THE STATE OF THE ART ON NUCLIDES SEPARATION IN HIGH LEVEL LIQUID WASTES BY TRUEX PROCESS

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ABSTRACT

For the advancement of the back-end of nuclear fuel cycle, novel CMPO–TRUEX process was studied for separating minor actinides from fission products in high level liquid waste using real radioactive solutions from PUREX experiments, so as to support PNC's actinides recycling program using fast reactor. The present PUREX process was also studied to improve the separation of ^{237}Np, ^{106}Ru and ^{99}Tc, the most interfering-natured nuclides in both PUREX and TRUEX processes, by utilizing electrochemistry-based salt-free methods which can eliminate the secondary radioactive waste.

The state of the art of separation technologies are described by summarizing the extraction behaviors of nuclides in recent hot counter-current runs using CMPO–TRUEX process with mild salt-free stripping reagents. The degradation and regeneration characteristics of CMPO/TBP/n-dodecane mixture solvent were also simulated by semi-hot experiments. Several experiments to separate minor actinides and lanthanides from the TRUEX mixture product using aqueous aminopolycarboxylate complexant, DTPA, resulted in reasonable MA/Ln separation profiles in multiple mixer-settler stages and allowed a unique separation flowsheet adaptable to the TRUEX process to be proposed.

Application of electrochemistry to assist both solvent extraction processes, *e.g.*, "anodic oxidation" to destroy PUREX and TRUEX solvent waste in the presence of electron transfer mediator Ag^{2+} or "cathodic reduction" for electrolytic extraction of Pd^{2+}, $RuNO^{3+}$ and $^{99}TcO_4^-$ from 3 M nitric acid medium is under study.

1. Introduction

Radioactive waste, especially high level liquid waste (HLLW) containing α emitters, have become a central issue from the interest in decreasing long lived toxicity on their long term storage and reducing the cost of the nuclear fuel cycle. Minor actinides (MA), usually lower than 1 % by weight, will sustain major toxicity of vitrified HLLW; actinides practically account for *ca.* 45 % of the total initial toxicity (one year after storage), but their contribution will increase up to *ca.* 70 % over 100 years for the case of LWR–HLLW. Such α toxicities of HLLW lie in MA, ^{241}Am, ^{244}Cm, ^{237}Np, and also $^{238, 241}$Pu derived from the PUREX process. The researches regarding α- and salt-free HLLW will become a key for a new reprocessing system.

Characteristics such as excellent extractability from highly acidic solutions, sufficiently fast kinetics for mass transfer, high radiolytic/hydrolytic stabilities and biological safety of extractants are essential for the process design of any novel solvent extraction system. An extraction process using neutral bifunctional organophosphorus Octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (OØD(iB)CMPO or simply CMPO) [1, 2] is a candidate to satisfy such requirements.

The first questions about the TRUEX process are its efficiency as a separation tool in a highly acidic and very complicated solution mixture for producing α-free HLLW, and the second is the quality of the recovered actinides if they are recycled in a reactor. For this evaluation, both optimization of the main TRUEX chemical flowsheet and introduction of a complexant to separate lanthanides (Ln) from MA were carried out by counter-current experiments. This paper describes the state of the art on TRUEX process development at PNC. The first part deals with some flowsheet improvements of the TRUEX process for actinides separation in a real highly active raffinate (HAR) solution, the second part describes the application of a chelating reagent, diethylenetriaminepentaacetic acid (DTPA) to a TRUEX flowsheet for MA/Ln separation. Auxiliary electrochemical process to assist both PUREX and TRUEX processes are thirdly described. All information is abstracted in attached summary tables.

2. TRUEX as a Tool for α-free Radioactive Wastes

2.1 Fundamental distribution properties of actinides and fission products

Fundamental distribution ratios (Ds) of 4f, 5f elements and fission products were verified in 0.2 M CMPO/1.0~1.4 M TBP/n-dodecane using not only real FR–HAR but also concentrated LWR–HLLW. Element compositions and concentrations of HAR and HLLW are shown in Figure 1, where a HLLW was obtained by commercial LWR spent fuel (less than 33000 MWD/T) reprocessed in the Tokai Reprocessing Plant (TRP) and HAR was originated in reprocessing experiments of FR Joyo spent fuel (burn up at *ca.* 55000 MWD/T, cooled for *ca.* 4 years). Relationships between various parameters such Ds and nitric acid concentration have already been given in other papers [3, 4]. The distribution characteristics of trivalent f-elements: ^{241}Am, ^{244}Cm and Lns are moderate, suggesting that they will be well extracted and recovered very simply by changing aqueous nitric acid

concentration from *ca.* 5 M to 0.01 M in the general TRUEX flowsheet.

Especially, the increase of nitric acid concentration causes desirable effects in decreasing the extractability of Ru and increasing that of Np. Distribution ratio of Np was confirmed at each acidity by equilibrating both phases over 24 h. At high acidities disproportionation of Np^{5+} into Np^{4+} and Np^{6+} might shift the valency of Np to Np^{6+}, which is easily extracted. An opposite tendency of Ru against Np was found either in batch experiments using trinitratonitrosyl ruthenium, $RuNO^{3+}$, and in counter-current tests using real HAR containing ^{106}Ru. These results suggested that different kinds of extraction mechanisms were operative for Ru and Np, and specific variation in distribution tendencies of Ru seemed to be attributed to the diversity of ruthenium species that were affected by even slight differences in extraction conditions. Since Ru behaved similar in batch and counter-current experiments, we concluded that Ru behaved in the form of $RuNO^{3+}$ in counter-current runs. Simple adjustment of the feed solution higher than 5 M nitric acid concentration was therefore recommended as an effective method to handle these two key nuclides. Neutral bidentate organophosphorus CMPO alone could make this procedure possible.

The Ds of all other major elements were measured for diluted LWR–HLLW using normal TRUEX solvent (0.2 M CMPO/1.0 M TBP/n-dodecane). Dilution was necessary for preventing third phase formation. It was confirmed that there was little difference in Ds of trivalent f-elements and Ru for HAR or HLLW in the range 0.5~4 M nitric acid. Third phase limit concentrations almost agreed with the predictions from mono element solution system. This suggested that there were probably no mutual interactions among these elements in HLLW and also among the extracted species [5].

