

## Research on PARC process for future reprocessing

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**Abstract** – In JAERI, PARC process based on PUREX technique has been studied to as the basis of future reprocessing. The key of concept is to obtain the products, U and Pu, within only a single extraction cycle by separating Np and Tc from U and Pu before U/Pu partition. Two flow-sheet tests on the process were performed with 44 GWd/t PWR spent-fuel solutions. It was demonstrated that remaining Np in raffinate from co-extraction could be decreased to 13 % compared to the dissolver solution with increased solvent flow rate and with increased nitric acid concentration of FP scrubbing solution. It was demonstrated that Np separation (selective reduction by n-butyraldehyde) efficiency could be improved from 36 % to 78 % by flow-sheet modification; increasing reductant concentration and scrubbing solution flow rate. The feasibility of the Tc separation technique by high acid scrubbing was demonstrated.

### INTRODUCTION

In JAERI (Japan Atomic Energy Research Institute), PARC (Partitioning Conundrum-key) process based on PUREX technique has been studied to as the basis of future reprocessing. The future separation process should be adaptable to spent fuels from both LWR and FBR. The future process is also requested to be more economical, producing fewer amount of waste, and safer than present one. Separation concept in PARC process is illustrated in figure 1. The key of concept is to obtain the products, U and Pu, within only a single extraction cycle by separating Np and Tc from U and Pu before U/Pu partition. Such simplification will enhance economy and reduce waste. Separated Np and Tc will be transmuted by an accelerator driven system (ADS) to reduce the radio-toxicity of high level waste.

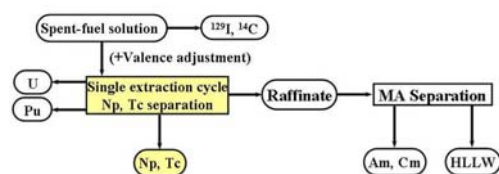


Fig. 1 Separation concept in PARC process.

Extraction behavior of Np in PUREX process is fairly complicated one, because it depends on the valence state of Np. It is known that Np can take several oxidation states, tetravalent to heptavalent, in aqueous solution [1]. A dissolver solution contains several compounds, which may act as Np oxidant or reductant. For

example, nitric acid oxidizes tetravalent Np (Np (4)) to pentavalent Np (Np (5)), nitrous acid, radiolysis product from nitric acid, reduces hexavalent Np (Np (6)) to Np (5), and hydrogen peroxide, radiolysis product from water, reduces Np (5) to Np (4) [1]. From nitric acid solution, Np (4) and Np (6) are easily extracted by TBP, but Np (3) and Np (5) are hardly extracted [2]. It is quite difficult task to measure directly the valence state of Np because of its small amount. Separation technique of Np (6) extracted by TBP together with U (6) and Pu (4) has already been developed. By using a decomposable organic reagent, n-butyraldehyde, Np (6) can be reduced selectively to Np (5), not to Np (4) [3]. Np (5) can be stripped from the solvent with aqueous scrub. This reagent does not reduce U (6) and Pu (4). Thus, the interruption to the extractive behavior of U and Pu can be limited. Feasibility of the technique has been examined in flow-sheet experiment with low burn-up (8 GWd/t) PWR spent fuel solution [4].

As for Tc, existing in a pertechnetate form, it can be co-extracted. Pertechnetate can be stripped from the U/Pu loaded solvent by scrubbing with high concentration of nitric acid. High concentration of nitric acid scrubbing is effective to strip Tc from the solvent [3, 4].

In this paper, the most recent results of spent fuel tests on the extraction process to examine the feasibility of the separation technique of Np and Tc are described. Two test runs were performed under two different flow-sheets to optimize flow-sheet conditions.

## EXPERIMENTALS

### General Description of Tests

Two flow-sheet tests, test #1 and #2, were performed with spent-fuel solutions using three miniature mixer-settlers type liquid-liquid extractor (twenty extraction banks, respectively) in a shielded cell at NUCEF (Nuclear Fuel Cycle Safety Engineering Facility) [5]. The first mixer-settler (MS) was used as co-decontamination and FP scrubbing steps. The second one was used as Np separation and Tc separation, and the third was used as U/Pu partition. PWR spent-fuels with burn-up of 44 GWd/t were dissolved and supplied as feed solutions for these tests.

Prior to the respective test, especially the test #2, flow-sheet for the test was examined with the help of ESSCAR (Extraction System Simulation Code for Advanced Reprocessing)-II.

