

SESSION II

PARTITIONING

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The field of hydrometallurgical processes continues to be very active.

- The MA partitioning at JNC comprises an improved version of the PUREX process and the TRUEX process for extraction and separation of the trivalent MAs from the high active raffinate issued from the PUREX process.
- In the four-group partitioning process at JAERI, the first active test of the process has been performed successfully in the BECKY hot-cell facility in NUCEF (Tokai-mura).
- The work in the field of partitioning in Europe is carried out within the European research programme “NEWPART” and at the CEA.
- A two-step partitioning process is under study within the NEWPART programme co-ordinated by the CEA. The first step is the co-extraction of the trivalent MAs and the trivalent lanthanide (Ln(III)) from a high active effluent issuing from the PUREX process using a malonamide extractant (DIAMEX process). The second step is the selective extraction of the trivalent MAs over the Ln(III). Important results include: (i) the first hot test of the DIAMEX process using centrifugal extractors at the ITU, Karlsruhe (Germany); (ii) the first inactive test of the DIAMEX process using an optimised malonamide extractant at the CEA/Marcoule; (iii) the first test using synthetic spiked solutions of an An(III)/Ln(III) group separation process using new aromatic diorganyldithiophosphinic acids at Jülich, Germany. For the first time successful separation performances were obtained for a feed with a high nitric acid concentration.
- The SESAME process at the CEA aims at Am/Cm or Am/Cm and Ln separations, and based on the extraction of oxidised form(s) of Am. Hot tests were carried out successfully at Marcoule in 1998.

The field of pyrometallurgy has recently been attracting more and more attention.

- The results of a study in CRIEPI were presented. The mass balance of TRUs during the implementation of the partitioning process was shown based on the distribution of MAs between a LiCl, KCl eutectic fused salt and fused metal.
- A new concept for nuclear fuel cycle in Russia was presented. The concept involves a molten salt reactor which is compatible with P&T strategy.
- In the Czech Republic, the experience of dry reprocessing based on fluoride salt volatility was accumulated in collaboration with the former SSSR. This can be useful for future strategies of nuclear waste management.

It can be concluded that the lectures presented in Session II reflected the important world-wide activities in the field of partitioning.

**A NEW REPROCESSING SYSTEM COMPOSED OF PUREX AND TRUOX PROCESSES
FOR TOTAL SEPARATION OF LONG-LIVED RADIONUCLIDES**

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Abstract

Actinides-FP separation technologies based on the TRUOX and PUREX processes were summarised. Minor actinides were recovered from HLLW by ADvanced TRUOX flowsheet adopting salt-free reagents. Np was recovered by ADvanced PUREX flowsheet into the Pu-product fraction. Electrolytic extraction was prospective to separate several rare metals including some LLFPs from HLLW. CMPO/TBP/n-dodecane was decomposed by mediatory electrochemical oxidation, where major products of them were identified to be CO₂ and phosphoric acid. Medium and long term (~2030) scenario for TRU-LLFP recycling has been newly considered.

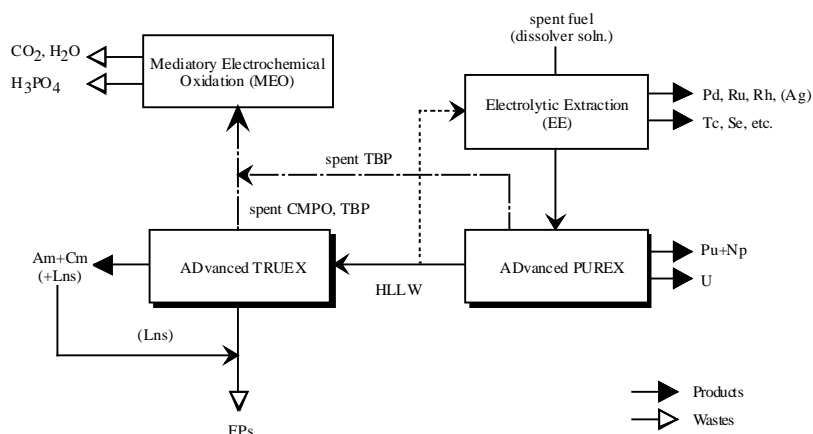
Long-lived nuclides separation system

A dual solvent extraction (SX) system has been proposed for enhanced governance of actinides in the spent fuel for the coming back-end fuel cycle. In this scheme, actinides (U, Pu, Np) are separated from dissolver solution by ADvanced PUREX process. Residue of them and all of Am and Cm are additionally recovered from high level liquid waste (HLLW) by the ADvanced TRUEx process. By such an “actinides recycling”, high radiotoxicity of the vitrified HLLW during ultra long terms is expected to be lowered to permit the reduction of the human being's supervision. The proposed concept as an advanced reprocessing system is shown in Figure 1.

While present research priority should be given to minor actinide separation, separation of fission products (FP) is necessary to further minimise hazard indexes of HLLW. This challenge will include to recover strategic platinum group elements (platinoids), technetium and the other rare metals as well as to separate long-lived fission products (LLFP). LLFP should be transmuted to short-lived or stable nuclides by fast reactor and/or another technics.

Among the targets, three nuclides, ^{107}Pd , ^{99}Tc and ^{79}Se , are ultra LLFP. Especially, enhanced removal of ^{99}Tc and ^{106}Ru will provide special advantages to raise the total decontamination factors to realise shorter SX process. Hence, the present study is focused on separating dissolved platinoids, technetium and rare metals in the dissolver solution and HLLW.

Figure 1. An Advanced Reprocessing Concept (PUREX-TRUEx Integrated Separation System)



In situ aqueous electrolytic extraction (EE) method can separate metals having noble redox potentials for M/M^{n+} couples, and has an advantage to generate less secondary radioactive wastes (*i.e.* salt-free). Platinoids, technetium and some rare metals dissolved in the nitric acid would meet with this technics.

One of the disadvantages on the SX process lies in the unsophisticated treatment manner for the final radioactive organic wastes. Application of mediatory electrochemical oxidation (MEO) method has been developed by several researchers to reduce PUREX solvent waste composed of TBP/n-dodecane, and shown the prospect to burn their hydrocarbon moiety in the aqueous phase.

