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Separation of actinides and fission products in high-level liquid wastes by the improved TRUEX process

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Abstract

With the aim of establishing an advanced fuel cycle enabling us to utilize all actinides in the spent fuels, separation of minor actinides in high-level liquid wastes (HLLW) has been studied using a CMPO/TBP mixture extractant. A novel flowsheet is being developed, by counter-current experiments using real HLLW from PUREX experiments, characterized by employing acidification for enhancing extraction of actinides with increasing $RuNO^{3+}$ decontamination, and a few mild salt-free reagents for fractional stripping and solvent clean-up steps. The flowsheet can give α- and salt-free HLLW providing a $DF_{Am} \geq 10^3$. In the counter-current experiments for SETFICS a flowsheet has been developed to separate An(III) and Ln using DTPA, Am and Cm was recovered without light lanthanide, and the applicability of hydroxylamine nitrate as a salting-out reagent was confirmed. © 1998 Elsevier Science S.A.

Keywords: Partitioning; HLLW; Minor actinide; CMPO; Improved TRUEX; Salt-free; Hydrazine oxalate; Hydrazine carbonate; Tetramethyl ammonium hydroxide; DTPA; SETFICS

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1. Introduction

Radioactive waste, especially high-level liquid waste (HLLW), is always at the heart of nuclear issues, with growing concerns about decreasing ultra long-lived α toxicity as well as reducing the liquid volume of it. The α nuclides and salt in the HLLW lie in inextractable minor actinides MA (^{241}Am, ^{244}Cm, ^{237}Np) and also ^{238,241}Pu, and sodium nitrate leaking from the traditional TBP-PUREX process. Research regarding α- and salt-free HLLW are important for establishing a new reprocessing system. A currently developed solvent extraction process using neutral bifunctional organophosphorus octyl[phenyl]-*N*,*N*-diisobutylcarbamoylmethyl-phosphine oxide (OØD(iB)CMPO or simply CMPO) [1–3] is a candidate for realizing α-free HLLW.

The present scientific questions about the ‘CMPO-TRUEX’ process relate to, firstly, keeping high α separation compatible with enhanced waste minimization (e.g., by salt-free), and, secondly, the quality of the recovered MA when they are recycled and burned in fast reactors etc. This paper focuses on the state of the art of the CMPO-TRUEX process development in PNC; the first part deals with improved TRUEX flowsheets by utilizing salt-free type reagents; the second part describes An(III)/Ln separation using aminopolyacetic acid.

2. Salt-free TRUEX process for secondary waste minimizing

2.1. γ irradiation of solvent and its impact on extraction/back-extraction

γ radiolysis of TRUEX solvent and its effects on the extraction/back extraction behaviors of typical Lns and FPs were studied. Irradiation was made using a γ-ray of ^{60}Co source (ca. 7×10^4 Ci) on pure CMPO crystal or on a 0.2 M CMPO/1.0 M TBP/*n*-dodecane mixture solvent which was pre-equilibrated with 3 M nitric acid for 30 min.

The gas chromatograph (GC) chart showed 32 peaks, 2 distinct peaks indicating the higher molecular weight between TBP and CMPO retention time assigned to be neutral methyl(*n*-octyl)(phenyl)phosphine oxide (MOØPO: $M = 252$) and *n*-octyl(phenyl)isobutylcarbamoylmethyl-

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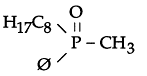
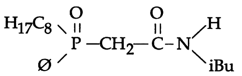
phosphine oxide (OØ(iB)CMPO: $M=351$) using a mass spectrometer (MS).



$H_{17}C_8(\text{Ø})P(=O)-CH_3$

[MOØPO]



$H_{17}C_8(\text{Ø})P(=O)-CH_2-C(=O)-N(H)(iBu)$

[OØ(iB)CMPO]

These peaks became intensified by irradiation at 1.1×10^7 R (1 R=258 μC/kg). The explosive nitrobenzene ($M=123$) was not recognized under the denoted irradiation level (~1.1×10^7 R), and that was attributed to the fact that the cleavage at the carbonyl or phosphoryl moiety took preference to the aromatics moiety [1,9]. An anionic chromatograph identified HDBP, H2MBP and another 4 peaks (probably carboxylic acids), with their extension becoming significant at 1.1×10^7 R irradiation. TBP's γ radiolysis was more substantial than CMPO's.

