

Some Modifications of the TRUEX Flowsheet for Partitioning of Actinides Elements in High Level Liquid Waste

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ABSTRACT

PNC has been promoting actinides partitioning studies as a part of advanced reprocessing system development efforts since 1990. Concurrently, the general TRUEX process was investigated as a reference partitioning tool. A concentrated high level liquid waste (HLLW) from LWR fuel reprocessing and a highly active raffinate (HAR) from FBR spent fuel PUREX experiments were nominated as target waste solutions. A mixed solvent composed of 0.2 M CMPO - 1.0- 1.8 M TBP in n-dodecane was tested as a TRUEX solvent. Counter-current tests aimed to improve the TRUEX process, using a real HAR generated from the PUREX process, were performed in the Chemical Processing Facility (CPF), Tokai Works. In these experiments, very high α - decontamination with explainable extraction profiles of tri-valent actinides and rare earth elements were obtained, but some retentions of Pu and Ru in the organic phase was recognized as a major issue of the TRUEX process. In the current investigation, however, it was found that the conventional solvent regeneration step can be an effective "barrier" for these nuclides' retention in the waste solvent.

INTRODUCTION

PNC has been carrying out basic experiments for the purpose of separating actinides from HLLW since 1990, as a part of an effort to increase the fuel utilization efficiency and to widen the options for waste management in the future¹⁾. Due to its high compatibility to the present PUREX process, PNC's current strategy is to apply the general TRUEX process, originally developed by Horwitz, et al.²⁾ to the actinides partitioning process..

The concept of an "Advanced reprocessing system" (Fig. 1) shows that the PUREX and TRUEX processes should be developed in parallel. The PUREX especially should be improved by focusing on lightening the load on the succeeding partitioning process. Generating simpler compositions with smaller amounts of HLLW is a major goal for improving the process. For this purpose, the methods using sodium-based reagents should be avoided, and Np should be co-extracted into the product Pu-streams in the Purex process. One