MEO of $\text{O}\phi\text{D}[\text{IB}]\text{CMPO}$ (hereafter CMPO: Octyl[phenyl]-N, N-diisobutylcarbamoylmethyl phosphine oxide) has been parametrically studied in the presence of $\text{Ag}^{+/2+}$, $\text{Co}^{2+/3+}$ or another mediators in nitric acid media. Ultimate volume reduction and mineralisation by the total burning of hydrocarbon moiety of CMPO, TBP and n-dodecane is highly expected.

The-state-of-the-art of the JNC's separation techniques

The recovery ratios and separation factors on actinides and FPs are summarised in Table 1, which indicates R&D levels currently reached for individual techniques.

Table 1. **Summary of recovery ratio of target nuclides/elements in JNC's reprocessing-nuclide partitioning techniques**

Elements/ Nuclides	Method	R&D level					Recovery ratio (RR)/ Separation factor (SF)	Remarks
		N	A	B	C	D		
Actinides								
U, Pu	PUREX					X	RR > 99.5%	in Pu-products in Pu-product stream
MA (NP)	PUREX					X	RR ~ 40%	
	AD PUREX				X		RR ~ 100%	
	(Advanced PUREX)							
MA (Am)	AD TRUEX				X		RR ≥ 99.9%	as T a
MA (Np, Cm), U, Pu	AD TRUEX				X		RR ≥ 99.9%	
MA/Ln	SETFICS				X		SF > 100	for Am/Ce for Am/Eu for Am/Eu for Eu/Am
	Cyanex301			X			SF > 6000	
	TPTZ			X			SF ~ 10	
	ODP			X			SF ~ 25	
Platinoid-FP, Tc ions								
Tc	EE (Electrolytic extraction)		X				N.C (Not confirmed)	RR for Re (Tc) ~ 45%
Pd, Rh, Ru	EE		X				Pd _{RR} ~ 95% Ru _{RR} ~ 30% Rh _{RR} ~ 35%	in simulated HLLW in simulated HLLW in simulated HLLW
Long-lived FP								
Se-79	EE		X				N.C	Se _{RR} ~ 50% in Simulated HLLW
Zr-93	–	X					–	Re _{RR} (simulated Tc) ~ 45% Pd _{RR} ~ 95% in Simulated HLLW
Tc-99	EE						N.C	
Pd-107	EE		X				N.C	
Sn-126	–	X					–	N.C
I-129	PUREX					X		
Cs-135	MC (Macrocycles)		X					
Other FP								
Sr-90	MC		X				N.C	
Cs-137	MC		X				N.C	

Level N: Not researched.

Level A: "Cold" level (nitric acid or simulated HLLW)/Labo. scale (tube test).

Level B: "Tracer" level / Labo. scale (system).

Level C: "Hot" level (real HLLW or dissolver Soln.)/Labo. scale (system).

Level D: "Commercial" level.

Major achievements and evaluation are briefly described for each technologies.

Solvent extraction systems

ADvanced TRUEX

The requirements for the newly developing SX process for radionuclides are summarised as follows:

- a.* Ligands should have properly excellent extractability ($10 < D_M < 10^2$) for the target metals with effective stripping method (in view of process design).
- b.* Material transfer rate should be properly fast (in view of process and equipment design).
- c.* Hydrolytic and radiolytic stability should be tolerable (in view of process and safety design).
- d.* Good compatibility and interface with the counter process (in view of process design).
- e.* Minimum amount of secondary radioactive effluents (in view of process design, waste treatment design).
- f.* Low biological toxicity (in view of process handling and environmental safety).

Requirements of *a.* to *e.* are closely related to process economy. Among more than 20 methods developed so far, CMPO-TRUEX was primarily nominated because it will meet with the requirements *a.*, *b.* and *d.* CMPO's advantage is definitely well because it will not require the dilution of HLLW due to its high extractability in highly concentrated nitric acid media, hence helpful to the simple reprocessing process design.

Actual R&Ds have been pursued at the hot lab. in the CPF (JNC's Chemical Processing Facility in Tokai-mura) using real HLLW (HAR from PUREX tests with "Joyo" FR spent fuels, and concentrated HLLW from commercial reprocessing at "TRP (Tokai Reprocessing Plant)" with LWR spent fuels [1]). Five TRUEX runs and two An(III)/Ln separation (SETFICS) runs were carried out so far. Major lessons from the process flowsheet study are summarised as follows:

- i)* An and Ln were successfully separated from highly active raffinates by ADvanced TRUEX process with S.F. $> 10^3$, and they were fractionally stripped by contacting with salt-free reagents in series [1,4,8].
- ii)* Pu and RuNO^{3+} were satisfactorily controlled in the flowsheet, while some portion of multi-valent transition elements, Zr^{4+} , Mo^{6+} and TcO_4^- , were extracted and contaminated MA products with Lns [1,4].
- iii)* Separation of An(III) from light Ln^{3+} (La ~ Nd) was achieved by the SETFICS method using DTPA with SF more than several tens. About 80% of Lns was separated from Am [6,8].
- iv)* Some sort of "soft" donor ligands, purified Cyanex301[7] and ODP (octyl diphenyl phosphoric acid) [5], proved excellent Am/Eu separation.

The SETFICS parameter will be polished to increase the recovery of An(III) in the product solution.

ADvanced PUREX

Two ADvanced PUREX runs were carried out aiming at enhancing extraction of Np by salt-free methods [2].

- i) Quantitative extraction of Np was confirmed by increasing acidity (e.g. up to 5.6 M H⁺) and temperature (e.g. 100°C) in the dissolver solution without adding any chemical reagents, whilst allowing the formation of some portion of Pu (VI).
- ii) Co-extracted Np(VI) and Pu(IV, VI) were reductively stripped by contacting with HAN. Np was split into one fraction of Pu/Np/U product and was not detected in U fraction.

As a total assessment of the ADvanced PUREX and ADvanced TRUEX studies, no redox reagents was necessary to extract TRU (especially on Np (V)), and the recovery ratio of >> 99.9% for Np will be possible when two SX processes are combined. SF > 103 for MA (Am, Cm) by laboratory test would be feasible in the industrial plant provided that the experienced scale-up factor ca. 6000 (CPF → TRP) with mixer-settler contactor. Recovery ratio of U and Pu will also be >> 99.9% if all of effluents will be gathered to one HLLW effluent.