To investigate the effect of solvent degradation on the extractability/back extractability of the metals, $RuNO^{3+}$, Zr^{4+}, Ce^{3+} and Eu^{3+} were chosen as representatives of major FPs, and light and middle Lns. The aqueous phase contained 0.02 M of each element ions, 3 M nitric acid, with/without 0.02 M oxalic acid. Both phases were mixed (A/O=1, 30 min) and metal concentration was analyzed by inductively coupled plasma spectrometry (ICP) in both phases after 60 min settling. Back extraction was made by six successive contacts with 0.01 M nitric acid by the same manner.

The extraction efficiency (E, %) of metals was evaluated against γ irradiation to the solvent. As the irradiation increased, E of Ce and Eu slightly decreased, but were always kept higher than 85%. However, that of the Ru conversely increased from 30% (at non-irradiation) to over 40% (at 1.1×10^7 R) independent of the presence of oxalic acid. In the case of Zr, its quantitative (more than 95%) extraction constantly occurred under any irradiation; nevertheless, the presence of the equimolar of oxalic acid particularly limited its E to be around 60% even at the irradiation level 1.1×10^7 R. Namely, the Zr^{4+}-oxalato complex, e.g. $Zr(C_2O_4)_2$, seemed to be more stable than that of $RuNO^{3+}$, Ce^{3+} and Eu^{3+}, and the Zr^{4+}-oxalato complex was certainly superior to its complexation with such acidic degraded products as HDBP or H_2MBP. Hence, the effect of irradiation on Zr^{4+} extraction can be hidden in the presence of oxalic acid.

The typical back extraction efficiency (BE, %) of metals from irradiated (1.1×10^7 R) solvent indicated that the BE of Lns were fairly sensitive to the nitric acid concentration in the loaded solvent; i.e., their perfect stripping followed the completion of stripping of nitric acid. In contrast, Ru and Zr were not dependent on acidity at all. About 70% of Zr in the loaded solvent was unstrippable by 0.01 M nitric acid, where Zr^{4+} might form stable $Zr(DBP)_4$ complex. Small BE, kept less than 10%, of Ru was essential by its ($RuNO^{3+}$) distribution property. Hence, stripping of Zr^{4+} and $RuNO^{3+}$ requires other reagents after completion of MA/Ln back-extraction with 0.01 M nitric acid.

2.2. Salt-free solvent clean-up as a back-extraction step

Clean-up behaviors of $RuNO^{3+}$, Zr^{4+}, Ce^{3+} and Eu^{3+}, and degraded substances by salt-free reagents were studied with reference to sodium carbonate. The reagents, composed of non-metallic cations and being electrochemically destructible to gaseous molecules, are nominated as 'salt-free' ones. After contact three times with 0.01 M nitric acid, loaded organic phase was mixed with the reagents (O/A=1, 20 min mixing/60 min settling). Metal concentrations in the organic phase irradiated by 1.1×10^7 R were: $RuNO^{3+}$, 0.005 M; Zr^{4+}, 0.015 M; Ce^{3+}, 0.005 M; and, Eu^{3+}, 0.004 M; respectively. Clean-up of Lns from irradiated solvent by lower concentration 0.02 N of Hdz. car. (hydrazine carbonate: $(N_2H_5)_2CO_3$) and Hdz. oxa. (hydrazine oxalate: $(N_2H_5)_2(COO)_2$) preliminarily suggested that these practically occurred regardless of the irradiation levels and the kinds of reagent with their clean-up efficiency (CE, %) kept higher 80%. Table 1 summarizes the effect of concentration of salt-free reagents on CE of the most unstrippable $RuNO^{3+}$ and Zr^{4+}. Apparently, increasing the concentration of reagent (as well as pH) results in increases of the CE. When the reagents concentrations were 0.2 N or more, Hdz. oxa. (pH=6.32), Hdz. car. (pH=7.71) and TMAH ($[(CH_3)_4N]OH$, pH=13.43) would offer almost the same CE for Zr^{4+} as that of Na_2CO_3. As for Ru, high-pH scrubbing was preferable, by Hdz. car., TMAH and Na_2CO_3, by turning hydration transformed extractable trinitratonitrosyl $RuNO^{3+}$ into less-extractable di- or mono-nitratonitrosyl species. TMAH can, due to its highest pH value, attain the highest CE for these FPs. If the salt-free reagent should be decreased in order to minimize its quantity to be destructed afterward, use of Hdz. oxa. of 0.02 N is recommendable.