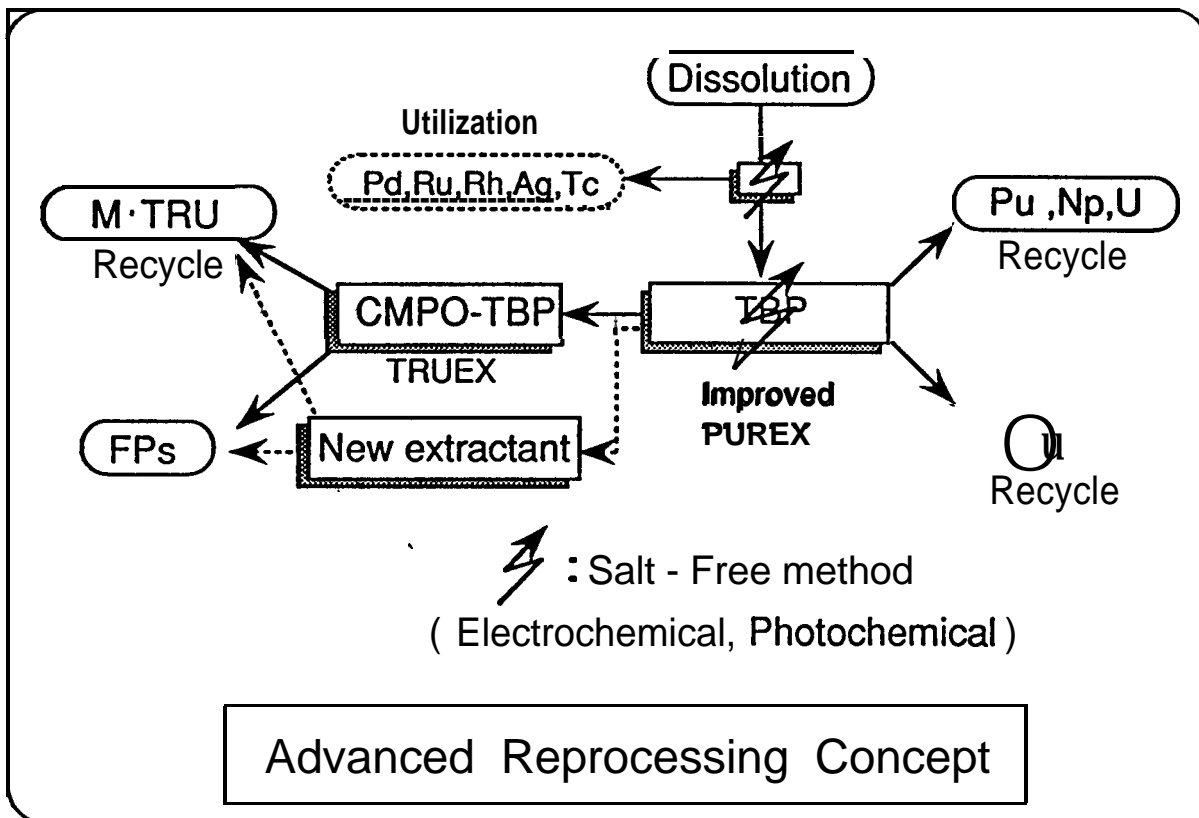


Fig.1 Advanced Reprocessing System

method to achieve this goal is to adopt “salt-free” reagents and in-situ electrochemical processes to the PUREX process³⁾. Being troublesome in the aspect of decontamination for the PUREX and TRUEX process in common, Ru, Rh, Pd and Tc should be removed prior to solvent extraction cycles. This will help simplify the extraction system of the PUREX process. A technique which will not introduce foreign materials into the solvent extraction and thus will not generate secondary waste should be incorporated in the upper part of the solvent extraction process. Electrolytic extraction of such precious metals from the dissolver solution will meet such a requirement. A basic potentiostatic test using a simulated dissolver solution and HLLW suggested that Pd, Rh and Ag can be deposited quantitatively on Ta or Ti electrodes without decreasing acidity by polarizing the electrode potential to be negative. On the other hand, Ru deposition efficiency was small, but a large portion of the ionic state of Ru can be transformed to another state with diaphragmless electrolysis⁴⁾.

TRUEX EXPERIMENTS

The TRUEX process is characterized by the use of the bifunctional extractant CMPO, octyl(phenyl)-N,N-diisobutylcalbamoylmethylphosphine oxide, with a PUREX solvent in combination, which will extract tri-, tetra- and hexa-valent actinides from various kinds of solution. The main purpose of our study was to identify the R&D items and then to improve TRUEX process, in applying it to the actinides partitioning process for HLLW. Thus, the counter-current tests using real HAR originating from FBR spent fuel PUREX reprocessing was carried out to meet that purpose.

A mixture composed of 0.2 M CMPO and 1.0-1.5 M TBP in n-dodecane was tested as a TRUEX solvent for the measurement of distribution ratio and third phase split boundary, As for counter-current tests, a mixture composed of 0.2M CMPO and 1.0M TBP in n-dodecane was adopted. The HAR was derived from PUREX reprocessing experiments of FBR-Joyo MK-II spent fuel burned up to ca. 54000 MWD/T and cooled for 2~ 4 years. In the counter-current tests, the HAR was used without adjusting acidity, but with

adding small amounts of **Pu** and oxalic acid which inhibits **Zr** and **Mo** from **coextraction** with the **actinides**. The mixer-settlers employed had **19** stages for extraction-scrubbing and 16- 19 stages for stripping including solvent regeneration. The volume of one stage of **the** mixer-settler was 23 mL. All the experimental apparatus was installed in a shielded **cell**. Based on the distribution values obtained by batch tests, three counter-current mixer-settler runs were carried out.