### Test #1

The flow-sheet for test #1 is shown in figure 2. It should be noted that flow rate of main solvent (MS No. 1) is fairly high. This condition was determined to examine enhancement of Np extraction. The concentration of HNO<sub>3</sub> in FP scrubbing solution (4 M) was determined for the same purpose.

The test was performed about 5 months after dissolution. After 10 hours of dissolver solution feed, MSs were stopped and samples were taken from respective 60 banks as 60 organic samples and 60 aqueous samples.

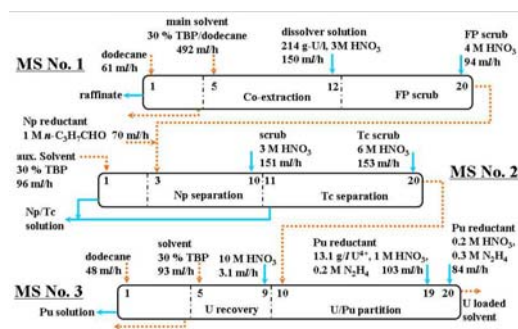


Fig. 2 Spent fuel test flow-sheet #1.

### Test #2

In figure 3, the flow-sheet for test #2 is shown. In this flow-sheet, the flow-rates of Np reductant and Np scrubbing solution were higher than those in test #1. These will enhance Np separation. On the other hand, the flow rate of main solvent is lower. This condition was determined to examine restriction of Np

extraction in MS. 1. The concentration of HNO<sub>3</sub> in FP scrubbing solution is moderate, 3 M. At first, lower concentration as 2 M was considered also to restrict Np extraction. The concentration, however, was altered to 3 M because U and especially Pu accumulation in the FP scrub part was expected with 2 M HNO<sub>3</sub> scrub from ESSCAR-II calculation.

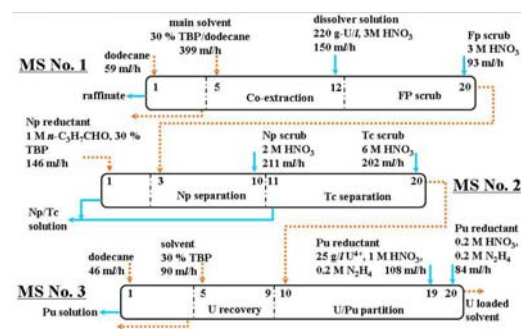


Fig. 3 Spent fuel test flow-sheet #2.

The test was performed about 1 year after dissolution. After 9.5 hours of feed, 120 samples were taken as in test #1.

### Analysis

Concentrations of Np in the dissolver solution and high active aqueous samples taken from extraction banks No. 1-12 in MS No. 1 were determined by ion exchange and direct measurement of alpha activity of Np-237. For the remaining samples, gamma activities of Np-239, already contained in the dissolver solution as daughter nuclide of Am-243, were measured. These values were converted into Np concentration values using isotopic ratio of Np-237 / Np-239 calculated by ORIGEN-II code. The concentrations of Tc were determined by ICP-AES and Tc-95m tracer.

## RESULTS AND DISCUSSION

### Np Extraction

In figure 4, concentration profiles of Np in MS No. 1 (co-decontamination and FP scrub parts) in test #1 are shown. Some examples of calculated profiles by ESSCAR-II code are also shown in the figure. As shown in the figure, percentage of Np remaining in the raffinate was estimated to be 13.2 % of that contained in the dissolver solution. To obtain this value, mass flow rates (concentration × flow rate) of Np in respective solutions were calculated. For the raffinate, concentration value of aqueous sample of bank No. 1 was used. It can be said that high solvent / dissolver solution flow rate ratio and the increase

of HNO<sub>3</sub> concentration in FP scrubbing solution improve the extraction percentage of Np, comparing to the previous results [5].

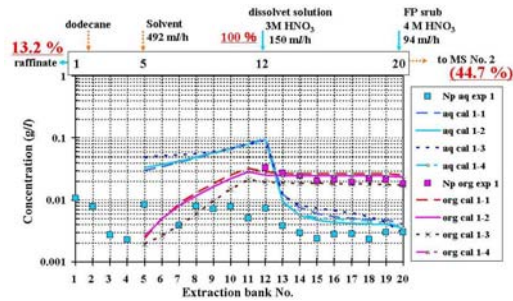


Fig. 4 Results of test #1. Concentration profiles of Np in MS No. 1.