Requirements of *c.*, *e.* and *f.* are currently focused in the JNC, and very prospective data have been obtained. Flowsheet simplification is one of the issues to consider process economy. Mathematical modelling and simulation of MA and FP extraction with CMPO-TBP-n-dodecane system is in progress with precisely evaluating water activity and activity coefficient of nitric acid, which are necessary for calculating distribution coefficients of them.

Electrochemical separation steps

Electrolytic extraction of fission products

Among ca. 35 fission products in spent fuel, target rare elements and platinoids are specified by their noble redox potentials for Mⁿ⁺/M couples in acidic media. Incentives on FP separation are that element recovery of rare metals (Ru, Rh, Pd, Se, Tc, Te) for resource, radionuclide separation (¹⁰⁷Ru, ⁹⁹Tc) for increasing DFs for SX, and pre-element separation of LLFP (¹⁰⁷Pd, ⁷⁹Se, ⁹⁹Tc) followed by isotope separation.

Figure 2 shows EE behaviours of target ions from simulated HLLW containing 2.5M nitric acid under the following EE condition; cathodic current density: 500 mA/cm², temp.: 50°C, Ti cathode, each ion concentration corresponds to HLLW composition, cathode/vol. ratio: 0.07 cm⁻¹. The typical EE yields for Ru, Rh, Pd, Se and Te resulted in 23%, 28%, 94%, 50% and 68%, respectively. Trend for EE yield agreed well with each redox potentials, and at least ≥ 0.7 V (vs. NHE) was necessary. However, except Pd deposition, their EE yields should be further improved. For promoting EE yield of Ru and Re, increasing of current density from 10 to 700 mA/cm² or lowering acidity from 3 to 0.5 M was effective, but both were not preferable in the operational point of view [3].

Figure 2. Relation between Deposition Yields and Standard Redox Potentials (E^0) of Several Elements in the 3hr. Electrolysis in the Simulated High Level Liquid Waste

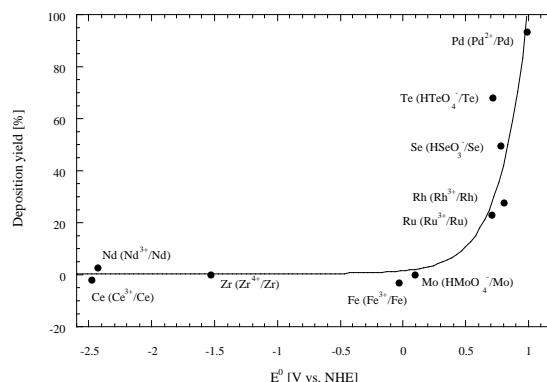
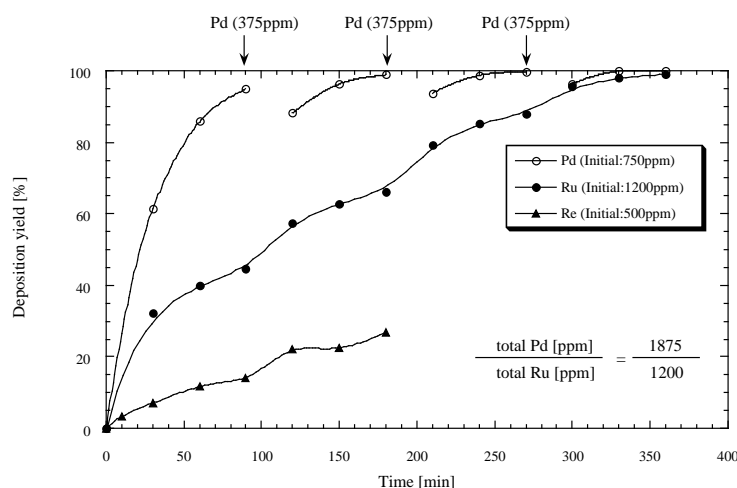


Figure 3. Time dependency of Ru and Re deposition yields with addition of Pd^{2+} ion in 2.5N HNO_3 Pd/Ru mixture or Pd/Re mixture solution



An unique acceleration effect of Pd^{2+} on the EE of $RuNO_3^{3+}$ and ReO_4^- was newly found as shown in Figure 3 [9]. In the case without addition of Pd^{2+} (initial Pd/Ru=0.6, Pd/Re=1.5), EE yields were only ca. 45% and 14% for Ru and Re, respectively. When 375 ppm of Pd^{2+} was added (Pd/Ru=0.9, Pd/Re=2.3), EE yields of Ru and Re were improved in giving EE yields of 66% and 27%, respectively. After more two times additions of Pd^{2+} (Pd/Ru=1.6), 99% of Ru was finally deposited. When the initial Pd/Ru was 1.6, however, only 74% of Ru was deposited. This suggests that co-existence of Pd^{2+} was effective, probably owing to either Pd_{adatom} on the cathode surface or their ionic interactions (reduction/ complexing) in the bulk solution. Such an acceleration effect was also observed on Rh^{3+} , but less or negative effect was found for Te^{4+} , Se^{4+} , Nd^{3+} , Zr^{4+} , Mo^{6+} , Fe^{3+} and Ce^{3+} . As was confirmed that it was extremely easy to recover from spent fuel, Pd^{2+} would be a “promoter” for fractional extraction of Ru, Rh and maybe Tc by its recycling.

As current data are limited to the “cold” test, the real effect of co-existing ions with α/γ irradiation on deposition will be defined through the “hot” tests using real dissolver solution or HLLW, and the total evaluation will be possible in the series test of *in situ* EE prior to SX process.

Mediatory Electrochemical Oxidation of Waste Solvent

Under the presence of small amount of Ag^+ or Co^{2+} , it has been confirmed that the dispersed CMPO/decalin was decomposed by electrolysis in the anolyte with 3M nitric acid. The decomposition was confirmed by analysing P in the anolyte. In comparing with direct electrolysis, current efficiency by MEO for CMPO decomposition was significantly improved from 13% to 75% with Ag^{2+} mediator. A redox ion couple in $\text{M}^{n/n+1}$ form with E^0 nobler than 1.8V would act as mediator for in this electrolysis. Another couples disturbed the decomposition, vice versa [3].