Although tetra- and hexavalent elements needed no special treatment for their forward extraction, perfect back extraction of these might require either strong complexants or higher pH reagents, such as salt-free hydrazine oxalate or hydrazine carbonate as previously reported [4]. The suitable concentrations are different for each reagent; recommended concentrations of these salt-free reagents are for example 0.5 M (at least higher than 0.2 M) to obtain 90% stripping of $RuNO^{3+}$ and Zr^{4+} at trace level in a single contact with TRUEX solvent, even with irradiated solvent by 10^7 R.

2.2 Improved TRUEX flowsheet based on "Salt-Free" concept

Several TRUEX counter-current runs employed to partition actinides in real HAR led to the flowsheet "TRUEX PNC Salt-Free Version" [6, 7]. Its block flow and typical material balance are shown in Figure 2. The feed composition of HAR is indicated in Figure 1. The higher acidity (*ca.* 5 M) was selected for the feed HAR due to the aforementioned reasons and the dual scrubbing was employed to decrease extraction of both $RuNO^{3+}$ and free nitric acid. Addition of oxalic acid was minimized to eliminate oxalate precipitation of f-elements, in spite of concerns of lowering decontamination factor of fission products (DF_{FPs}) and causing accumulation of extractable species. Expecting complete fractional stripping, we prepared 3 banks composed of 51 stages in total, despite having only 6 stages for extraction in this case. Material balance was made based on the flow rates and α, γ and element concentration. Experimentally, steady state operation had been confirmed within 4–5 hours from the start. Each sample was taken from the settlers after ten hours operation.

Although there was some experimental fractiousness, it was confirmed that most of the f-elements were extracted within the 6 extraction stages, and they were quantitatively recovered again in the aqueous phase. Extractability of Np from highly acidified HAR was sufficiently high in the presence of oxalic acid in the aqueous phase as confirmed by no leakage in the raffinates. Stripping of Np however unexpectedly occurred with dilute nitric acid prior to the contact with HAN. The neighboring transition elements, Zr^{4+}, Nb^{4+}, Mo^{6+} and TcO_4^-, were also extracted in this condition. Once extracted in the solvent phase, Zr and Mo were retained until strip-III, the scrubbing of hydrazine oxalate. Therefore more sensible management is necessary for both elements because of their abundance in spent fuel.

The typical stripping profile for major nuclides indicates that the organic concentrations of $^{238, 239, 240}Pu$ and ^{106}Ru were peculiarly high in the stripping banks until strip-III. In normal TRUEX process Pu and Ru used to be retained in the spent organic phase at *ca.* 20 – 95 % and *ca.* 2 – 8 % respectively after stripping with dilute nitric acid. For Ru, however, hydration seemed to transform extractable trinitrato nitrosyl species into less extractable mono- or dinitrato nitrosyl species in the alkali scrubbing stages (strip-III and IV) [8]. Consequently, high decontamination of ^{106}Ru could be attained by high pH scrubbing with hydrazine carbonate at the end of solvent regeneration step, offering $DF_{Ru\text{-}106} > ca.\ 10$, by combining high acidity scrubbing at scrub-1 banks with $DF_{Ru\text{-}106} > 10^2$. The stripping behavior of Pu was similar to that of ^{106}Ru; namely, DF_{Pu} was *ca.* 10 with hydrazine oxalate and *ca.* 20 with hydrazine carbonate. These steps were also capable of removing UO_2^{2+}, HDBP and other acidic degraded species. Scrubbing efficiency of HDBP was tentatively *ca.* 60 % in the two steps of solvent regeneration.

In this modified TRUEX flowsheet, where complex ions composed of hydrazine oxalate and hydrazine carbonate worked well under high pH conditions, the final amounts of remaining Pu and Ru were respectively reduced to 0.5 % and 0.25 % of their initial concentrations. They are, then, no longer troublesome nuclides in this salt-free TRUEX flowsheet and the final two steps of solvent regeneration become an effective "plutonium/ruthenium barrier". Generally, while the addition of complexants will have trade off the elements between precipitation and third phase formation, the elimination of precipitates highly helped to improve the recovery rates of the elements in this case. The actinide concentrations in the raffinate were usually lower than the detection limits (around 10^4 Bq/mL), giving a DF_α of $\geq 10^3$, a few more stages would be necessary to absorb process fluctuations.

2.3 Stability and safety of CMPO

Solvent degradation of CMPO/TBP by γ radiolysis/hydrolysis and its effects on the stripping of the extracted elements were studied. Irradiation experiments using a ^{60}Co source (*ca.* $7x10^4$ Ci) on pure CMPO and on 0.2 M CMPO/1.0 M TBP/n-dodecane mixed solvent preequilibrated with 3 or 5 M HNO_3 showed that two major peaks, assigned to neutral methyl(n-octyl)(phenyl)phosphine oxide (MOØPO) and n-octyl(phenyl)isobutyl-carbamoylmethylphosphine oxide (OØ(iB)CMPO), were distinct and such radiolytical damage became dominant over 10^7 R. For irradiations higher than 10^7 R, the practical radiation bounds in partitioning process, TBP's damage was more substantial than CMPO's. Alkali scrubbing with sodium carbonate, tetramethyl ammonium

hydroxide (TMAH) and hydrazine oxalate offered quantitative scrubbing effects only for the former degradation species (probably in the form of octyl(phenyl)phosphinic acid) as well as for Ru, Zr and HDBP. The slow kinetics of each scrubbing treatment necessitated sufficient contact time (> *ca.* 10 min.) and concentration for each reagent (> 0.2 M). Neutral degradation species are generally very lipophilic, therefore some solid absorbents such as magnesium silicate or activated alumina are recommended as a secondary clean up system.

Thermochemical data [6] of OØD(iB)CMPO, obtained by thermogravimetric analysis and differential thermogravimetry (TG-DTA), indicated that its degradation exothermally proceeded in two steps at least, around 260 °C and 294 °C, and was completed at 300 °C even in the form of amorphous of it with TBP and Ru. The flash and combustion temperatures of CMPO were also quite a bit higher than those of TBP. These results indicate that CMPO is thermochemically stable in the usual operation.