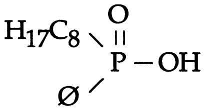
The clean-up behaviors of degraded substances of solvent were confirmed by the following steps: solvent irradiated by 1.1×10^7 R was preliminary contacted with 0.01 M nitric acid three times (each 20 min mixing), and was subsequently contacted with 0.5 N of the salt-free reagents (O/A=1, 20 min mixing/60 min settling). Clean-up behavior was determined by the difference of area of each peak of the GC chart before and after scrubbing. Among nineteen small peaks, those corresponding to molecules lower than TBP did not change during the scrubbing. However, several peaks of the higher molecules

Table 1
CE (%) of Ru and Zr with salt-free reagents

Metal	Reagent conc.	Hdz. oxa.	Hdz. car.	TMAH	Na_2CO_3
$RuNO^{3+}$	0.02 N	51.5	28.7	48.6	37.4
	0.2 N	66.7	87.2	99.1	88.2
Zr^{4+}	0.02 N	56.9	19.5	52.1	43.1
	0.2 N	89.0	91.0	>99.9	91.4

Solvent was irradiated by 1.1×10^7 R.

arising from CMPO degradation quantitatively decreased with high-pH scrubbing by TMAH. Especially, neutral MOØPO can also be scrubbed by four reagents, except for citric acid (pH = 1.93 at 0.5 M) and tartaric acid (pH = 1.80 at 0.5 M). One possible explanation was that a successive oxidation of MOØPO occurred leading to an acidic molecule such as octyl(phenyl)phosphinic acid.



[Octyl(phenyl)phosphinic acid]

These two acidic reagents reversely increased the peak corresponding to MOØPO with the other 2 peaks. Interfacial crud or stable emulsion was commonly observed, and their quantity was proportional to the level of irradiation, but higher concentration ($\geq$0.2 N) of TMAH would keep them at a minimum. OØ(iB)CMPO was not scrubbed by any reagents. Generally, neutral degradation species are very organophilic, hence some solid absorbents, such as magnesium silicate or activated alumina, should be equipped as a secondary clean-up system.

The TMAH is presently considered as the best reagent, but its safety properties relating to the actual PUREX–TRUEX environment are not yet well investigated. Therefore, due to their mild and electrochemically well destructible property, Hdz. oxa. and Hdz. car. were firstly devoted to the following hot counter-current experiments.

2.3. Actinides/FPs balance in salt-free TRUEX flowsheet

Distribution ratios (D_S) of actinides and fission products verified by 0.2 M CMPO/1.0–1.4 M TBP/*n*-dodecane using real FR-HAR and concentrated LWR-HLLW were reported elsewhere [3,4]. The issues of relevance are that the D_s of Am^{3+}, Cm^{3+} and Ln^{3+} vs. nitric acid are moderate suggesting their extraction and back extraction are possible simply by changing the aqueous nitric acid concentrations from ca. 5 M to 0.01 M, and the acidification of the feed encourages decreases in the extractability of $RuNO^{3+}$, whereas it increases that of NpO^{2+}. In actual fact, at $\geq$5 M, the apparent D_{Np} shows more than 10, assuming acceleration of disproportionality of inextractable NpO_2^+ into Np^{4+} and NpO_2^{2+} which might shift the valence of the Np_{mix} to be rich in extractable VI.