RESULTS AND DISCUSSION

The distribution ratio (D) values for actinides, **Pu(III)**, **Pu(IV)**, **Np(IV)**, **Np(V)** and **Np(VI)**, and for the other impurities as a function of nitric acid are shown in Fig. 2⁹. **Pu(III)** and **Np(V)** were obtained by adding an excess of Hydroxyl Amine Nitrate (HAN) to **Pu(IV)** and **Np(mix)** solution. **Np(mix)** was prepared by equilibrating Np in nitric acid solution about 24 hours without adding redox agents. Similarly, **Np(IV)** and **Np(VI)** were obtained by contacting with **Fe(II)** and **Cr(VI)**. It can be seen that it's quantitative extraction at 3M nitric acid is possible if Np **valency** is adjusted to IV and VI, otherwise probably **Np(mix)**. **Np(V)**, on the contrary, showed sufficiently low distribution ratios to suggest that quantitative stripping would be expected. The **D_{Pu(mix)}** showed still larger than 10 even at 0.1 M nitric acid concentration, thus indicating that the reductive stripping, unlike in the PUREX process, must be carried out in very low nitric acid conditions. Although not clearly shown herein, higher than 5 M nitric acid concentration seems to be effective in inhibiting its extraction.

Fig. 3 shows the **flowsheet** conditions for counter-current tests of each run. In the scrubbing bank, dual scrubbing using two different concentrations of nitric acid was adopted to improve Ru decontamination and to avoid **oxalate** precipitation in the second and third runs. In the third run, the acidity of the feed solution was increased from 4 M to 7 M for the purpose of increasing Ru decontamination and accelerating Np extraction. In order to confirm the