The biochemical data [6] represented by 50% lethal dose, LD_{50}, also suggest that OØD(iB)CMPO should be categorized neither as a poison nor as a toxin, and that it is as safe as TBP whose LD_{50} for rats has been reported to be 3000 mg/kg. Furthermore, negative results in reverse mutation assay for Salmonella Typhimurium and DNA molecular repair assay for Bacillus subtilis indicated that CMPO is neither a chemical carcinogen nor a hereditary toxicant.

3. Actinide (III) and Ln Separation in CMPO Mixed Solvent System

3.1 Criteria for Am and Cm recovery

In our "Advanced Fuel Recycle System" which is based on MOX fuel, Am is recycled in fast reactors, and Cm is stored for several decades, waiting for ^{244}Cm decay [9]. The incineration of Am needs to separate Cm and lanthanides from Am. On the other hand, contamination with Ln would be allowed in Cm recovery.

It is considered that there is quite a large difficulty in Am/Cm separation by solvent extraction. Thus, TRUEX process must be coupled with some Am/Cm/Ln separation methods. If light lanthanides which are major fission products were removed, the scale of Am/Cm separation process could be reduced. For totally process simplification, it is favorable to add a function of lanthanides rejection to the TRUEX process.

3.2 Utilization of DTPA

A chelating reagent diethylenetriaminepentaacetic acid (DTPA) has been utilized in An(III)/Ln separation based on cation exchange and solvent extraction such as the TALSPEAK process. In a neutral extractant TBP system, DTPA is used with high concentration of nitrate as a salting out reagent [10].

Light lanthanide elements are less selectively extracted by CMPO than heavy lanthanides from nitric acid solution, and tend to make strong complexes with DTPA. Therefore it is expected that light lanthanides could be rejected in CMPO extraction system, utilizing DTPA complexation. In the studied process, the nitrate concentration was lowered and a higher pH than in the TBP system was used in the extraction experiment.

In order to realize the process using DTPA, stabilization and/or control of pH in the separation process is essential. Certainly, basic distribution data for CMPO–TBP mixed solvent / DTPA–nitrate solution are

required.

3.3 Control of pH

One of the advantages of CMPO is the extraction ability from high acidity solution. However, as the loaded solvent which is contacted with highly acidic waste solution contains considerable amount of nitric acid, it would interfere DTPA–metal complexation. Therefore, it is needed to reduce the acid concentration in the organic phase. Fortunately, the extent of distributions of metal and acid differ using nitrate salt at low acidity. It is considered that the selective stripping of acid from the loaded solvent can be conducted by using proper concentration of nitrate solution.

DTPA has carboxyl groups. Since the first and second dissociation constants are around two, buffering effect could be expected in the acidity range near 0.01 M which is appropriate for separation.

3.4 Basic data on lanthanide distribution

Since the separation system is rather complicated, many factors affect the distribution of trivalent metals. The acidity of the aqueous phase is the most important parameter. In Figure 3, the distribution ratios of four lanthanide elements are plotted as a function of pH. As pH become higher, dissociation of DTPA proceeds, resulting in a decrease of the distribution ratios. And the effect of metal complexation emerges as the difference of the values. As the stability constants of Dy is near that of Am, it is expected that Am could be stripped while major light lanthanides such as Ce and Nd would be kept in the organic phase. The separation factors are almost consistent with the ratio of stability constants of metals. Then it is considered that the separation is mainly governed by selectivity of DTPA complexation.

The higher nitrate and lower DTPA concentration enhance the extraction of metal. Higher temperatures lower the distribution ratios. And the kinetics of stripping of metal from loaded solvent are rapid enough for the use of mixer-settlers as contactors.

3.5 Concept of flowsheet

We made a basic flowsheet for An(III) recovery with lanthanides rejection using DTPA–nitrate solutions. The process is composed of four sections; namely, extraction–scrubbing, acid stripping, An(III) stripping and Ln stripping as shown in Figure 4.

In the first extraction–scrubbing section, the trivalent metals are extracted from acidic solutions. The operation procedure is basically the same as the original TRUEX. The acid in the loaded solvent is removed in the second acid stripping section using a nitrate solution of low acidity. The aqueous waste solution will contain only little activity. Trivalent actinides are back extracted in the third An(III) stripping section with a DTPA–nitrate mixed solution, the pH of which is adjusted around two. It is anticipated that mid lanthanides such as Sm and Eu would be simultaneously recovered with Am and Cm in a certain extent. As the product solution contains a high concentration of nitrate, further treatment will be required to obtain nitric acid solution as product. With dilute nitric acid, retained lanthanides in the organic phase are stripped in the fourth Ln stripping

section. (Recently, we call this process flowsheet as SETFICS * for convenient.)

* Acronym of "Solvent Extraction for Trivalent f-elements Intra-group Separation in CMPO–complexant System"

3.6 Results of counter-current experiment

Based on the conceptual flowsheet as stated before, we conducted counter–current hot experiments using a TRUEX product which was previously obtained in the hot tests and acidified to 2 M HNO_3 for extraction. The trivalent metals were well extracted in the first section. In the second stripping section, 0.5 M $NaNO_3$ solution (pH 2.0) was used. Since re-extraction was not conducted from experimental restriction, approximately 10 % of the metals were streamed into aqueous waste. The acid concentration of discharged solvent was lower than 0.01 M.

In Figure 5, the profiles of concentrations and distribution ratios of major nuclides are plotted. The composition of the An(III) stripping solution was 0.05 M DTPA–4 M $NaNO_3$ solution (pH 2.0). Americium-241 and ^{244}Cm were stripped into product solution while ^{144}Ce was retained in the organic phase. As the behavior of ^{155}Eu was similar to that of ^{241}Am, the greater part of ^{155}Eu was recovered with An(III) product. The distribution ratio was varied with acidity of aqueous phase. The pH value became higher in the upper stream of solvent feed point. This tendency resulted in a decrease of distribution ratios and an increase of An(III) recovery.

