

The progress of TRUEX process improvement in PNC
- The applicability of "Salt-free" reagents-

Hiroyasu Hirano, Kazunori Nomura, Yoshikazu Koma, Shinichi Nemoto,
Masaki Ozawa and Akio Togashi

Reprocessing Technology Development Division
Power Reactor and Nuclear Fuel Development Corporation (PNC)
Tokai-mura, Ibaraki-ken, Japan

ABSTRACT

PNC has been promoting actinides partitioning studies as a part of advanced reprocessing system development efforts since 1990.¹⁾ Concurrently, the general TRUEX process was studied as a reference partitioning tool. In the counter-current flow-sheet tests using mixer-settler, some portion of U, Pu and Ru used to remain in the solvent by conventional stripping methods. Therefore a new "Salt-free" solvent-washing methods were studied to remove these nuclides and Zr from TRUEX solvent. Hydrazine oxalate was tested for U. Hydrazine oxalate, hydrazine carbonate and TMAH (tetramethylammonium hydroxide) were tested for Ru and Zr. The stripping behavior of Pu by hydrazine oxalate was studied through the counter-current test. It was concluded that various "Salt-free" reagents will be effective, if these are used in combination manner, for reducing these nuclides retention in the solvent.

INTRODUCTION

Partitioning of actinides in the High Level Liquid Waste (HLLW) is one of the key technology to achieve advanced reprocessing system in which recovered minor actinides will be recycled to reactor with U and Pu. This system is named "Actinide Recycle System". Such an innovative reprocessing may contribute to increase the fuel utilization efficiency and to decrease potential radioactive hazard of vitrified HLLW.

PNC has been studying the applicability of the TRUEX process²⁾ as a method for removal of actinides in the HLLW from the PUREX process. The batch-wise basic tests and the counter-current tests using the real highly active raffinate (HAR) derived from the PUREX process of FBR spent fuel have been carried out.

In these tests, the extraction behavior of actinides, lanthanides and some fission products became almost clear; Actinides and lanthanides were extracted quantitatively from HAR in the extraction bank and a high α -decontamination factor, $>ca.10^3$, was obtained.³⁾ Trivalent actinides and lanthanides were co-recovered from the loaded solvent in the stripping bank using dilute nitric acid. On the other hand, some portion of U, Pu and Ru were difficult to remove from the solvent by conventional stripping methods. In former counter-current test^{3),4)}, dilute nitric acid, HAN (Hydroxylamine nitrate), oxalic acid and sodium carbonate were tested as stripping reagents. Sodium carbonate seems to be highly effective at least in reducing amount of Pu as well as Ru in the solvent.^{3),4)}

Sodium carbonate has been employed as the solvent-washing reagent in PUREX process. From a view of a secondary waste generation, sodium-based reagents should be avoided. Therefore "salt-free" solvent-washing reagents, which were able to be decomposed to gaseous material by an electrochemical process, etc., were adopted to PUREX process⁵⁾ and were tested in the TRUEX process.

EXPERIMENTAL

Two kinds of tests were carried out. The objective element of the first test was U, and the second ones were Ru and Zr which were also troublesome fission products in PUREX and TRUEX processes. These two tests were carried out in a batch-wise method. The other kind of tests was the counter-current test using real HLLW aiming to evaluate an effect of salt free reagent on Pu and Ru stripping.

In U test, hydrazine oxalate was tested and compared with sodium carbonate, and a mixture solvent was composed 0.2M CMPO-1.0M TBP in n-dodecane. The test was performed at a room temperature(R.T.) and the organic/aqueous ratio (O/A ratio) was 1.

In Ru and Zr test, hydrazine oxalate, hydrazine carbonate and TMAH were tested. The reference alkali reagent was sodium carbonate. The solvent composed 0.2M CMPO-1.0M TBP in n-dodecane was irradiated up to 10^7 R by γ - ^{60}Co . The test was performed at R.T. and the O/A ratio was 1.