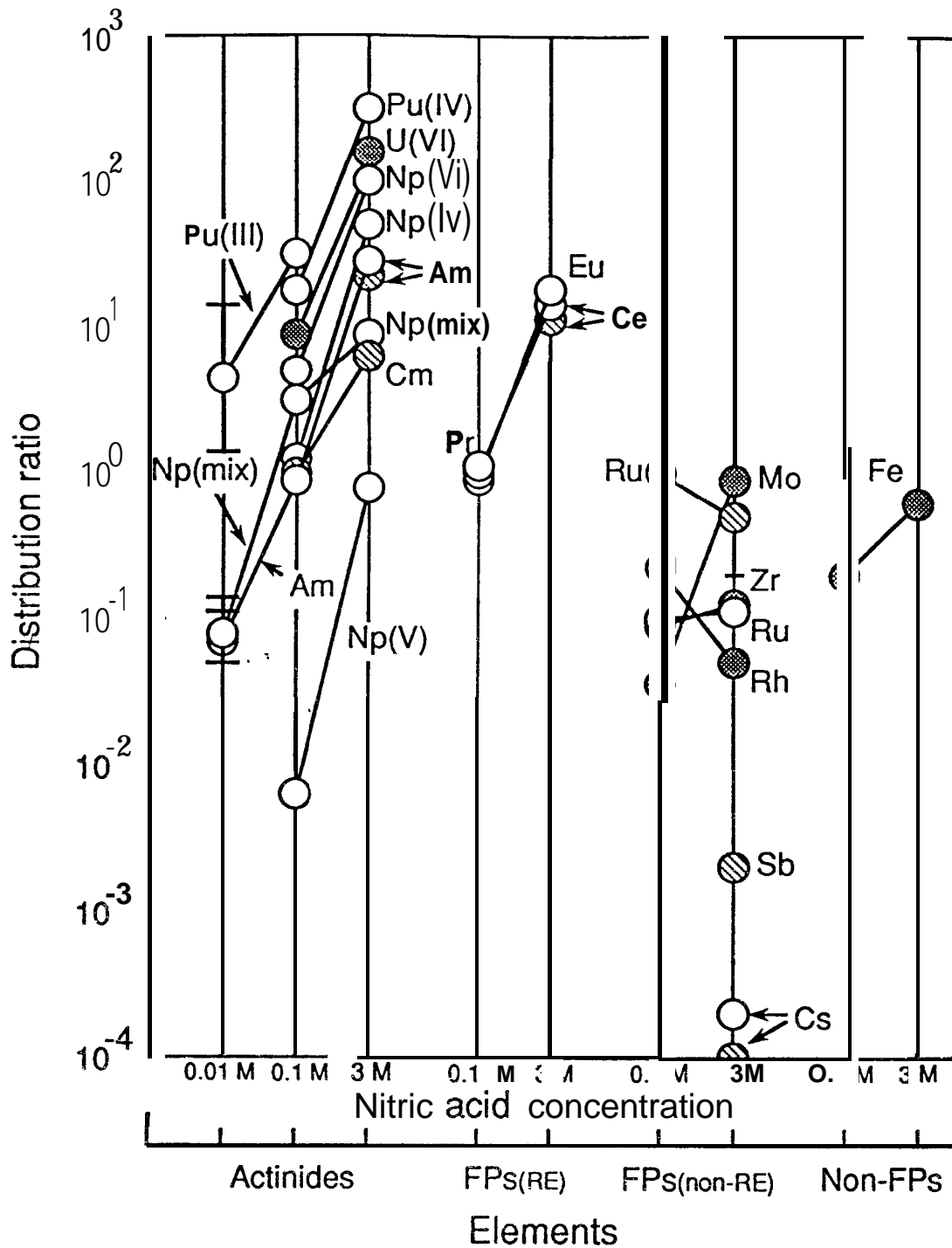
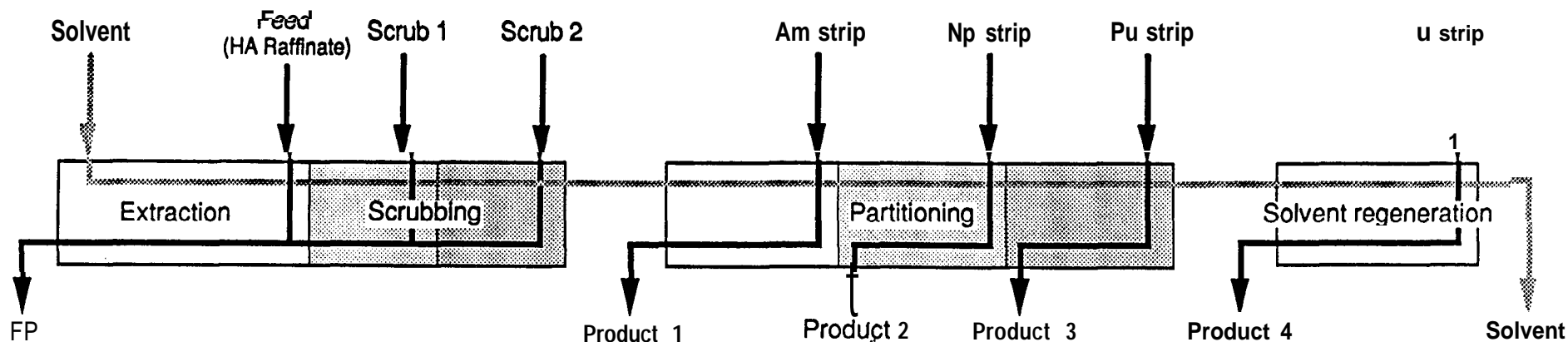


Fig. 2 Acid dependency of distribution ratios of major components in HLLW

- D without oxalic acid
- D with oxalic acid
- ◐ D_M with oxalic acid (Mixer-settler test)



Run	Feed (HAR)	Extractant	Scrub -1	Scrub -2	Am strip	Np strip	Pu strip	U strip
1st	"Joyo" MK-II 54100 MWD/T 1500d cooling H ⁺ : 4,0 M	0.2M CMPO 1.0M TBP n-dodecane	—	0.3M HNO ₃ 0.1 M H ₂ C ₂ O ₄	—	—	0.01M HNO ₃	—
	196 mL/h	87 mL/h		40 mL/h			106 mL/h	
2nd	"Joyo" MK-II 54100 MWD/T 1500d cooling H ⁺ : 4.5 M 0.02M H ₂ C ₂ O ₄ Pu addition	0.2M CMPO 1.0 M TBP n-dodecane	7.7M HNO ₃ 0.03M H ₂ C ₂ O ₄	0.3 M HNO ₃	—	—	0.01M HNO ₃	—
	196 mL/h	119 mL/h	12 mL/h	16 mL/h			79 mL/h	
3rd	"Joyo" MK41 54100 MWD/T 1500d cooling + "Joyo" MK-II 54700 MWD/T 700d cooling H ⁺ : 7,0 M	0.2M CMPO 1.0M TBP n-dodecane	7.7M HNO ₃ 0.03M H ₂ C ₂ O ₄	0.3M HNO ₃	0.01M HNO ₃	0.3M HNO ₃ 0.1M HAN	0.5M HNO ₃ 0.1 M H ₂ C ₂ O ₄	0.1M Na ₂ CO ₃
	200 mL/h	100 mL/h	30 mL/h	30 mL/h	100 mL/h	50 mU/h	50 mL/h	50 mL/h