Figure 4. Mediatory electrooxidation of TRUEX solvent composed of 0.2M CMPO/1M TBP/n-dodecane; off-gas generation rate and decomposition ratio

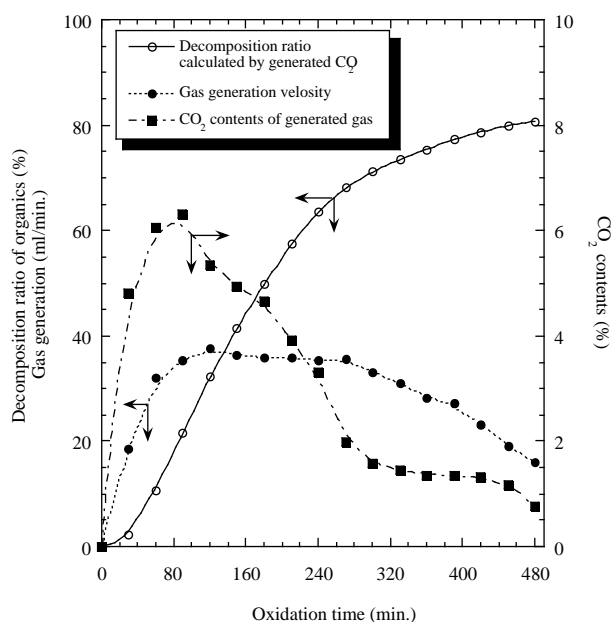


Figure 4 shows the typical example of the off-gas behaviour during the MEO of TRUEX solvent (0.2M CMPO/1M TBP/n-dodecane) dispersed in the anolyte with 3M nitric acid. The MEO condition was that anodic current density: 500 mA/cm^2 , temp: 50°C , Pt-Ti anode, Ag^+ : 0.5M, devoted TRUEX solvent: 0.447 g, anode/vol. ratio: 0.07 cm^{-1} . CO_2 release pattern was different for each MEO of TBP or CMPO. Sufficient analysis have not done yet, TBP and CMPO were seemed to be perfectly decomposed by analysis of P in aqueous phase, but the total decomposition yield was remained to be 80% from the estimation of CO_2 evolution. Only one peak was found and assigned to inorganic phosphoric acid by ^{31}P -NMR measurement in the aqueous phase, whereas several intermediates were recognised in the organic residues. The energy demand for the MEO was still high $5.6 \times 10^{-3} \text{ g/Ahr}$, and the current efficiency was low 4.5%.

Ongoing R&D programs and scenario

Owing to the present plan to renew or exchange process equipments in the cell of CPF, “hot” experiment using real dissolver solution and HAR will be started after 2001. Therefore, latest R&D programs are focused on “soft” work or “tracer” level test in the other facilities.

During 1998-2005, (i) TRUEX mathematical modelling and simulation on MA extraction followed by process design code, (ii) basic An(III)/Ln separation using DTPA or novel ligands, and (iii) organic waste decomposition, will be more active in JNC. Separation of fission rare metals, including LLFP will be continued. MA separation in pyrochemical process will be also considered.

As a long-term scenario, engineering scale tests will be expected in the phase 2005-2010 for precise evaluation of the system safety and cost on the TRU-LLFP recovery. In the next phase 2010-2030, “tracer/hot” engineering test should be carried out probably in the JNC’s existing facility. LLFP separation from real waste will be carried out in this period. After 2015, TRU and LLFP will be recovered from real HLLW and be fed to the fast reactor MONJU via TRU/FP target fabrication process.

Conclusion

Present TRU/FP separation technology based on the TRUEX process was summarised. TRU would be recovered from spent fuel by ADvanced PUREX and TRUEX process flowsheets. Electrolytic extraction was prospective to separate several rare metals including some LLFPs. Organic waste composed of CMPO/TBP/n-dodecane was decomposed to CO₂ and phosphoric acid by mediatory electrochemical oxidation. Medium and long-term (~2030) scenario for TRU-LLFP recycling using existing facility is under consideration in JNC.

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**SEPARATION OF MINOR ACTINIDES FROM GENUINE HLLW
USING THE DIAMEX PROCESS**

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Abstract

In the present work a counter-current extraction experiment, MA separation from real high-level PUREX raffinate, is reported. HLLW feed, obtained from small scale PUREX reprocessing of commercial LWR fuel (45.2 GWd/tM) in a centrifugal extractor battery, was used without further treatment for the DIAMEX process which was carried out in the same 16-stage centrifugal extractor set-up.

With up to six extraction stages, feed decontamination factors above 400 for lanthanides and above 1 000 for minor actinides were reached. Co-extraction of Mo and Zr was efficiently prevented using oxalic scrubbing. The back-extraction proved to be very efficient, yielding in four stages more than 99.9% recovery of MA and lanthanides. Co-extracted Tc, Ru and Pd were less efficiently stripped

Introduction

The potential harmfulness of the wastes generated by reprocessing are primarily due to the presence of minor actinides, MA, and they are of special concern regarding separation and transmutation.

Two step processes are at present considered necessary combining i) a separation of lanthanides and actinides from high acidity HLLW, ii) a separation of actinides from lanthanides at lower acidity. Several extraction processes have been investigated for use in the first step, the best known being the TRUEX process based on CMPO, n-octyl(phenyl) N,N diisobutyl carbamoylmethylphosphine oxide [1]. The TRPO process developed in China utilises a trialkyl (C6-C8) phosphine oxide extractant [2]. DIDPA, diisodecyl phosphoric acid, extracts actinides from feed solutions from 0.5 M nitric acid and offers thereby also the potential to be used in a one-stage process [3,4]. Of these three the TRPO process is the best compromise between extraction and back-extraction and CMPO is the only one capable to extract from a high acidity feed. However, due to a strong complexation, the CMPO shows accumulation in the back-extraction section of a continuous multistage process [5].

The French DIAMEX process uses at present dimethyl-dibutyl-tetradecyl malonamide, (DMBDTDMA) as reference molecule [6] in a completely combustible solvent (CHON principle). Similar to CMPO, actinides and lanthanides are extracted from a high acidity PUREX raffinate (3-4 M HNO₃). Batch experiments have indicated [5] that also the back-extraction is very efficient, similar to TRPO.

