of Tc by utilizing ESSCAR. Two calculations for Run No. 2 were performed as an example. In the first calculation, the distribution of Tc was described as $D_{Tc} = D_{Tc, Zr} + D_{Tc, 0}$, thus, only the synergistic extraction effect of Zr together with the intrinsic Tc extraction was considered (refer to eq 1). The results are represented as the lines noted as "Zr-effect" in Figure 5. In the second, only the synergistic extraction effect of U was considered, namely $D_{Tc} = D_{Tc, U} + D_{Tc, 0}$, and the results are similarly noted as "U-effect" in the figure. The lines for "Zr-effect" show that Tc will be extracted in the decontamination part with. On the other hand, the lines for "U-effect" show that Tc will not be extracted. In the scub part, the lines for "Zr-effect" shows that Tc will be back-extracted and be restricted to flow out as an organic solution. The lines for

Figure 5. Tc concentration calculated by ESSCAR code.
Zr-effect: Tc distribution coefficient calculated from synergistic effect of Zr only.
U-effect: Tc distribution coefficient calculated from synergistic effect of U only.
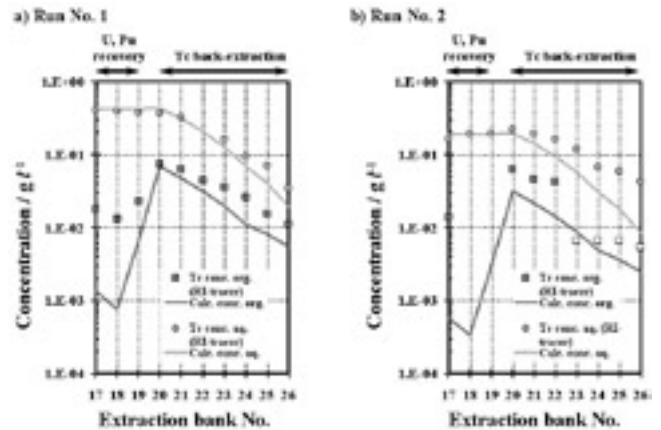
Figure 6. Tc concentration in the extraction banks No. 17–26, U, Pu recovery part and Tc back-extraction part. Experimental values expressed as plot symbols, and calculated values expressed as lines. a) Run No. 1 and b) Run No. 2.

"U-effect" show that the Tc concentration in organic solution does not significantly decrease. Therefore, ESSCAR calculation results clearly present that;
1. The phenomenon of Tc extraction in the co-decontamination part is dominated by the synergistic extraction effect of Zr, not that of U;
2. The phenomenon of extracted Tc passing through the scrub part is dominated by the synergistic extraction effect of U, not that of Zr.

4.2. Tc Separation. In Figure 6, the Tc concentration profiles at the U, Pu recovery part (the extraction banks No. 17 to 19) and the Tc back-extraction part (the extraction banks No. 20 to 26) obtained from two experimental runs are summarized as Figure 6a for Run No. 1 and Figure 6b for Run No. 2. The Tc concentration values are respectively expressed as the plot symbols in the figures, the squares for organic solutions and the circles for the aqueous solutions. The open plots, again, represent the values under detection limit. It is clear from these figures that the Tc concentration in the organic solution steadily decreases in the Tc back-extraction part as the bank number increases from No. 20 to 26, but that Tc still flows out as the organic solution especially in the case of Run No. 1. In the U, Pu recovery part, the extraction banks No. 17–19, the Tc concentration in the aqueous solution maintains almost constant value and Tc flows out as the aqueous solution, too. The recovery of
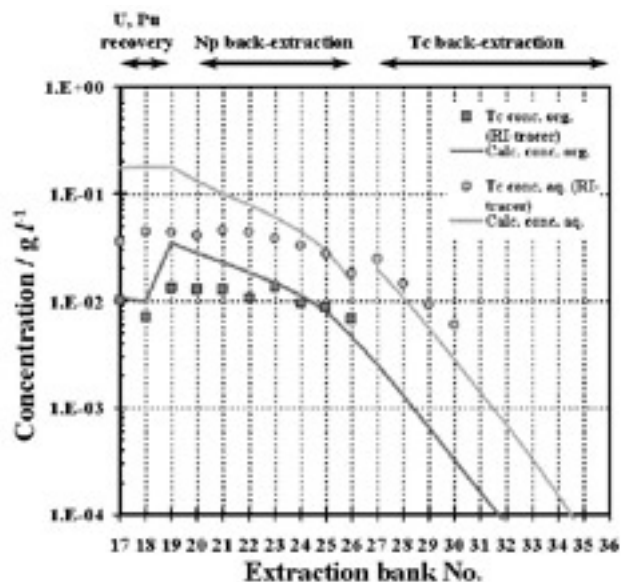
Figure 7. Tc concentration in the extraction banks No. 17–36, U, Pu recovery part, Np separation part and Tc back-extraction part, in Run No. 3. Experimental values expressed as plot symbols, and calculated values expressed as lines.

Tc in the product solution is calculated to be 68.7% for Run No.1 or 54.2% for Run No. 2, respectively, in the same manner as sect 4.1, and is not sufficiently high. The calculated concentration values agree fairly well with the experimental ones, except those for the organic solutions at U, Pu recovery part. Therefore, it is confidently said that Tc can be separated from U and Pu and be recovered as Tc product and the recovery can be increased by adding more extraction bank for Tc back-extraction.

Figure 7 shows the concentration profile of Tc in bank No. 17 to No. 36 in Run No. 3. From this figure, it can be noted that significant amount of Tc was back-extracted in the Np separation part (banks No. 19 to No. 26) and flowed out as Np product. It is expected that such undesirable Tc loss in the Np product can be avoided by exchanging the order of the two separation parts, a Tc separation part before a Np separation part. Although the agreement of calculation results with experimental ones is not very well, the trend is represented. In extraction banks No. 27 to 36, Tc separation part, the concentration of Tc in aqueous solution significantly decreased and the remaining Tc in organic solution was under detection limit (9×10^{-4} g l^{-1}). Thus, it can be said that Tc is sufficiently back-extracted. The experimental results in Tc separation part, only those for aqueous solution being available here, agree very well with the calculated ones. The back-extraction in this part seems to be more efficient than that for Run No. 1 or No. 2 shown in Figure 5a or 5b. This difference can be explained by the lower U load in the solvent in the case of Run No. 3 (approximately 50 g l^{-1}) than that in the case of Run No. 1 or No. 2 (approximately 65 g l^{-1}).

5. Conclusion

We performed Tc extraction-separation experiments, basing on PUREX techniques, using spent UO_2 fuel with burn-up of 44 GWd t^{-1}. We performed simulation calculations by ESSCAR, too, and the results can be summarized as follows.
1. Tc is extracted by TBP with significant efficiency from a dissolver solution. Quantitative extraction of Tc is feasible.
2. Tc is extracted in a co-decontamination part by the synergistic extraction effect of Zr. Tc passes through a scrub part by the synergistic extraction effect of U.
3. Extracted Tc is separated from U and Pu as a product by additional scrub. Quantitative recovery of Tc is feasible, too.
Here, because of low Pu concentration, (only 1% of U), the synergistic effect with Pu was not discussed. Scoping for the future when MOX fuel is widely utilized with innovative light water reactors or fast breeding reactors as nuclear power plants, the synergistic effect of Pu will be a quite important factor to describe Tc extraction behavior.

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