Fig. 3 Flow conditions for counter-current tests

fundamental stripping behaviors, rather simple dilute nitric acid was used in the partitioning banks during the first and second runs. In the third run, however, in addition to dilute nitric acid, HAN, oxalic acid and sodium carbonate were applied to determine the appropriate selective stripping method of actinides.

The extraction profiles obtained by mixer-settler runs indicated that the extraction of all of actinides and tri-valent rare earths were completed within a few extraction stages as expected. These nuclides were never found at the aqueous outlet stage of the extraction bank. ^{137}Cs and ^{125}Sb were confirmed to be completely retained in the aqueous phase. As a result of dual scrubbing, extracted portions of ^{106}Ru became low from over 10% to 6%, and 2% by increasing the acidity of the feed solution to 7 M.

The typical partitioning profiles of actinides and FPs are shown in Fig. 4. The tri-valent actinides, ^{241}Am , ^{244}Cm , and rare earth, ^{144}Ce , were stripped out with dilute nitric acid as expected. However, insufficient recovery rates of these nuclides, ca. 50 to 80%, would attribute to the small accumulation of these in the organic extraction banks. Organic Pu concentration, on the contrary, was almost constant even though it was contacting with dilute nitric acid, HAN and oxalic acid in series. After scrubbing with sodium carbonate solution, however, Pu concentration was considerably decreased. When stripping is carried out using only dilute nitric acid, more than 95% of Pu was allowed to be retained in the organic phase, but a combination of reduction of Pu valency from IV to III by HAN with sodium carbonate scrubbing gave a high recovery rate, more than 80% of Pu. Such a balance with reductive stripping of plutonium was consistent with the distribution data of Pu(III) at 0.01 M HNO_3 , obtained by the batch test.

The organic ^{106}Ru profile indicated that very little unstrippable species existed in spite of exposing with any kind of chemical reagent. Considerable effects, however, resulting from sodium carbonate scrubbing could be attributed to similar effects observed in the PUREX system (higher Ru scrubbing can be obtained in higher pH scrubbing regions with any kind of reagent⁹). The same pH dependency of Ru scrubbing ratio was obtained in the