The hot counter-current runs were carried out in hot cells at the Chemical Processing Facility (CPF) in the Tokai Works, PNC. Salt-free type reagents, oxalic acid, HAN (hydoxylammonium nitrate), Hdz. oxa. and Hdz. car., were preferentially used in the flowsheet [5]. The feed HAR from reprocessing of the fast reactor spent fuel was spiked by U and Pu, and slightly acidified (ca. 5 M) due to the aforementioned reasons. The typical block flow diagram is shown in Fig. 1, where four banks composed of 35 mixer–settlers were devoted, expecting complete fractional stripping, despite there being only one bank of six stages for extraction. The dual-scrubbing (first, 8 M nitric acid with 0.03 M oxalic acid; second, 0.05 M nitric acid) was used to decrease extraction of both $RuNO^{3+}$ and free nitric acid. The amount of added oxalic acid was limited to minimize oxalato precipitation of f-elements in the scrubbing banks. As for fractional stripping, 0.01 M nitric acid for MA^{3+} and Ln^{3+}(strip-I), 0.01 M HAN for Pu^{4+} and NpO_2^{2+}(strip-II), 0.2 M Hdz. oxa. for Zr^{4+} and Pu^{4+} (strip-III), and 0.2 M Hdz. car. for $RuNO^{3+}$, Pu^{4+} and UO_2^{2+}(strip-IV) were individually employed. A material balance was made based on the flow rates and samples were taken from the settlers at steady-state 10 h from the start of operation. Typical results are summarized thus:

1. The total-α concentrations in the raffinate were lower than the detection limits (around 10^4 Bq/ml), resulting in giving a DF_{Am} of 10^3.
2. Acidified HAR with the first high-acid scrubbing resulted in a decrease of Ru extraction offering $DF_{106Ru} \geq 10^2$, and in high *E* (%) of Np.
3. Large *E* (%) of multivalent transition FPs, ca. 85% of Zr^{4+}, 55% of MoO_2^{2+}, and 70% of TcO_4^-, was observed, despite the presence of oxalic acid. TcO_4^- might accompany with highly extractable UO_2^{2+}, Pu^{4+} and Zr^{4+}.
4. Recovery ratios of MA and Ln were 80–110% at strip-I. Quantitative stripping of Np and transition elements was also achieved here.
5. Pu and Ru were strongly retained in the organic phase by ca. 20–95% and ca. 2–8% during strip-I. *BE* of 0.01 M HAN for Pu was unexpectedly low at strip-II.
6. The stripping profile of Pu was similar to that of Ru; DF_{Pu} was ca. 10 at strip-III and ca. 20 at strip-IV. DF_{Ru} was ca. 10 at strip-IV and ca. 2 at strip-III.
7. Overall *CE* (%) of HDBP was ca. 60% during strip-III and strip-IV.
8. The final retained Pu and Ru in the recycle solvent can be determined to be 0.5% and 0.25%. Hence, the latter two strip steps acted as an effective 'Plutonium (α)/Ruthenium (γ) Barrier'.

In general, stripping of multivalent transient cations and degraded acidic organics are considered to be governed by some complexation and/or pH of aqueous effluents. In strip-III, oxalic acid from Hdz. oxa. acted as an effective complexant, particularly for M^{4+} and M^{6+}, even in rather low pH conditions. In strip-IV, however, the higher pH condition given by Hdz. car. was preferable to strip out $RuNO^{3+}$ by possible hydration and acid dissociation of HDBP. Carbonate ions, furthermore, were more suited to complexing with UO_2^{2+}. In the design concept of salt-free reagents, metallic cations such as Na^+, K^+, etc., can be replaced by non-metallic $N_2H_5^+$, etc., due to the fact that the cation does not directly participate in the chemical reaction [5].