Table 1 Material balance and decontamination factor

Material balance ;

unit : %

	^{144}Ce	^{154}Eu	^{155}Eu	^{241}Am	^{242}Cm	^{244}Cm	La	Ce	Pr	Nd	Sm
Feed						100					
Acid waste	9.0	8.9	9.5	6.2	6.4	8.6	10*	10*	10*	10*	10*
An(III) product	0.89	45	46	64	56	67	1.2	<6.1	2.3	1.4	27
Ln waste	85	15	15	5.6	1.6	0.75	52	97	69	71	34
Total	94	68	70	76	64	77	63	<110	81	82	72

* Evaluated values equal to those of radionuclides

Decontamination factors to ^{241}Am ;

^{144}Ce	^{154}Eu	^{155}Eu	^{242}Cm	^{244}Cm	La	Ce	Pr	Nd	Sm
72	1.4	1.1	1.1	0.95	52	> 10	28	46	2.3

The material balance and decontamination factors are summarized in Table 1. Because of the short operation time, the steady state was not attained. Especially, the sum of the output of An(III) and Eu was quite

low. The decontamination factors of light lanthanides were obtained in several tens, and, at least, 80 % of lanthanide were removed from An(III) product solution. Therefore, the main contaminants of An(III) were Sm and Eu.

3.7 Further subjects

It has been found that CMPO mixed solvent / DTPA–nitrate solution system has a potential for light lanthanides removal. It is considered that the improvement of An(III) recovery and the reduction of nitrate in stripping solution should further be studied.

4. Supporting Electrochemical Technique for Separation Process

4.1 Electrolytic extraction of platinum group elements and technetium

Precious metals such as Ru, Pd, Rh, Ag and Tc amount to several kilograms per ton of ordinary spent fuel. The ionic state of these elements, especially extractable $RuNO^{3+}$ and TcO_4^-, behave in a rather complicated manner and eventually dominate the final decontamination factors of the PUREX and successive TRUEX processes. In that sense, their separation prior to both solvent extraction processes is meaningful and worthy to improve decontamination in a limited number of extraction stages and cycles as well as to prepare future multiple usage of precious metals from spent fuel.

Pure cathodic deposition behaviors of Ru^{n+} and Pd^{2+} in 3 M nitric acid were studied using Pt-Ti cathode (20 cm^2) in an electrolysis cell equipped with cation exchange membranes. The volume of catholyte and anolyte was 100 ml each, temperature was set at 50 °C, and Ru^{n+} and Pd^{2+} were mixed together at 100 ppm each. In accordance with electrolysis time, both metals were deposited dendritically together. A yield ≥ 90% was obtained for both Ru and Pd in a few cases employing high cathodic current density ≥ 100 mA/cm^2 during 3 hours. In the case of low 10 mA/cm^2 electrolysis with less amount of hydrogen evolution, only Pd was deposited with the same high yield. Low deposition yield of Ru (less than 30%) suggests that its redissolution might occur at such a cathodic density. The reported value of E^0 for the amorphous TcO_2/TcO_4^- electrode is 0.746 V (vs. SHE) [11],

$$TcO_4^- + 4H^+ + 3e^- \leftrightarrow TcO_2 \cdot xH_2O + (2\text{-}x)H_2O$$

thereby suggesting electrochemical deposition of Tc in nitric acid. The further electrochemical tests by cyclic voltammogram (CV) measurement and galvanostatic electrolysis are in progress for Pd^{2+}, $RuNO^{3+}$, $^{99}TcO_4^-$ and ReO_4^- with 3 M nitric acid.

4.2 Mediated electrochemical destruction of solvent waste

Electrolysis tests were carried out to search for the possibility of electrochemical destruction of PUREX and TRUEX solvent waste [12]. Cyclic voltammogram measurements suggested that adsorption and the direct oxidation of emulsified CMPO (and also TBP) by Pt anode in nitric acid (3 M) was easier than that of n-dodecane.

About 90% of CMPO was decomposed within 3 hours electrolysis with much excess of Ag^{2+} (initial

Ag^+/CMPO/decalin molar ratio was 1500 : 1 : 30), 500 mA/cm^2, 50 °C in 3 M nitric acid. Mainly phosphoric acid (*ca.* 80 %) and carbon mono-, dioxide (*ca.* 10 % in total) were detected in the aqueous phase and in gas phase, respectively. The presence of Ag^{2+} mediator in the electrolysis system considerably accelerated oxidation kinetics by *ca.* 5 times and improved current efficiencies as compared to that from the direct electrode reaction. Nevertheless, still lower individual current efficiency calculated on the basis of gaseous compositions with the following assumed reactions suggests that electrolysis conditions can furthermore be improved.

Anodic reactions;

$$H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$$

$$Ag^+ \rightarrow Ag^{2+} + e^-$$

$$CMPO + 51H_2O \rightarrow 24CO_2 + 1/2N_2O_5 + 1/2P_2O_5 + 144H^+ + 144e^-$$

$$CMPO + 27H_2O \rightarrow 24CO + 1/2N_2O_5 + 1/2P_2O_5 + 96H^+ + 96e^-$$

Bulk reactions;

$$2Ag^{2+} + H_2O \rightarrow 2Ag^+ + 2H^+ + O\cdot$$

$$Ag^{2+} + H_2O \rightarrow Ag^+ + H^+ + OH\cdot$$

$$CMPO + 72O\cdot \rightarrow 24CO_2 + 21H_2O + 1/2N_2O_5 + 1/2P_2O_5$$

$$CMPO + 48O\cdot \rightarrow 24CO + 21H_2O + 1/2N_2O_5 + 1/2P_2O_5$$

The formation of O· and OH· radicals was essential in this mechanism (*i.e.*, double mediatory system), and cation exchange property of diaphragm was very important to prevent consumption of Ag^{2+} mediator in the anolyte. Mediation effect of Co^{3+} was lower than Ag^{2+}, and addition of Ni^{2+} or Ce^{4+} unexpectedly brought only negative effects.

Direct and/or mediated electroredox technique can push out separation function and provide new waste minimizing system in the solvent extraction process.