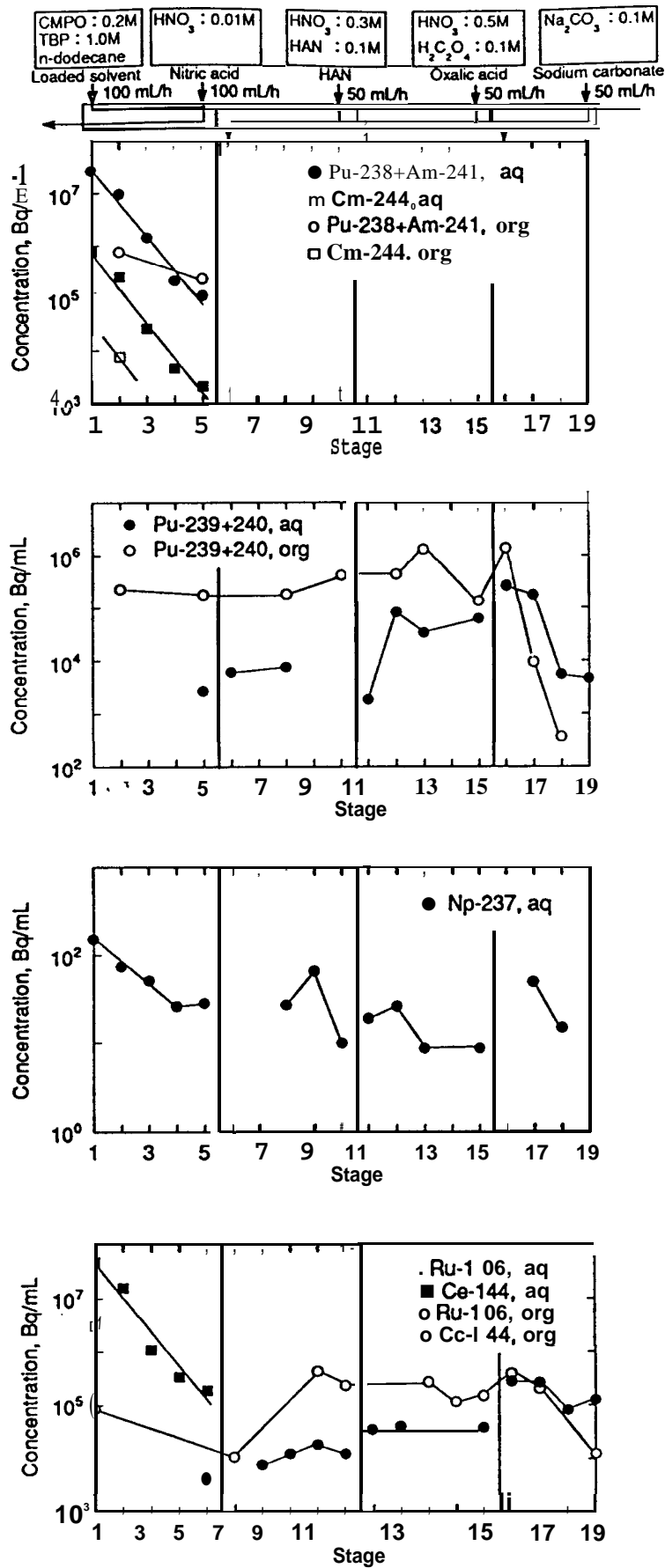


Fig. 4 Typical partitioning profiles of actinides and FPs in the 3rd counter-current test.

y -irradiated TRUEX solvent exposed with 10^7 R by sodium carbonate, hydrazine carbonate, etc. (as indicated in Fig. 5).

Through three mixer-settler runs, the third phase splitting was never found at the interfaces. The operation for higher metal concentration solutions, such as concentrated HLLW, will need more detailed examination for loading limits to avoid third phase splitting. As a result of tests using simulated HLLW, operating conditions with higher TBP concentration ($\geq 1.4\text{M}$) and higher operating temperature ($\geq 40^\circ\text{C}$) for instance, will be recommended unless the HLLW is diluted⁷⁾.

The decontamination factors for ^{241}Am and Total-a removal from HAR were both larger than 5×10^3 . The separation factors for FPs removal from ^{241}Am products were ca. 0.6, ca. 20 and larger than 4.5×10^4 for ^{144}Ce , ^{106}Ru and ^{137}Cs , respectively. These numbers closely agree with past data⁵⁾.

In the effort to discover another extractant for the partitioning, a concept of allosteric metal binding was newly proposed by Kobuke, et al.⁸⁾. The concept describes that a host with two metal binding sites, in which pre-binding of M_1 to the first site, influences the second site electronically and conformationally. This metal-assisted organization converts the second site from a weak binding site into a potent site for the cooperative binding of M_2 . The PNC/university collaboration work suggests that it is notable that copper (as M_1) - assisted coronands, e.g., bis(β -diketonato)-Cu-polyether 26, affords the most appropriate and selective binding site to alkali and alkaline earth metal ions (as M_2), especially for Sr^{2+} , as shown in Fig. 6.