In the present work, the DIAMEX process has been tested in continuous counter-current extraction experiments, using a centrifugal extractor battery installed in a hot cell. The feed was a genuine HLLW obtained from small scale PUREX reprocessing of commercial LWR fuel (45.2 GWd/tM).

The high radiation dose delivered, especially from alpha decay, as well as the complex chemical composition with respect to the speciation of a large number of elements, necessitates the verification of the process using a genuine HLLW solution.

Experimental

Fuel

The characteristics of the fuel are given in Table 1.

Table 1. **Characteristics of the reprocessed fuel**

Pellet characteristics

Density:	94.3-95.0 %TD
Grain size:	6.5-7.0 µm
²³⁵ U enrichment:	3.2 %
Diameter:	9.11 mm
He fill gas pressure:	2.21 MPa
Cladding material:	Zry 4

Irradiation conditions

Average burn-up:	45.2 GW/tM
Average cycle power	
Cycle 1:	35.8 kW/m
Cycle 2	28.8 kW/m
Cycle 3	23.9 kW/m

Chemicals

All reagents and chemicals were of analytical grade. Tributylphosphate >99%, TBP, used without further treatment, and dodecane >99% were obtained from MERCK (Germany). The nitric acid solutions were prepared either from dilution of concentrated nitric acid or from Titrisol ampoules. MQ grade water (18 M Ω /cm) was used for all dilutions.

The diamide, DMDBDTMA, of ca. 98% purity and TPH were obtained from PANCHIM (France). It was diluted with pentane and purified in an Alumina-B (ICN Biomedicals, grade super I) filled column. The pentane was removed by vacuum evaporation and the pure DMDBDTMA (2.1 M) was diluted into TPH (hydrogenated tetrapropene) to an approximate concentration of 0.5 M. The exact concentration was determined by titration using perchloric acid in acetic anhydride media.

Equipment and Procedures

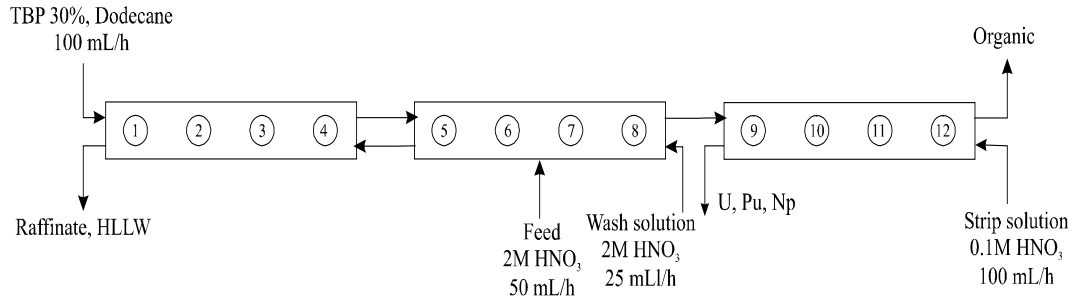
The centrifugal extractor equipment installed in the hot cells is described elsewhere [2]. For the present study, it was extended from 12 to 16 stages, divided into four batteries with four extractors each. Two different sampling techniques were used. When the system had reached steady-state conditions (ca. 1.5 h), samples were taken on-line from each stage. At the end of the experiment, usually three hours after introducing the feed, the centrifuges and pumps were switched off simultaneously and samples were taken from the mixing chambers (wells). In addition, the feed and all collected fractions were sampled.

All concentrations in the aqueous samples were determined by a quadrupole ICP-MS (Perkin-Elmer, ELAN250). Samples taken from the organic phase were back-extracted twice with 0.1 M HNO₃ prior to the analysis. The acidity profile was determined for the aqueous phase by titration.

PUREX process

The PUREX process flow-sheet is shown in Figure 1. The feed for the PUREX process was produced by dissolving 60 g of fuel (see Table 1) in 300 mL 4 M HNO₃.

Figure 1. Flow-sheet for the PUREX process



In total, 11 on-line samples were taken from the aqueous phase together with samples from the collected aqueous and organic effluents.

The decontamination factor of this process is defined by the equation (1):

$$DF = \frac{[M]_{Feed}}{[M]_{Raffinate}} \Theta \quad (1)$$

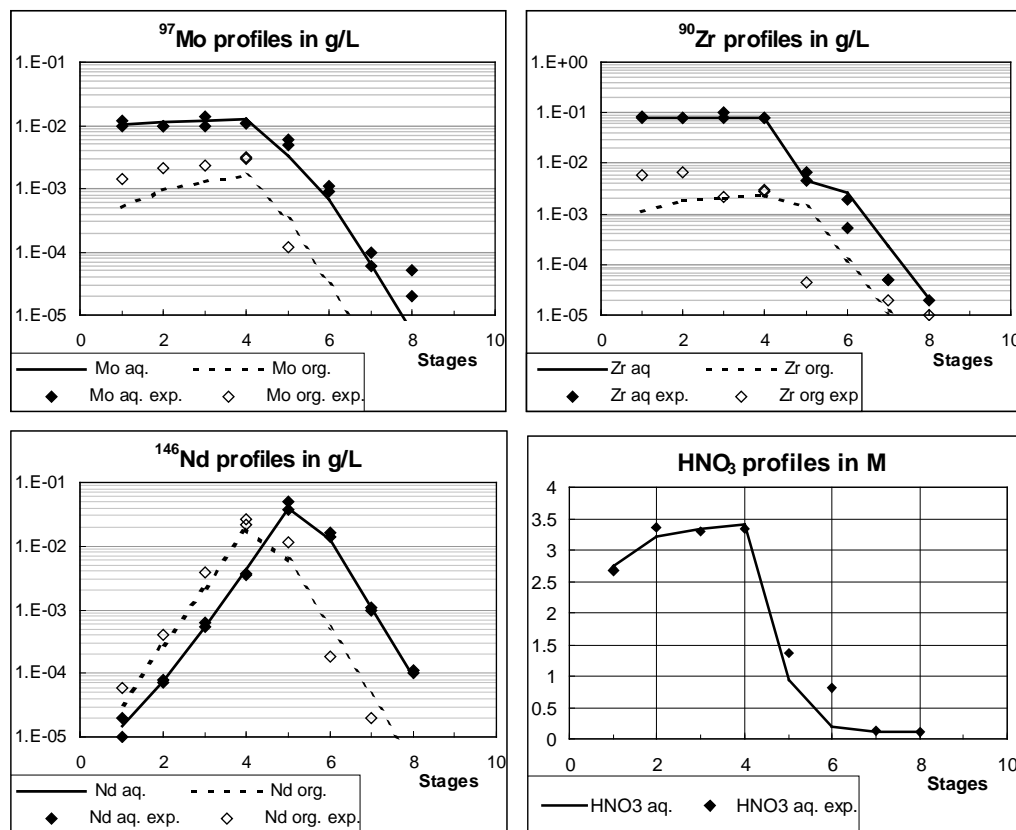
Θ is flow rate ratio between the raffinate and the feed.