5. CONCLUSION

Basic distribution studies of actinides and FP as well as several TRUEX counter-current runs using real HAR from PUREX experiments successfully led to an original flowsheet "TRUEX PNC Salt-Free Version". With this flowsheet, an α- and salt-free HLLW was obtained, ensuring a $DF_a \geq 10^3$. The DTPA has been successfully adapted with a reasonable separation of MA from light lanthanide in counter-current runs using TRUEX product solution. General process safety on the TRUEX process were preliminarily verified by original experiments. Electroredox methods for separating precious metals and destroying solvent waste have been studied in the frame of salt-free concept.

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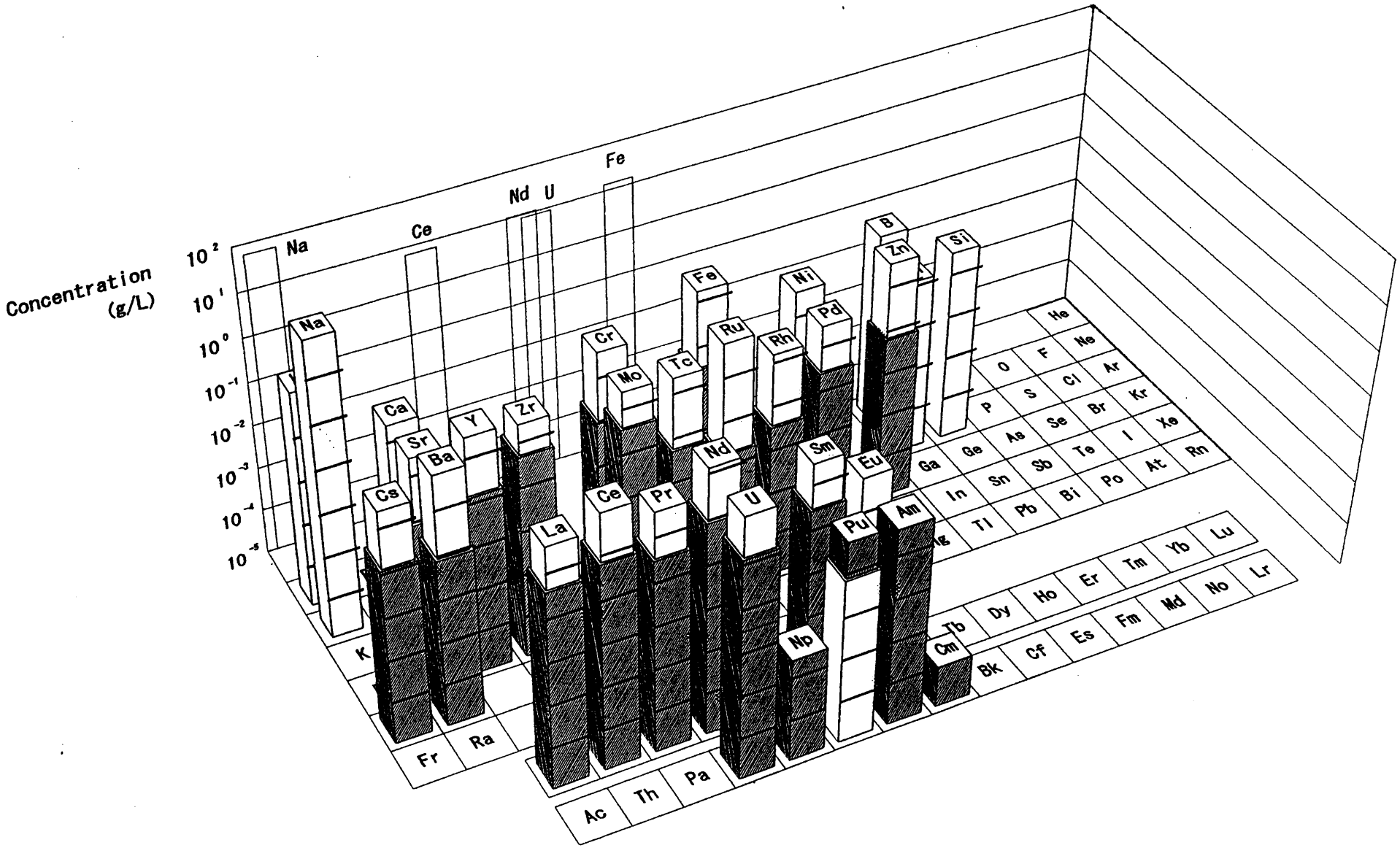