The improved TRUEX flowsheet, 'PNC Salt-Free Ver-

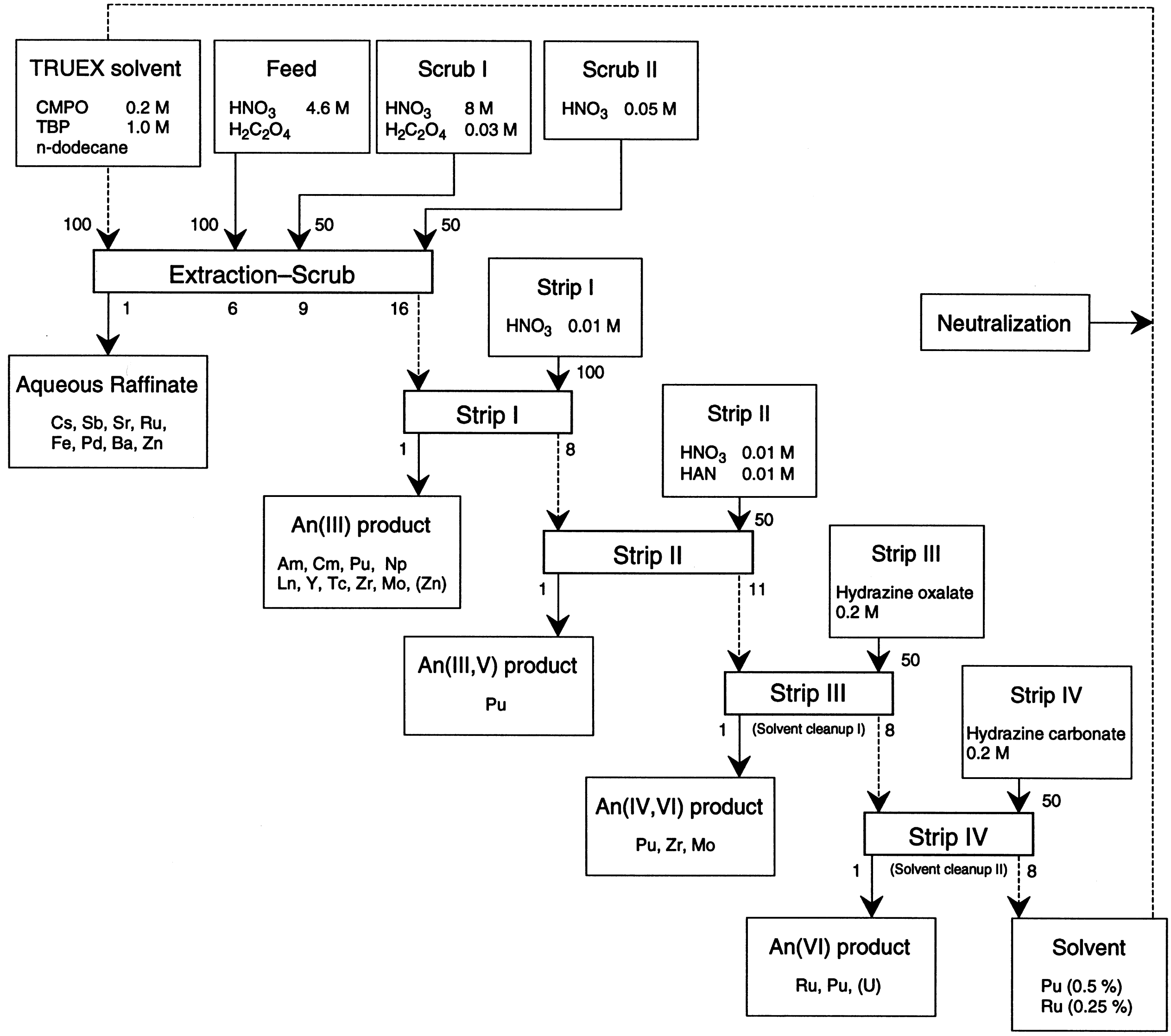


Fig. 1. Improved TRUEX flowsheet (PNC salt-free version).

sion', employed with simple feed acidification and combination of salt-free reagents for fractional stripping, successfully managed all of the actinides, lanthanides and troublesome FPs without generating secondary salt-wastes.

3. Application for An(III) and Ln separation–SETFICS

3.1. Process description and experimental flowsheet

Separation of trivalent actinide and lanthanide has been a major concern in the field of nuclear chemical engineering, and is essential for recycling Am and Cm in the MOX fuel system. The extractant CMPO has rather poor selectivity for those elements; thus, selective reagents have to be used in the CMPO extractant system for separation of those elements. The SETFICS flowsheet has been proposed to recover Am and Cm solutions which do not contain light lanthanides [6]. The principle of partitioning is different to the TALSPEAK process which uses acidic extractant [7,8]. The major reactions are extraction by CMPO and complexation with diethylenetriaminepentaacetic acid, DTPA, and are expressed in the following equations:

$$M^{3+} + 3NO_3^- + 3\overline{CMPO} \leftrightarrow \overline{M(NO_3)_3 3CMPO}, \qquad (1)$$

$$M^{3+} + DTPA^{5-} \leftrightarrow M\,DTPA^{2-}. \qquad (2)$$

In the SETFICS process, trivalent actinides are preferentially retained in the aqueous phase with complexation with DTPA, while lanthanides are extracted with CMPO. As the complexation with DTPA has to be done in low-acidity media, the CMPO mixed solvent is contacted with highly concentrated nitrate solution for enhancement of the salting-out effect.