In the counter-current test using mixer-settler at the chemical processing facility (CPF), hydrazine oxalate was tested as stripping reagent for Pu. Feed solution was a real HAR derived from FBR-PUREX reprocessing tests. This solution contained much amount of corrosion products, Fe,Cr,Ni, corresponded to the concentration in the real HLLW from LWR reprocessing plant. (Refer to figure 1) The amount of total metals in the feed solution was about 5 times higher than in normal FBR-HAR. The flow-sheet of this test was shown in figure 2. The mixed solvent was 0.2M CMPO-1.4M TBP in n-dodecane. The concentration of TBP was a little higher than the former tests^{3),4)} attempting to avoid a third phase split. The extraction/scrubbing bank employed 32 stages and the stripping bank employed 19 stages. The dual-scrubbing method offering two scrubbing solutions was employed for improved Ru decontamination in the same manner as former tests.³⁾ The stripping bank was divided in two parts, the former was the trivalent actinides and lanthanides stripping part using dilute nitric acid and the latter was the Pu and U stripping part using hydrazine oxalate.

RESULT and DISCUSSION

The distribution ratio of U vs. reagent concentration was shown in figure 3. When the reagent concentration was lower than 0.1M, hydrazine oxalate showed less efficient than sodium carbonate. However, the distribution ratio of U using hydrazine oxalate, ca.0.1, was enough low to reduce U retention in the solvent. When the reagent concentration exceeded 0.1M, which were much excess to U concentration in the solvent, hydrazine oxalate indicated a good efficiency of U stripping as well as sodium carbonate. This indication was considered from the results that almost U was formed a water-soluble complex with oxalate ion or carbonate ion and then removed from the solvent.

The stripping efficiencies of Ru and Zr using another salt-free reagents were tested. Figure 4 shows the stripping ratio vs. reagents concentration in the case of pre-irradiated TRUEX solvent. TMAH showed a higher efficiency. Ru was stripped quantitatively when the reagent concentration was higher than 0.1M. In the case of reagent concentration exceeded 0.2M, the stripping ratio by sodium carbonate and hydrazine carbonate also became sufficient (>90%). But, hydrazine oxalate was not effective to strip Ru. As reported in the former paper ³⁾, the efficiency of Ru stripping was affected by the pH-value of aqueous phase and the significant Ru stripping can be obtained in higher pH value conditions. Figure 5 showed the stripping ratio of Zr vs. reagents concentration in the case of pre-irradiated solvent. The strip tendency of Zr was essentially similar to Ru; the higher Zr stripping was obtained in the higher complexing reagent concentration, about more than 10 times the Zr concentration. In the results showed, hydrazine oxalate was more efficient for Zr than for Ru. A similar result was experienced in the PUREX process ⁵⁾. It was considered that the complex formation with oxalate ion contributed to be stripped Zr from the solvent. In the most case of Ru and Zr stripping test, the interfacial cruds formation was observed. While the behaviors of cruds formation and decomposition have not become clear yet, the control of cruds is one of the problems to solve for the application of salt-free reagent.

The material balance of main elements in the counter-current test was shown in Table 1. Trivalent actinides (Am, Cm), lanthanides (Eu) and Pu were extracted quantitatively from the HAR to the solvent. Fission products (Cs) were not extracted and then retained in the raffinate stream. Some portion of Ru was extracted to the solvent. In the strip bank used dilute nitric acid, some portion of trivalent actinides and lanthanides were stripped from the solvent. However, a major portion of these was leaked to the later strip bank used hydrazine oxalate. Both of Pu and Ru were not stripped by dilute nitric acid. Because of the large amount of metal leakage, a precipitation formed in the stripping bank used hydrazine oxalate. The amount of elements in the precipitation was not measured, thus the stripped portion by hydrazine oxalate in Table 1 was estimated from the balance of the other fraction.

Pu was completely removed from the spent solvent. However, Ru was not stripped sufficiently and almost of the extracted Ru was still remained in the spent solvent. The precipitation formation was observed in the stripping bank used hydrazine oxalate. However, hydrazine oxalate was proved to be effective reagent for Pu stripping. On the other hand, hydrazine oxalate was not sufficient for Ru stripping, and it was the same result that obtained in the batch-wise test.