Figure 1 Typical Composition of HAW

: HAR by FR reprocessing, volume: *ca.* 15 L/kg•SF

: HLLW by LWR reprocessing, volume: *ca.* 1 m³/t•SF

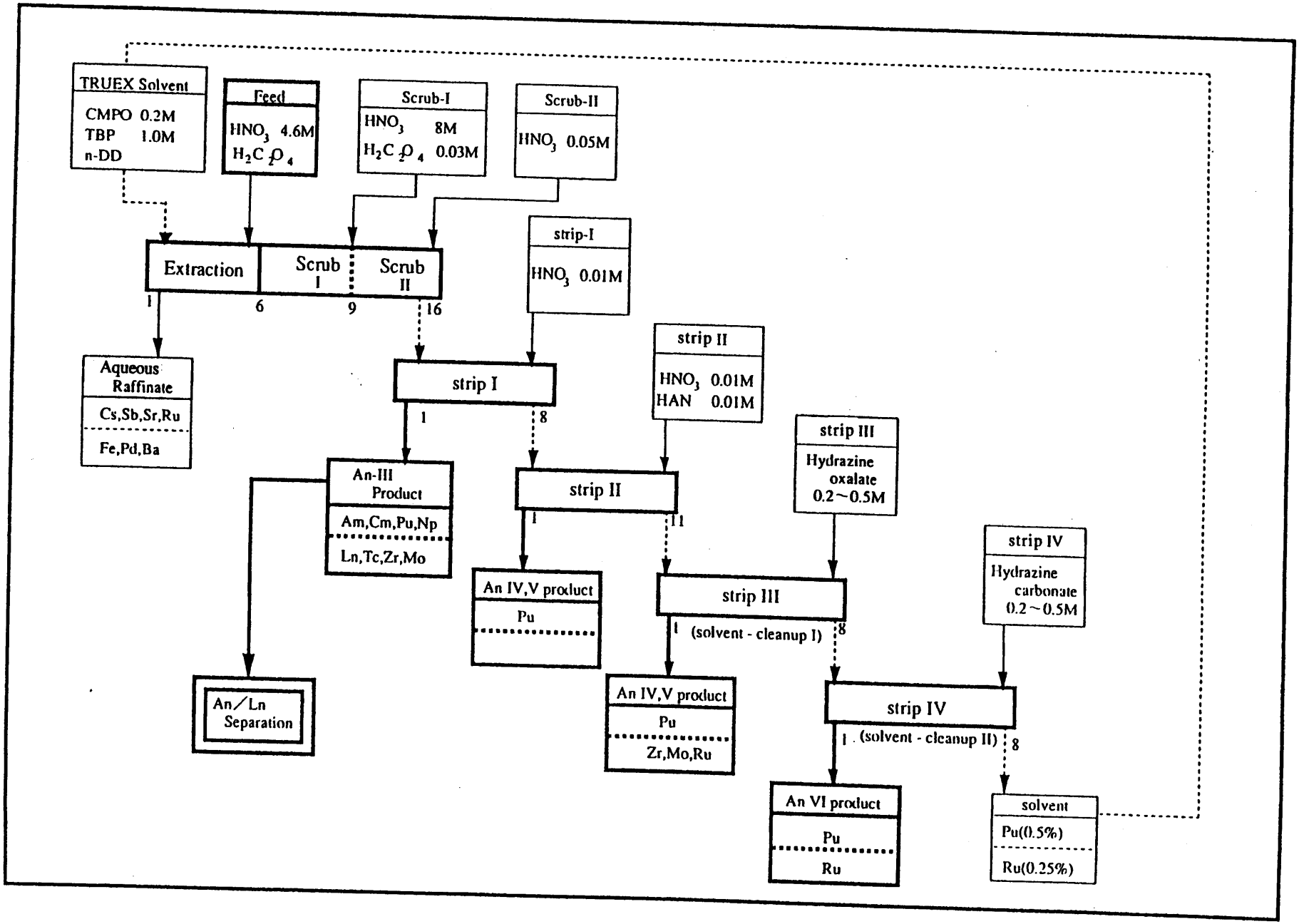

Figure 2(a) Improved TRUEX Flowsheet : PNC TRUEX Salt-Free Version

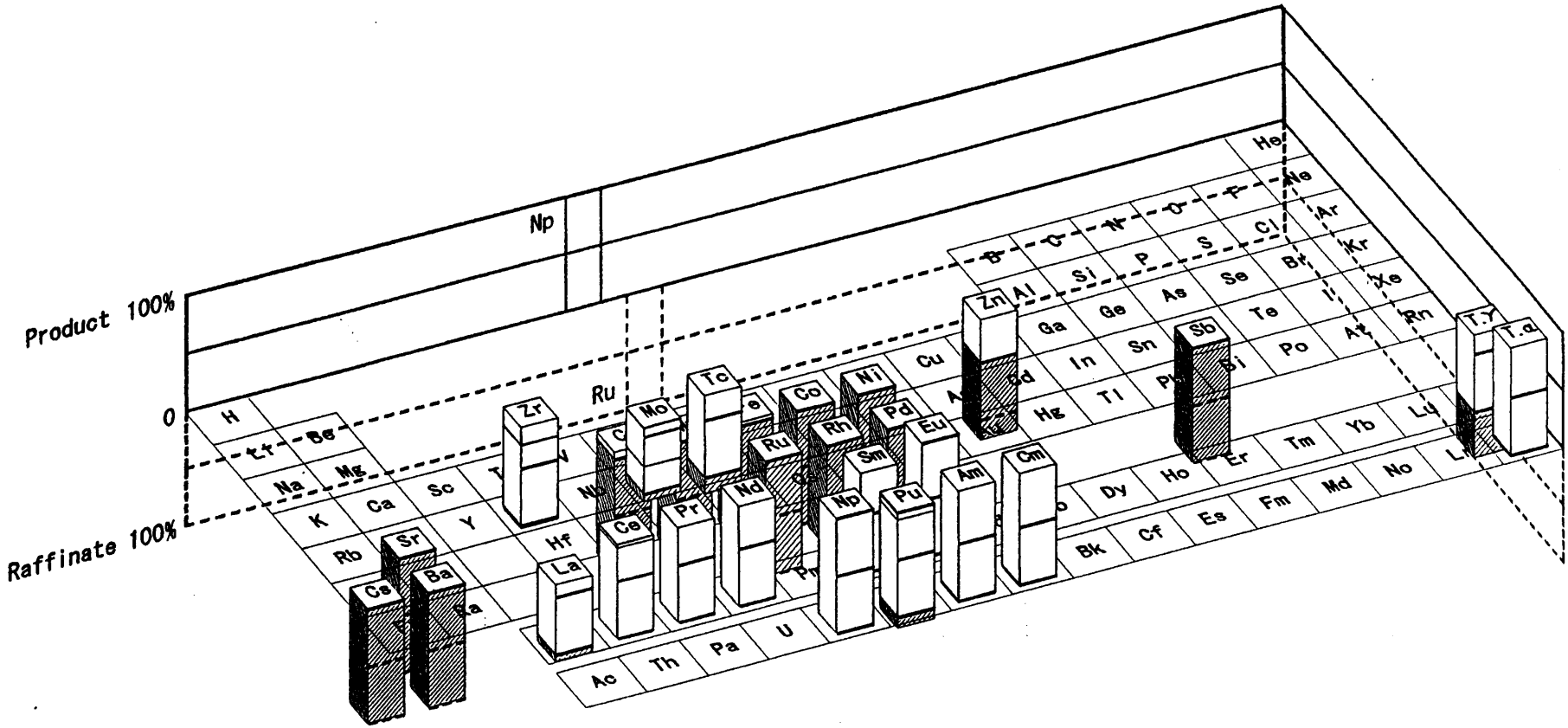

Figure 2(b) Typical Distribution of Elements
(TRUEX : PNC TRUEX Salt-Free Version)