DIAMEX process

The feed for the DIAMEX process is the HLLW fraction collected from the PUREX process. Before use the acidity was adjusted to 3.5 and 0.3 M in nitric acid and oxalic acid, respectively, avoiding significant dilution. Oxalic acid was added to prevent the extraction of Zr and Mo.

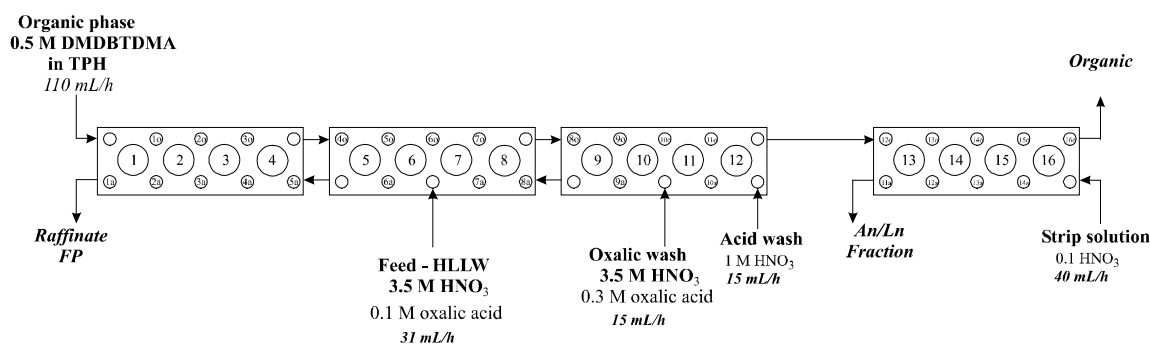
For the DIAMEX process the flow-sheet was optimised on the basis of data obtained from a cold test with a simulated lanthanide solution. The flow ratio in the extraction and in the back-extraction (with 0.1 M HNO₃) were 1.8 and 2.1 respectively. Figure 2 shows the profiles from this experiment in comparison to those calculated by means of the PAREX code [7].

Figure 2. Experimental and calculated (PAREX code) results from the cold test



It can be seen that the experimental concentration profiles are fairly well simulated. On the basis of this result, an optimised flow-sheet for a 16 stage counter-current process was designed (Figure 3).

Figure 3. Flow sheet used in the DIAMEX hot-test



The decontamination factor for this process is defined in the equation (1).

Titration and ICP-MS analyses of the aqueous well samples were performed. All out-going fractions were analysed including the solvent. On-line samples from stages 4a, 6a, 8a and 12o (a=aqueous, o=organic) were taken for comparison to the well samples. A good agreement was found in most cases, indicating that well samples taken after the experiment were also in extraction equilibrium conditions.

Results and discussion

PUREX

U and Pu were efficiently extracted in six stages, with decontamination factors (see eq. 1) of 10 [5] and 10 [3], respectively. Np was also extracted to about 70%. Of the fission products, only Tc was to some extent co-extracted. The composition of the feed and raffinate solutions for the PUREX process are tabulated in Table 2. It should be pointed out that the HLLW is diluted by a factor 2/3 versus the feed.

Table 2. Concentrations ($\mu\text{g/g}$) in the PUREX experiment

Isotope	Feed	HLLW
⁸⁵ Rb	33	30
⁸⁷ Rb	60	58
⁸⁸ Sr	89	92
⁸⁹ Y	111	101
⁹¹ Zr	128	112
⁹² Zr	136	117
⁹³ Zr	146	126
⁹⁴ Zr	154	134
⁹⁵ Mo	102	96
⁹⁷ Mo	104	94
⁹⁸ Mo	108	99
⁹⁹ Tc	101	57
¹⁰¹ Ru	52	47
¹⁰² Ru	55	49
¹⁰³ Rh	32	29
¹⁰⁵ Pd	44	38
¹⁰⁶ Pd	42	36
¹⁰⁷ Pd	24	21
¹⁰⁸ Pd	16	14
¹¹¹ Cd	2	2
¹¹² Cd	2	1
¹¹⁴ Cd	1	1
¹³⁰ Te	10	8
¹³³ Cs	168	135
¹³⁵ Cs	45	35
¹³⁸ Ba	229	179

Isotope	Feed	HLLW
¹³⁹ La	210	169
¹⁴⁰ Ce	215	169
¹⁴¹ Pr	243	188
¹⁴³ Nd	126	97
¹⁴⁴ Nd	256	193
¹⁴⁵ Nd	118	90
¹⁴⁶ Nd	130	99
¹⁵¹ Sm	2	1
¹⁵² Sm	19	14
¹⁵³ Eu	22	16
¹⁵⁶ Gd	23	17
¹⁵⁸ Gd	5	4
²³⁴ U	26	0
²³⁵ U	704	0
²³⁶ U	631	0
²³⁷ Np	222	62
²³⁸ U	130-543	2
²³⁸ Pu	38	0
²³⁹ Pu	673	1
²⁴⁰ Pu	364	1
²⁴¹ Am	94	91
²⁴² Pu	116	0
²⁴³ Am	24	21
²⁴⁴ Cm	6	5

Acidity (M)	1.98	1.94
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DIAMEX

Figure 4 shows the aqueous concentration profiles (in μg nuclide per g of solution) obtained for the minor actinides, and for some lanthanides. All minor actinides (Am, Cm and also Np) are efficiently extracted, similar to the lanthanides. The back-extraction of actinides and lanthanides is even more efficient, except for Np. The profiles for the lanthanides indicate a decreasing extraction with the element number.