After the operation of counter-current test used the HAR corresponding to the LWR-HLLW, the third phase splitting was observed in the half part of extraction/scrubbing bank, and then the third phase seemed to form during the operation. However, the extraction behaviors of main elements in the extraction bank were not significantly different from the former tests used the normal FBR-HAR^{3),4)}, in which the third phase was not observed. Though the third phase was not recognized to affect seriously for extraction in this test, avoiding the third phase formation might be important to obtain selective actinide fractionation according to their valency.

Considering the results mentioned above, the next counter-current test using the improved flow-sheet will be carried out in near future. In this test, three kinds of salt-free reagent will be tested; the first is HAN in dilute nitric acid for Pu stripping, the second is hydrazine oxalate for mainly U and Pu stripping and the third is hydrazine carbonate for Ru stripping.

CONCLUSIONS

Some salt-free reagents, which were used in the PUREX process, were tested for nuclei stripping from the TRUEX solvent in the batch-wise tests and the counter-current test used the FBR-HAR. Hydrazine oxalate was proved to be reagent sufficient for U and Pu stripping from the TRUEX solvent. Hydrazine carbonate and TMAH were sufficient for Ru and Zr stripping from the pre-irradiated TRUEX solvent. The efficiency of salt-free reagents was not much inferior to sodium carbonate. It means that conventional sodium-based reagent is able to be replaced by the salt-free reagent from a view of nuclei removal from the TRUEX solvent.

The optimization of the flow-sheet condition aiming complete "Salt-free" TRUEX process is in progress.

REFERENCE

- 1) T. Kawata et.al., "Preliminary Study on the Partitioning of Transuranium Elements in High Level Liquid Waste", Proc. First OECD/NEA Information Exchange Meeting on Separation and Transmutation of Actinides and Fission Products, Mito, Japan, Nov.6-8,1990
- 2) P.Horwitz et.al., "THE TRUEX PROCESS:A VITAL TOOL FOR DISPOSAL OF U.S. DEFENSE NUCLEAR WASTE", Proc. New Separation Chemistry for Radioactive Waste and Other Specific Application, Rome, Italy, May 16-18,1990
- 3) M.Ozawa, et.al., "Some Modifications of the TRUEX Flowsheet for Partitioning of Actinide Elements in High Level Liquid Waste", Proc. Second OECD/NEA Information Exchange Meeting on Separation and Transmutation of Actinides and Fission Products, Chicago, USA, Nov.11-13,1992
- 4) K.Nomura, et.al., "JAPANESE EXPERIENCE IN APPLICATION OF THE TRUEX PROCESS TO HIGH LEVEL WASTE FROM REPROCESSING", Proc.GLOBAL'93. Seattle, USA, Oct. 12-17, 1993
- 5) M.Ozawa, et.al., "MECHANISM FOR SOLVENT CLEANUP PROCESS USING SALT-FREE REAGENTS", Proc. RECOD'91, Sendai, Japan, 1991