CONCLUSION

Batch and counter-current tests based on the CMPO/TBP extractant have been carried out to provide data on the applicability of the TRUEX process performance for the actinides partitioning process for HLLW. Very promising results with D.F.'s of over 10^3 for major actinides separation from HA raffinate were obtained to support the TRUEX process. A combination of reductive

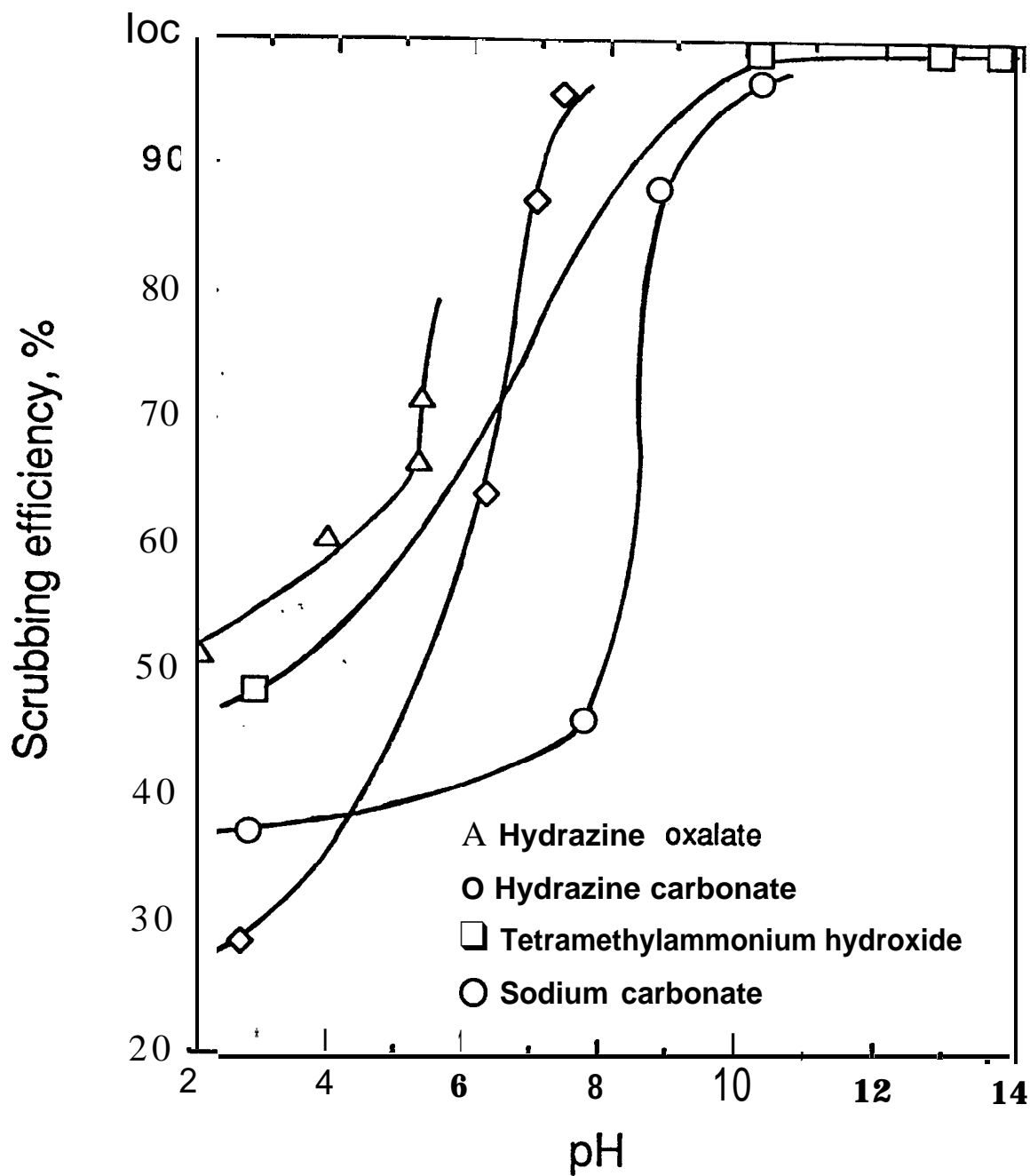


Fig. 5 The scrubbing efficiency of Ru in the degraded solvent by y-ray irradiation (107R).