In Figure 5 the profiles for some relevant fission products are shown. The oxalic scrubbing efficiently reduces co-extraction of Zr and Mo. The reduced acidity in the two acid wash stages has also a good scrubbing effect on these elements. In the scrubbing section the aqueous concentration of Zr and Mo decreases by several orders of magnitude with an almost complete wash-out.

Tc and Pd, and also to some extent Ru, are co-extracted and scrubbing is not efficient in this case. In the back-extraction section the Pd and Ru profiles indicate a slow back-extraction, and the efficiency could probably be increased using more stages. The Tc profile in the back-extraction section indicates an accumulation in the organic phase.

Figure 4. Actinide and lanthanide concentration profiles in the DIAMEX process

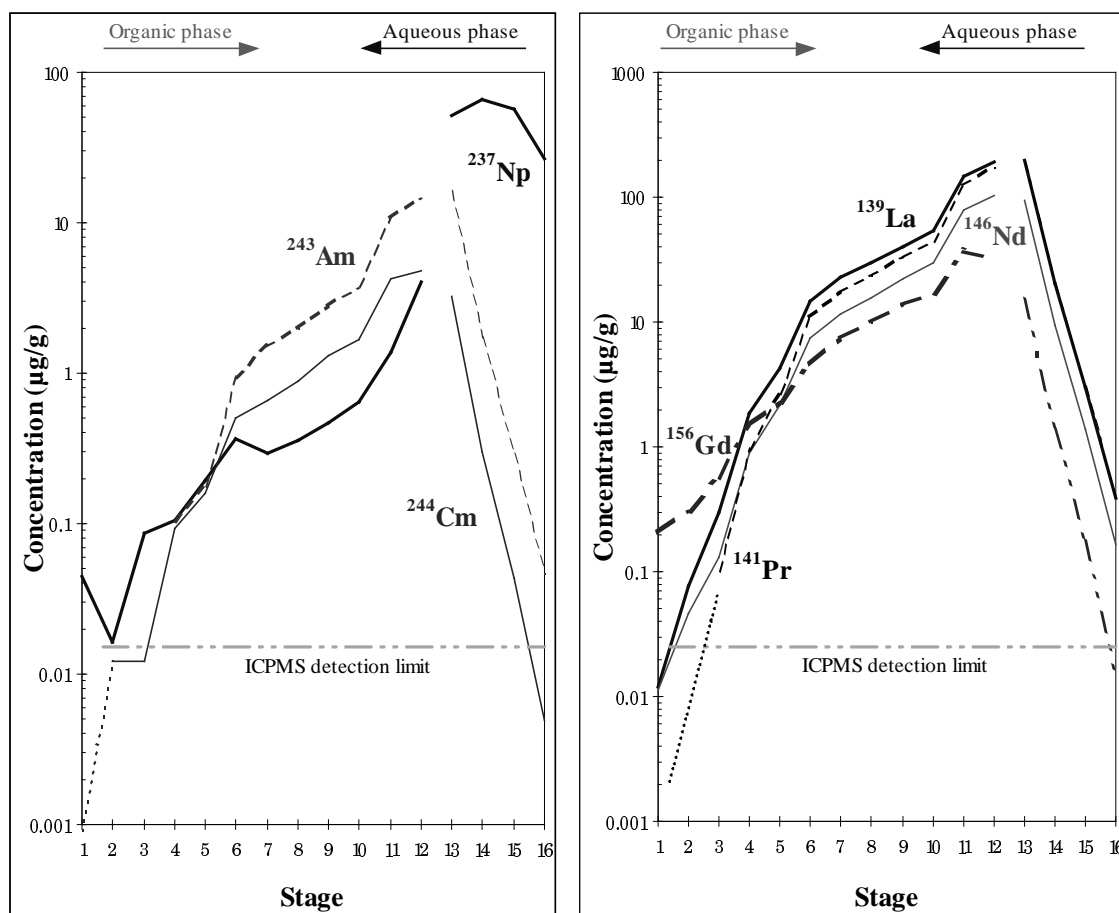


Figure 5. Concentration profiles for the light fission products in the DIAMEX process

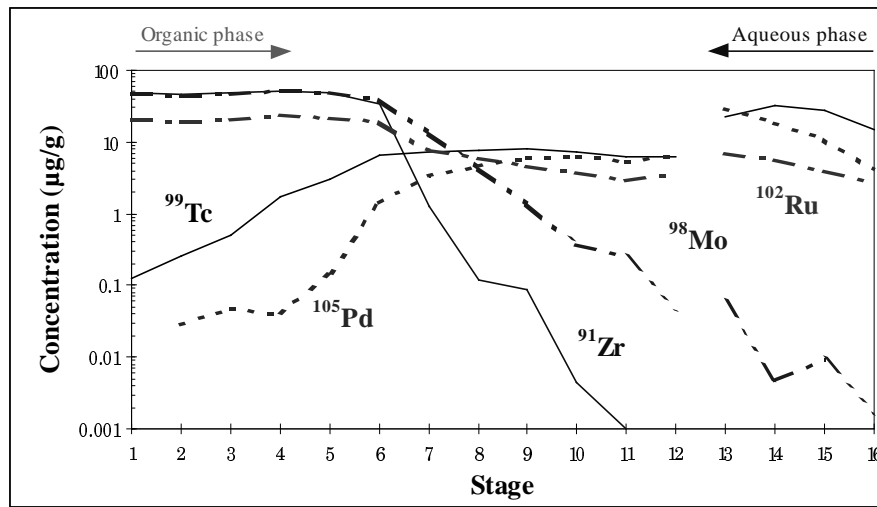
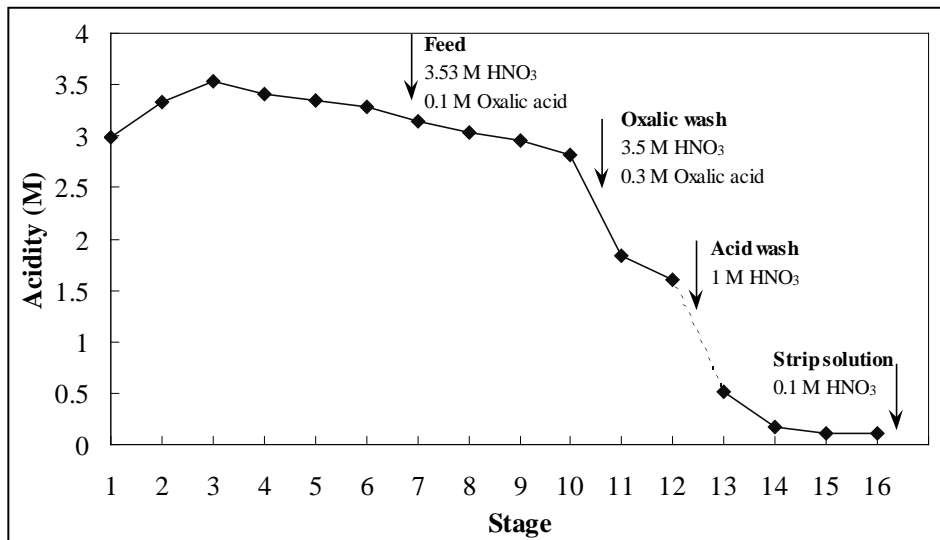