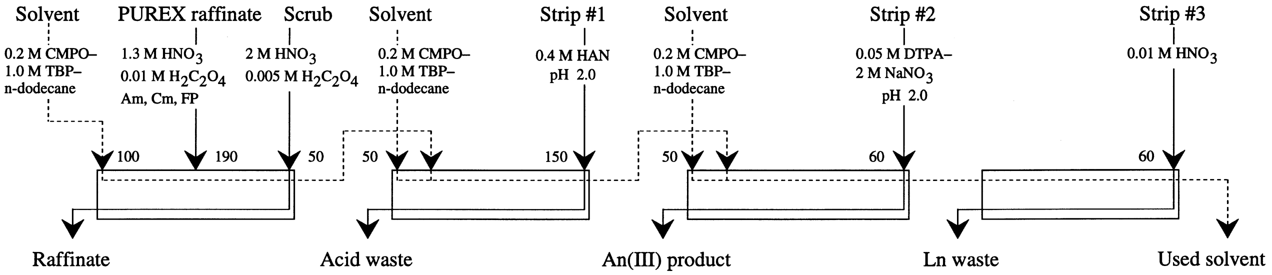


Fig. 2. Experimental flowsheet for trivalent actinide recovery from PUREX raffinate.

A basic flowsheet which was composed of four sections has been derived. In the first hot counter-current experiment, it had been found that the flowsheet was feasible and trivalent actinide was successfully separated from light lanthanides, such as La, Ce, Pr and Nd. The second counter-current hot experiments were conducted to improve recovery of An(III), apply hydroxylamine nitrate, HAN, as a salting-out reagent and trace the behavior of major FP elements.

The experimental flowsheet is shown in Fig. 2. The feed solution was obtained by diluting the raffinate which was generated in the preceding hot test for the PUREX process. The extracting solvent was prepared to 0.2 M CMPO–1.0 M TBP in *n*-dodecane.

In the first section, trivalent metals were extracted and most of the FP elements except for rare earth were decontaminated. For reduction of Zr and Mo extraction, oxalic acid was added to both the feed and the scrub solution. Prior to selective stripping of An(III), the acid concentration of the loaded solvent was reduced to stabilize pH in the partition using DTPA-nitrate mixed solution. In the 'acid stripping' section, 0.4 M HAN solution (pH 2.0) was used instead of the $NaNO_3$ solution which was adopted in the first test, and washing solvent was fed. For recovery of Am and Cm, 0.05 M DTPA-2 M $NaNO_3$ solution (pH 2.0) was used, and the concentration of $NaNO_3$ was lower compared to that of the first test. Any buffering reagent was not added and the pH was not actively controlled during the operation. Washing solvent was also used to reduce contamination with lanthanide. In the last section, the remaining lanthanide was stripped with 0.01 M HNO_3 solution. The hot operation was carried out for about 10 h. After the operation, the washing solution used in the An(III) stripping was found to contain a considerable amount of nitric acid.

3.2. Results

The mass balance of major components was obtained and is shown in Table 2. Trivalent metals were well recovered from the feed solution, and most of the FP remained in the aqueous raffinate, except for Ru. Some portion of Ru remained in the solvent after the last Ln stripping section. The fraction of trivalent metals in the 'acid waste' was very small, while the nitric acid which was contained in the solvent from the extraction–scrub section was successfully removed. As shown in Fig. 3, the extracted metals were kept in the organic phase. The availability of HAN for 'acid stripping' reagent was confirmed.

Table 2
Material balance of major components in the hot test

	Unit: %															
	^{106}Ru	^{125}Sb	^{137}Cs	^{144}Ce	^{154}Eu	^{241}Am	^{244}Cm	Zr	Mo	La	Ce	Pr	Nd	Sm	Eu	Y
Feed	100															
Raffinate	95	120	110	<0.3	<1.5	0.2	<0.9	99	86							
Acid waste	0.6	0.005	0.01	0.01	0.02	0.02	0.02									
An(III) product	<1.5	<0.2	<0.01	<0.1	84	160	200			<15	<6.2	<5.8	<5.2	38	100	120
Ln waste	<1.5	<0.2	<0.01	120	25	7.0	<0.2	<1.0	2.1	110	110	110	100	70	26	<2.9
Used solvent	38	0.02	0.002	<0.002	<0.01	0.01	<0.1									
	130	120	110	120	110	170	200	99	88	110	110	110	100	110	130	120

A blank indicates no analytical value.