Solvent: 0.2M CMPO + 1.0 M TBP in n-dodecane

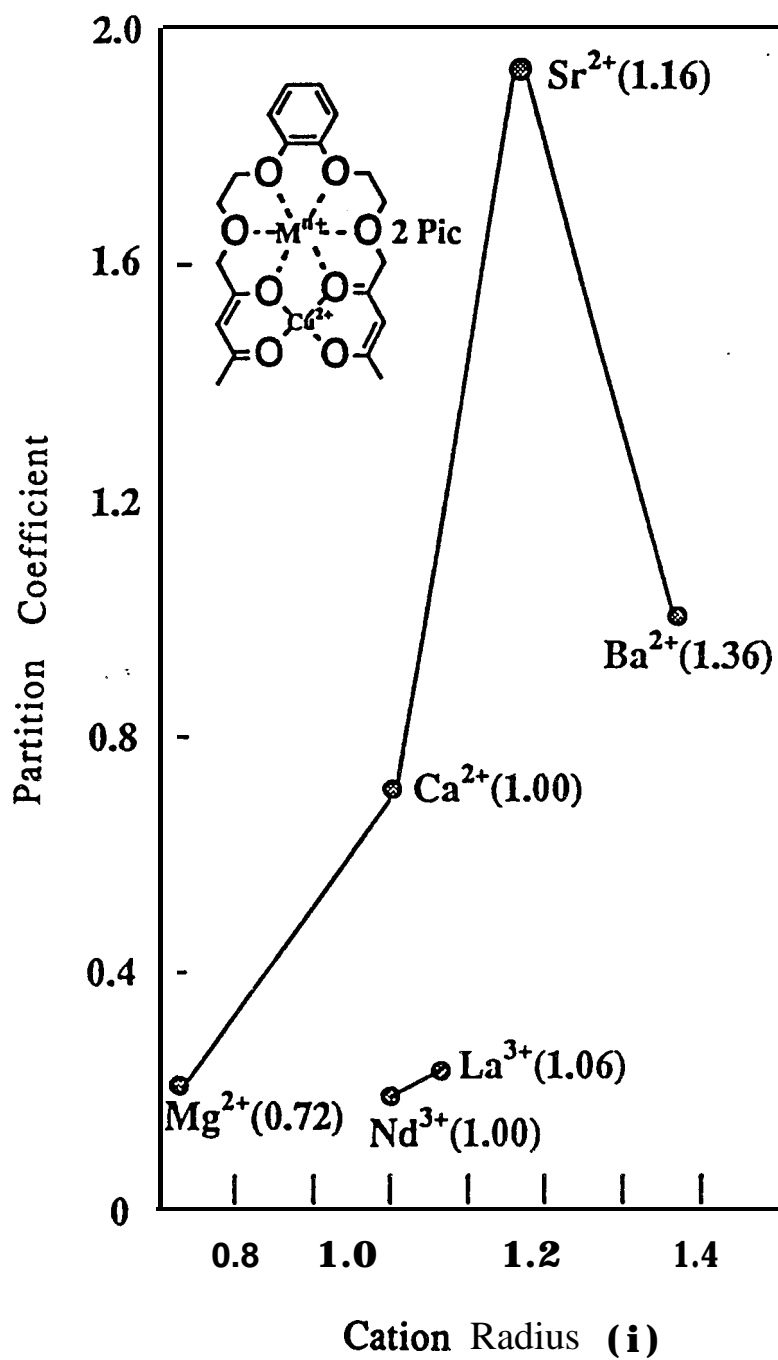


Fig. 6 Extraction of alkaline earth metal cation by bis(β-diketonato)-Cu polyether 26

stripping with sodium carbonate scrubbing caused quantitative Pu separation from the organic phase. High separation of RU was also obtained by sodium carbonate. Further efficiency, made possible by optimizing flowsheet conditions and replacing sodium-based reagent by salt-free reagents, will be the next step. New and innovative ideas for designing and synthesizing strong and selective **ligands** capable of facile synthesis is being studied. Study on separation techniques for **actinides** and rare earths will be **accelerated**.

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