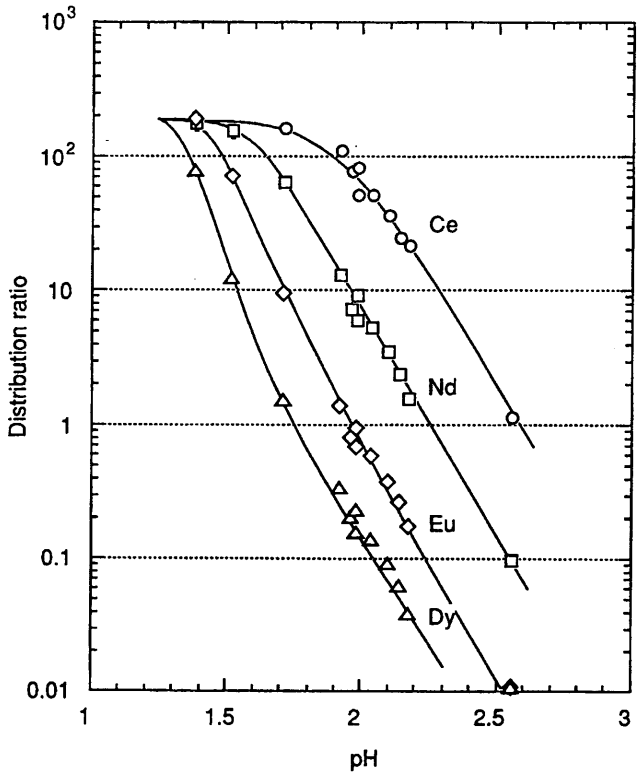

Figure 3 Lanthanide distribution between CMPO mixed solvent and DTPA–nitrate solution

Organic solvent : 0.2 M CMPO–1.0 M TBP–n-dodecane
Aqueous solution : 0.05 M DTPA–3 M $NaNO_3$