The percentage of Np extracted was estimated to be 44.7 % from the analytical result of Np concentration for the organic sample of bank No. 20 and solvent flow rate. Because the analytical method for the dissolver solution differs from that for the sample, the accuracy of this value should be treated as limited.

In figure 5, concentration profiles of Np in MS No. 1 (co-decontamination and FP scrub) in test #2 are shown. In this test, the percentage of Np in the raffinate was calculated to be 17.4 % of that in the dissolver solution. The percentage of extracted Np was calculated to be 45.4 %. The limitation of accuracy caused from the difference of analytical methods as before mentioned should be kept in mind, again.

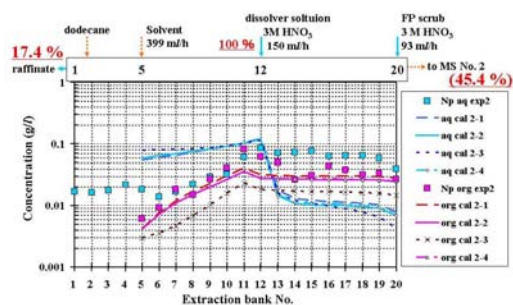


Fig. 5 Results of test #2. Concentration profiles of Np in MS No. 1.

### Np Separation

In figure 6, concentration profiles of Np in Np separation part (bank No. 3-10) and Tc separation part (bank No. 11-20) of MS. No. 2 in test #1 are shown.

It can be seen in this figure that Np concentration in the organic phase gradually decreases as the

bank number increases in the Np separation part. This implies that Np was back-extracted from the solvent in this part. On the other hand, the concentration increases in Tc separation part. This implies that back-extraction of Np did not work well in this part. In this part, the concentration profiles showed an accumulation pattern both in the organic phase and the aqueous phase.

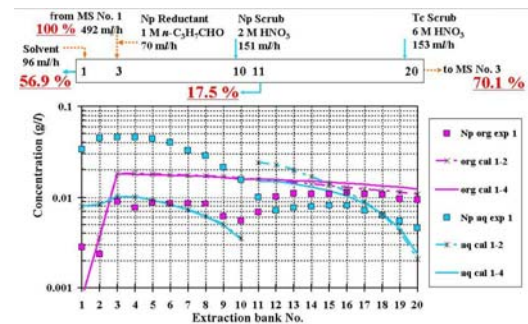


Fig. 6 Results of test #1. Concentration profiles of Np in MS No. 2.

The percentage values shown in the figure were calculated from mass flow rates, treating the value for extracted Np (calculated from the concentration in the organic sample of bank No. 20 in MS. No. 1) as 100 %. Percentage of Np separated in Np scrub part was 56.9 %, that in Tc scrub part was 17.5 %, and that remaining in the solvent was 70.1 %. The total of these values exceeds 100 %. This implies that Np behavior did not reach steady-state. It may be caused by its complicated redox behavior. Np separation efficiency was evaluated to be 39 % (56.9 / (56.9 + 17.5 + 70.1)) for the Np separation part.

Concentration profiles of Np in Np scrub and Tc scrub part of MS No. 2 in test #2 are shown in figure 7.

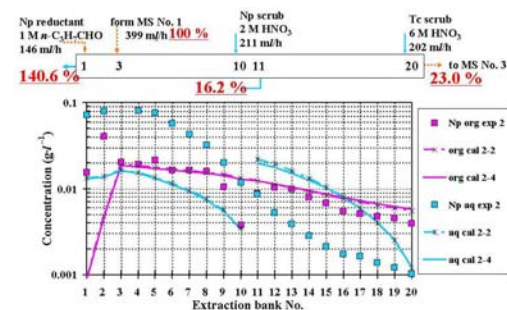


Fig. 7 Results of test #1. Concentration profiles of Np in MS No. 2.



Comparing with test #1 (Fig. 6), Np concentration in the organic phase decreased more rapidly in the Np separation part. This implies that Np back-extracting worked better in test #2. This may be attributed to the increased reductant concentration, increased Np scrub flow rate, and slight increase of resident time of solvent in the Np scrub part.

In the Tc separation part, Np concentration increased at banks No. 11 and 12 similarly to Fig. 6. The concentration, however, decreased again at banks No. 13 to 20. This implies that back-extraction of Np still worked in this part. The profiles showed an accumulation pattern only in organic phase.