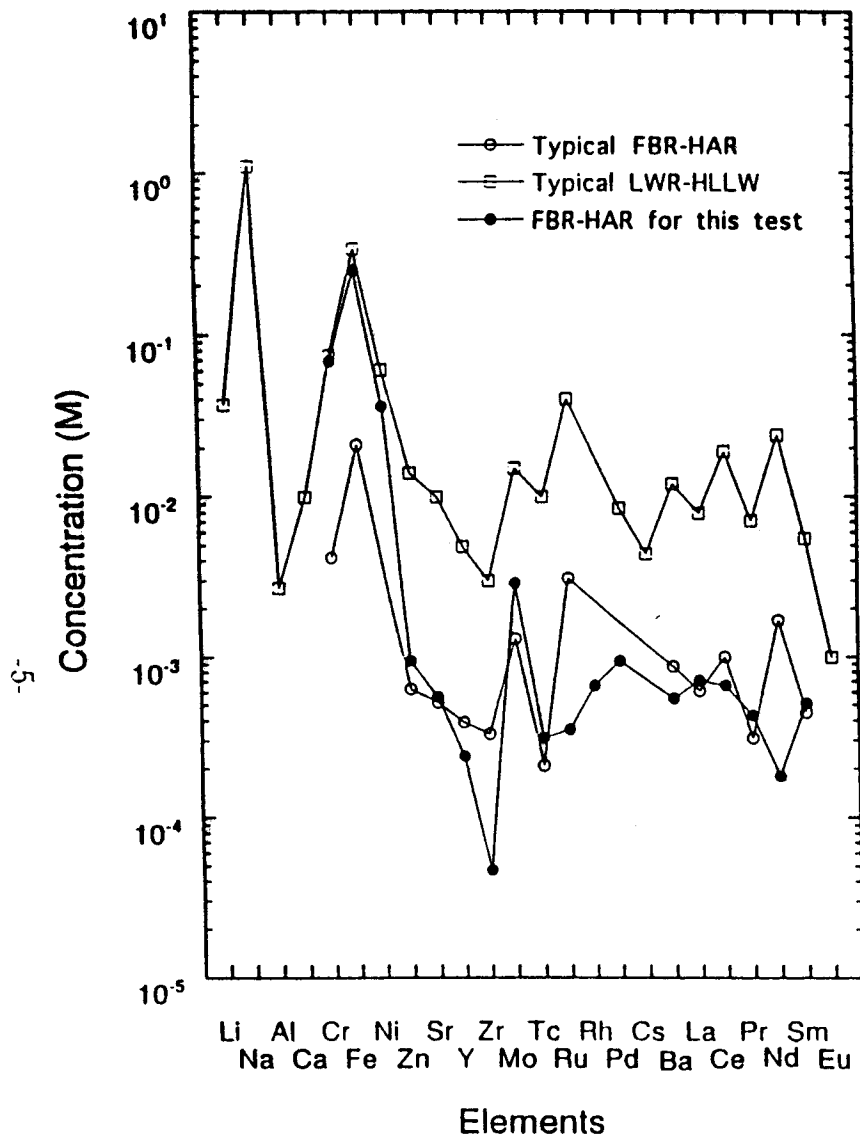


Figure 1 The composition of solution used for the counter-current test

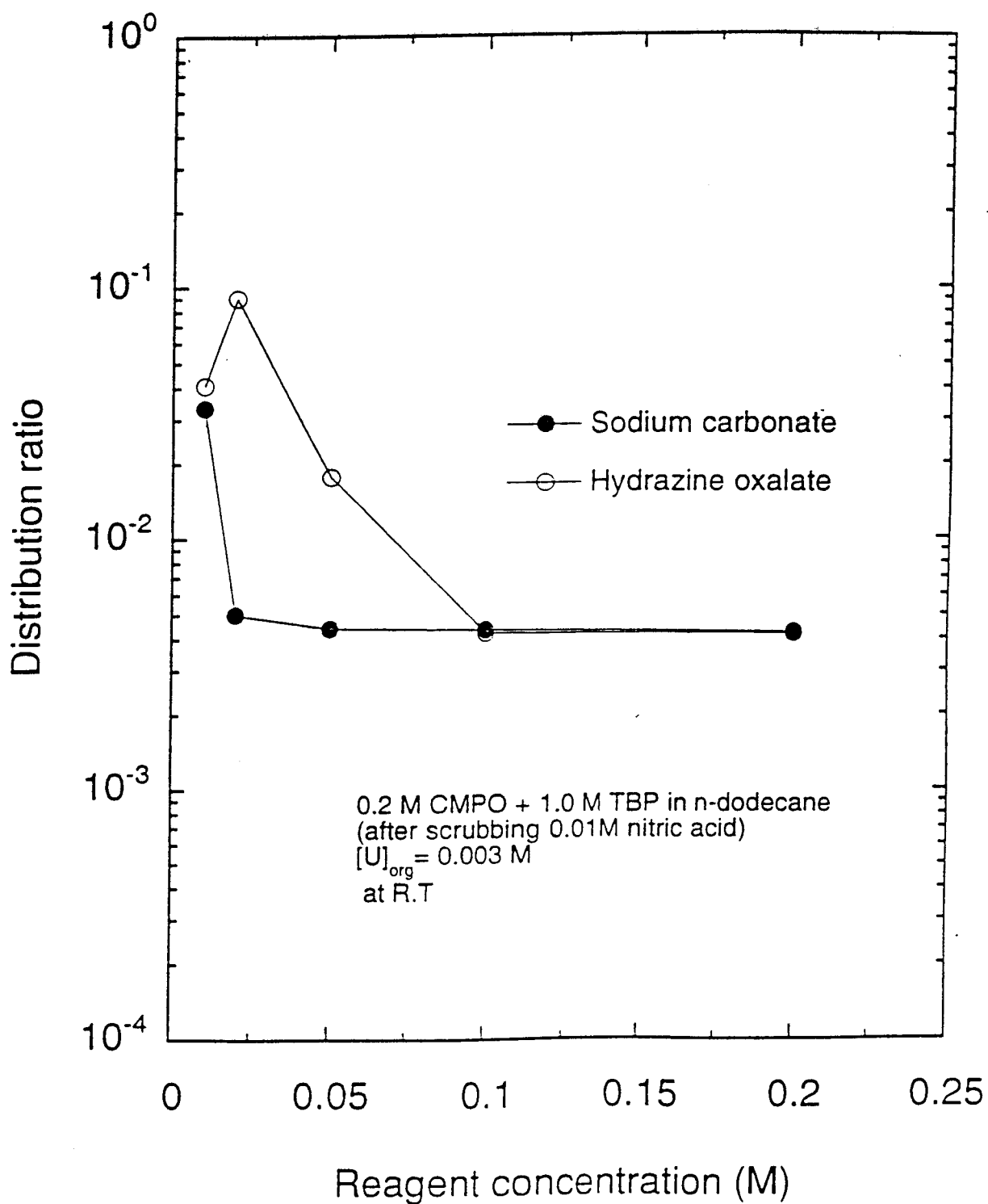


Figure 3 The dependency of U distribution ratio on reagent concentration

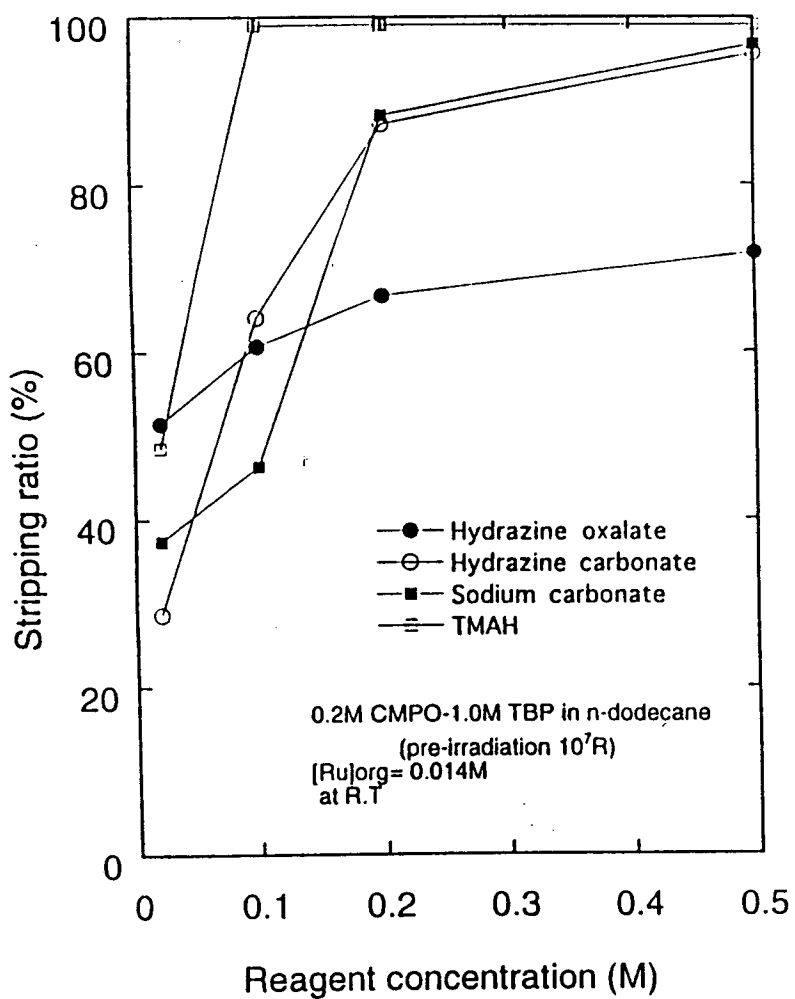