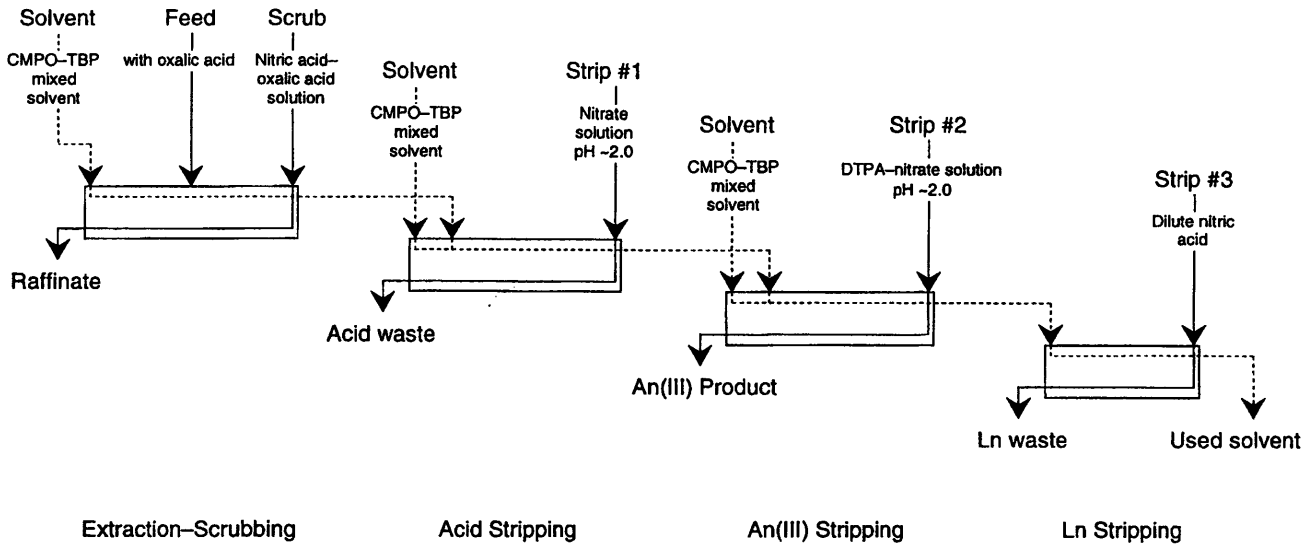

Figure 4 Conceptual flowsheet for An(III)/Ln separation

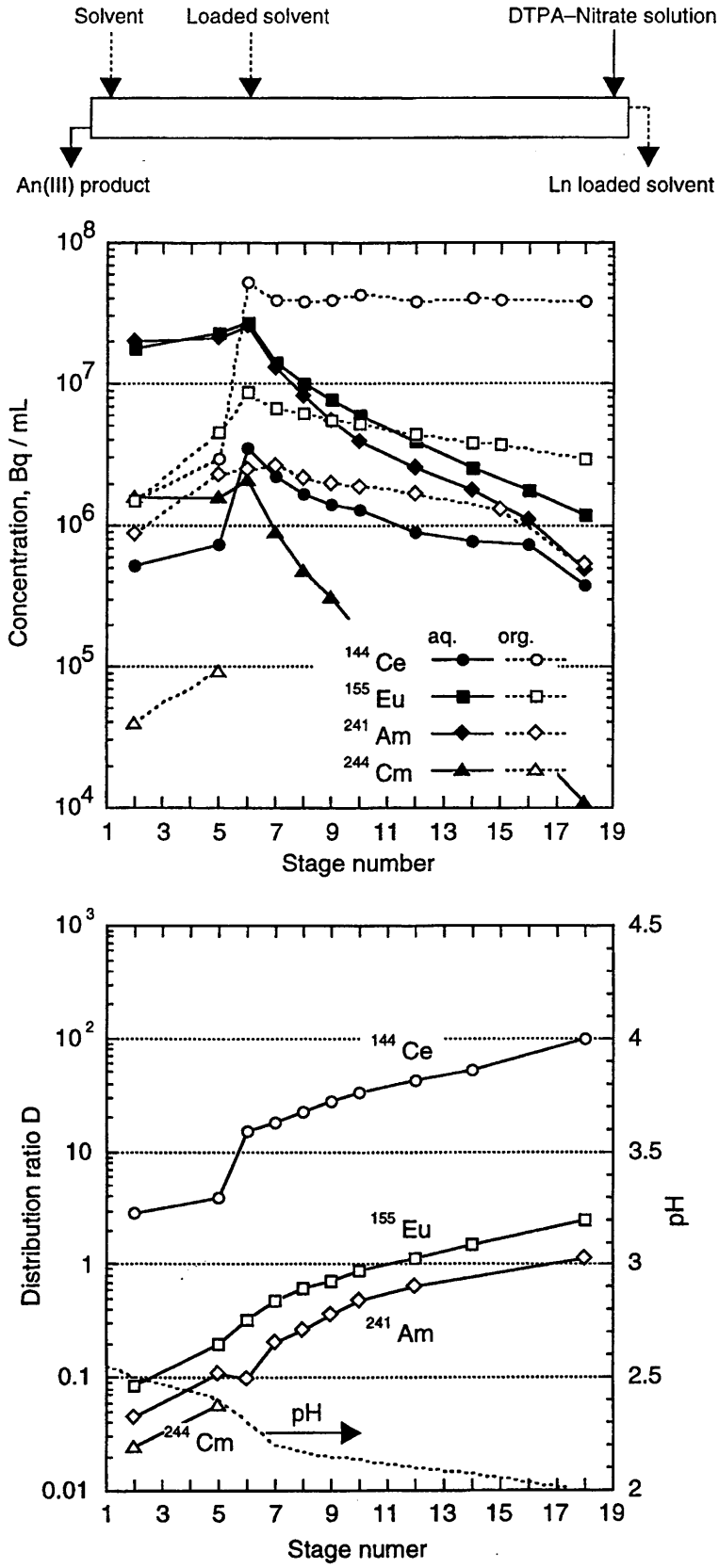

Figure 5 Profiles of concentration and distribution ratio of major nuclides in An(III) stripping Section

APPENDIX

Summary Table

	TRUEX	Others (reference)
Extractant	OØD(IB)CMPO	
Synthesis		
– Method (synthesis & purification)	established	
– Cost (as a mixed solvt.)	500$/kg= 41kYen/L	40$/kg=3kYen (diamide)
Stability		
– γ ^{60}Co	highly stable up to 10^7R (Over 10^7R, TBP as well as CMPO will be significantly degraded)	
– Nitric Acid	(acceptable up to 7 M HNO_3 in process)	
– Thermal decomposition temp.	272.3~313.2 ℃	
Solubility		
– Into$Ø_{AQ}$(at 0.01~ 3 M HNO_3)	TBP ≤ 300ppm CMPO ≤ 10ppm	
Toxicity		
– Mortality(LD_{50}) for		
5 mice (male): oral	> 3000 mg/kg 3000 mg/kg (for TBP)	
5 mice (male): dermal	> 2000mg/kg	
– Reverse mutation assay	negative	
– DNA repair assay	negative	
Burnability		
– Flash point	243.6 ℃	
Incinerability	imperfect (*e.g.*, Ag^{2+} process is under investigation)	perfect (diamide)
Process Flowsheet		
Solvent	0.2 M CMPO/1.0 ~ 1.4 M TBP	
Diluents	n-dodecane	
Target waste solutions		
– Highly active raffinate	applicable	
– HLLW	needs more investigations	
Feed adjustment	*ca.* 5 M HNO_3 with $H_2C_2O_4$	
Process sensibility for extraction	durable for acidity changes	

(continued)

	TRUEX
Typical mass transfer time	
Forward ext. at C_H 3 M	Nd (< 5 min) << Ru < Zr
Strip at C_H 0.2 M	Nd (< 5 min) << Ru, Zr
FPs scrubbing	"dual" scrubbing with a $H_2C_2O_4$
Selective stripping method	
→ 1st Step	dilute HNO_3 : 0.01 M HNO_3 * An^{3+}, Ln^{3+}, TcO_4^-, $Zr^{4+}$and Mo^{6+}were separated
→ 2nd Step	reducing reagent : 0.01 M HAN * $Pu^{4+}$was separated
→ 3rd Step	complexant : 0.2~0.5 M $(N_2H_5)_2C_2O_4$ * Pu^{4+}, Zr^{4+}, Mo^{6+}, $RuNO^{3+}$ were separated
→ 4th Step	high pH complexant: 0.2~0.5 M $(N_2H_5)_2CO_3$ * Pu^{4+}, UO_2^{2+}, $RuNO^{3+}$ were separated
Separability of actinides from FP	
– DF for actinides from HAR	> 10^3
– SF for Am/Cs	> 10^4
for Am/Tc, Mo, Zr	to be improved
for MA/Ln	to be improved
Separation of MA from Ln	Applicability of DTPA is under investigation
Third phase formation	
– Constituents (confirmed)	H^+, Ln^{3+}, Fe^{3+}, UO_2^{2+}
– Limit concentration (at 0.2 M CMPO/1.2 M TBP/nDD, C_H 3 ~ 6 M, 25 °C)	Nd^{3+}: 0.04~0.045 M (0.02 M *) Pu^{4+}: 0.03 M UO_2^{2+} : 0.025~0.03 M (0.012 M*) * in the case of 1.0 M TBP
Solvent clean up	
– Major degraded material identified at 10^7R	HDBP methyl(n-octyl)(Ø)phosphine oxide n-octhyl(Ø)isobutylcarbamoylmethylphosphine oxide
– Mass transfer rate of FPs during salt-free scrubbing for irradiated solvent at 10^7R.	
Scrub at $C_{HYD.CARB.}$	Nd (1 min.) << Zr, Ru (10 min.)
Scrub at $C_{HYD.OXAL.}$	Nd (1 min.) << Zr, Ru (20 min.)
→ 1st Clean up method	a salt-free method for acidic degraded materials and FPs. (see Step 3rd and 4th)
→ 2nd Clean up method	active Al_2O_3 or floridine