Table 3
Decontamination factor to ^{241}Am of major component in the hot test

^{106}Ru	^{125}Sb	^{137}Cs	^{144}Ce	^{154}Eu	^{241}Am	^{244}Cm	La	Ce	Pr	Nd	Sm	Eu	Y
>110	>700	>22 000	>2600	1.9	1.0	0.83	>11	>26	>28	>31	4.3	1.6	1.3

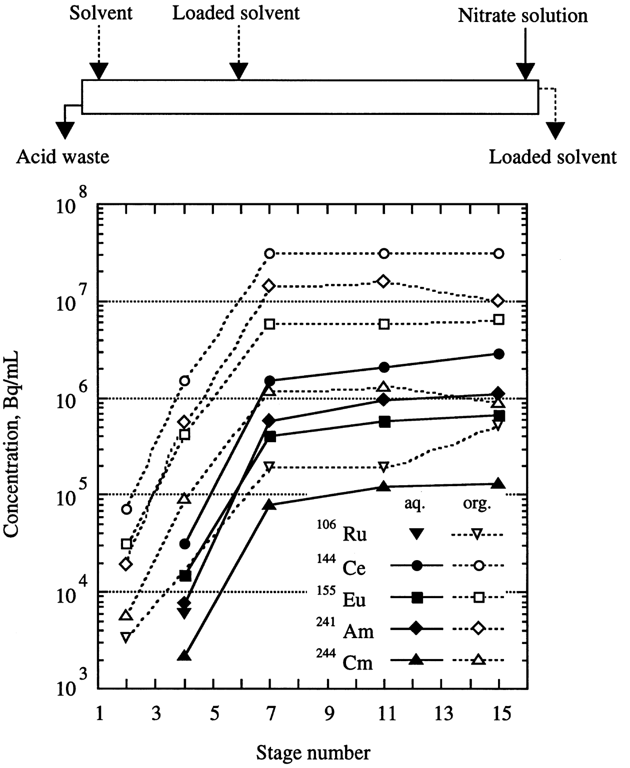


Fig. 3. Profile of concentration of some nucleides in the acid stripping section.

Most of the Am and Cm was recovered in the An(III) product solution, and the recovery was considerably increased compared with the result of the first test. However, a small fraction was streamed into the Ln waste solution, and further improvement is required. Although the acid in the washing solution affected the profile of acidity, the tendency for accumulation was observed slightly and any disturbance on recovery did not occur. The separation factor to ^{241}Am is shown in Table 3. Light lanthanides such as La, Ce, Pr and Nd were well decontaminated and values larger than 10 were obtained. Samarium, Eu and probably Gd was also contained in the An(III) product. For other FP components, the separation factors were very high.

By conducting two hot runs, it was verified that trivalent actinide can be recovered without light lanthanides in CMPO-TBP mixed solvent and DTPA-nitrite solution systems. For further investigation, optimization of the operating conditions and research into the principle of separation are required.

4. Conclusion

Basic study into salt-free reagents and several hot counter-current runs using real HAR from PUREX experiments led to an original TRUEX flowsheet. In this flowsheet, α- and salt-free HLLW was possible providing a $DF_{\mathrm{Am}} \geq 10^3$. In the hot run of the SETFICS flowsheet, Am and Cm was recovered without light lanthanides. The *DF* values for ^{241}Am were at least higher than 10 for La, Ce, Pr and Nd. Electrolytic extraction of precious (otherwise troublesome) RuNO^{3+}, Rh^{3+}, Pd^{2+} and TcO_4^- metals and mediatory electrochemical oxidation of organic wastes are under development as sub-systems of these solvent extraction processes [9]. Total destruction or reducing bulk of either organic additives (TMAH, DTPA, etc.) or spent extractants (CMPO, TBP, etc.) is key to establishing the ultimate waste-minimizing partitioning process.

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