Figure 4 The dependency of Ru stripping ratio on reagent concentration

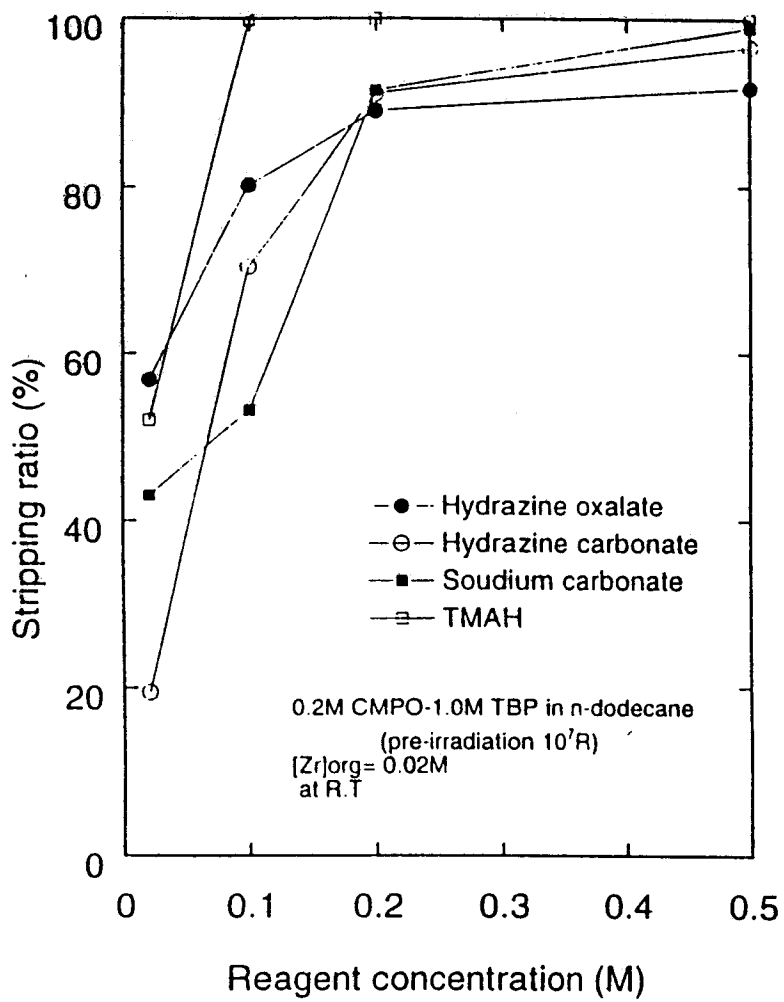


Figure 5 The dependency of Zr stripping ratio on reagent concentration

Table 1 The material balance for the main elements in the counter-current test

Elements	Strip(1)		Strip(2)	
	Raffinate	Diluted nitric acid	Hydrazine oxalate	Spent solvent
Cs	ca. 100%	-	-	-
Eu	-	ca. 5%	95%*	-
Am**	-	ca. 3%	97%*	-
Cm	-	ca. 4%	96%*	-
Pu	-	-	100%*	-
Ru	-	-	0~4%	~5%

Amount of feed = 100%

- : Not detected

* Calculated value : (100% - (Raffinate + Strip(1) + Spent solvent)

** Am-241 + Pu-238