The percentage values shown in the figure were calculated in the same manner as those in Fig. 6. Percentage of Np separated in Np scrub part was 140.6 %, that in Tc scrub part was 16.2 %, and that remaining in the solvent was 23.0 %. The total of these values exceeds 100 %, again.

For the test #2, Np separation efficiency was evaluated to be 78 % (140.6 / (140.6 +16.2 +23.0)) for the Np separation part.

### Np in U/Pu Partition

In figure 8, concentration profiles of Np in MS No. 3, U/Pu partition part, in test #1 is shown. The percentage values shown in the figure were calculated in the same manner as those in Fig. 6. The Np flowed into this part distributed both Pu solution and U loaded solvent.

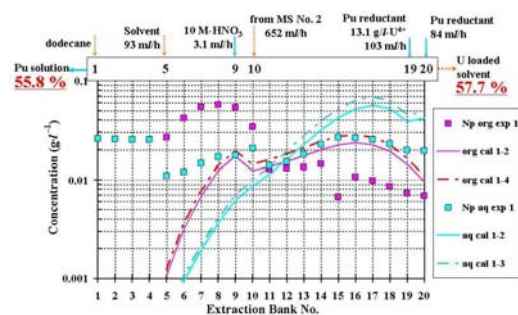


Fig. 8 Results of test #1. Concentration profiles of Np in MS No. 3.

In figure 9, concentration profiles of Np in MS No. 3, U/Pu partition part, in test #2 is shown. It seems that Np flowed into this part did not flow out yet.

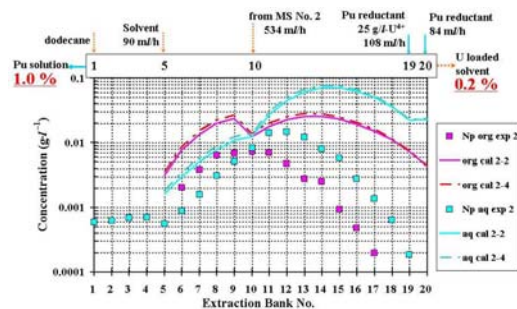


Fig. 9 Results of test #2. Concentration profiles of Np in MS No. 3.

### Tc Separation

In the two tests, sufficient results to demonstrate Tc extraction from dissolver solution were not obtained. Therefore, only the results about Tc separation in MS. No. 2 are described.

In figure 10, concentration profiles of Tc in MS No. 2, in tests #1 are shown.

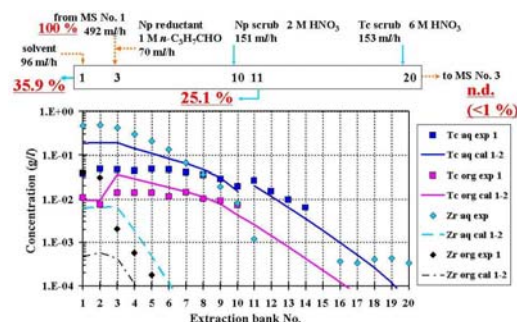


Fig. 10 Results of test #1. Concentration profiles of Tc in MS No. 2.

From this figure, it can be noted that substantial percentage of Tc was stripped from the solvent in the Np separation part together with Np. The rest of Tc was sufficiently stripped in the Tc separation part, and Tc remaining in the solvent was under the detection limit ( $9 \times 10^{-4}$  g/l).

### CONCLUSION

In this study, it was demonstrated that remaining Np in raffinate from co-extraction could decrease to 13 % compared to the dissolver solution with increased solvent flow rate and with increased nitric acid concentration of FP scrubbing solution in test #1. It was demonstrated that Np separation efficiency could be improved from 36 % in test #1 to 78 % in test #2 by flow-sheet modification; increasing reductant concentration and scrubbing solution

flow rate. As for Tc separation, the feasibility of the technique was demonstrated.

As a next task, valence adjustment of Np in dissolver solution should be examined to obtain higher Np extraction. Heating of dissolver solution will be good technique because it does not need extra reagent nor apparatus. To obtain higher Np separation efficiency, further modification of flow-sheet should be examined. Utilization of new faster reductant is also in our scope, although safety of the new reagent should be paid attention. Demonstration of Tc extraction from dissolver solution is still remaining as a task.

Late in this year, MOX spent fuel test is scheduled. Although the experiment will be performed under conventional PUREX flow-sheet, Np extraction and Tc extraction will be examined.

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#### ACKNOWLEDGEMENT

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