Figure 6 shows the acidity profile in the aqueous phase of the extractor battery. A slight co-extraction of HNO₃ is observed in the extraction and scrubbing section with a minimum at stage 3.

Figure 6. Nitric acid concentration profile in the DIAMEX test



The acidity in the lanthanide/actinide fraction is 0.5 M HNO₃. This is an acidity that allows a subsequent lanthanide-actinide separation process without or little adjustment of the feed. Table 3 shows the decontamination factors of the feed for the major isotopes analysed, calculated with eq. 1.

Table 3. Decontamination factors (DF) achieved in the DIAMEX process (Feed/Raffinate)

Isotope	DF
⁹¹ Zr	3.7
⁹⁸ Mo	3.8
⁹⁹ Tc	462
¹⁰¹ Ru	4.9
¹⁰⁵ Pd	610
¹³⁹ La	650
¹⁴⁰ Ce	815
¹⁴¹ Pr	835

Isotope	DF
¹⁴⁶ Nd	609
¹⁵² Sm	426
¹⁵³ Eu	438
¹⁵⁶ Gd	189
²³⁷ Np	1020
²⁴³ Am	1000
²⁴⁴ Cm	1167

MA elements show higher DF values compared to lanthanides. In the lanthanide series DF values vary with the element number with a maximum for Ce and Pr, see also Figure 4. This result can be explained by a different stability of the extracted complexes. From the analyses of aqueous and organic effluents, a recovery of more than 99.9% of Am and Cm in the process was calculated.

Table 4 shows the decontamination factors of the “loaded” organic phase. The DF’s of the lanthanides and Am are more than 22 000 which indicate a high back-extraction yield to the aqueous phase of these elements. This is also the case for Cm but for the extracted FP’s and Np, the DF’s are less than 100.

Table 4. Decontamination factor of the organic phase (loaded solvent/stripped solvent)

Isotope	DF
⁹⁹ Tc	30
¹⁰¹ Ru	61
¹⁰⁵ Pd	96
¹³⁹ La	> 46 000
¹⁴⁰ Ce	> 22 500
¹⁴¹ Pr	> 44 000

Isotope	DF
¹⁴⁶ Nd	> 50 000
¹⁵³ Eu	> 300 000
¹⁵⁶ Gd	> 300 000
²³⁷ Np	29
²⁴³ Am	> 25 100
²⁴⁴ Cm	

Conclusions

A 16 stage extraction process using a centrifugal extractor battery allows to efficiently separate MA from genuine HLLW, obtained from PUREX reprocessing of commercial LWR fuel. The process represents an excellent compromise between reasonably good extraction and even better back-extraction properties. Thus, recovery better than 99.9% for Am and Cm was achieved, i.e. the losses of these elements in the process are very low. The experiments confirm the previous results obtained in a mixer settler experiment [6]. Oxalic scrubbing showed to be very efficient in preventing co-extraction of Mo and Zr. For Tc, Ru and also Pd which are slightly co-extracted, a process optimisation is needed. The actinide/lanthanide fraction is collected with an acidity of 0.5 M HNO₃ and can thus be introduced in a subsequent actinide-lanthanide separation process, without or little feed adjustment.

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DEVELOPMENT OF THE FOUR GROUP PARTITIONING PROCESS AT JAERI

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Abstract

At the Japan Atomic Energy Research Institute (JAERI), a partitioning process has been developed to separate elements in a high-level liquid waste (HLLW) into four groups; transuranium elements (TRU), Tc-platinum group metals (PGM), Sr-Cs and the others. The present paper deals with objects of the partitioning, main characteristics of four group partitioning process, generation of solid materials after the partitioning and its positive effects on the management of high-level waste (HLW), and recent study on the four group partitioning process.

Objectives

The first objective of the partitioning is the reduction of long-term radiotoxicity of HLW to be disposed of into deep underground. The second one is the volume reduction of HLW by separate treatment of heat generating nuclides such as ^{90}Sr and ^{137}Cs . The third objective is the development of advanced waste management methods because the other groups containing about 70wt% of fission and corrosion products in HLLW might be disposed of directly without long-term cooling. The fourth objective is resourcefication of HLW by promoting beneficial uses of radioisotopes and noble metals in HLLW.

Basic way of thinking for the construction of the partitioning process

For the satisfaction of above objects the four group partitioning process has been developed at JAERI since 1985.

Following items have been considered for the construction of the partitioning process.

1. First priority separation of the TRU group because of its long-term and dominant radiotoxicity and suppressing its dispersion into other groups.
2. Waste minimisation, especially for the separation of the Tc-PGM and the Sr-Cs groups.
3. Use of reagents with high radiation durability and chemical stability.
4. No possibility of firing and explosion of the reagent and its degradation products. No use of reagent with phenyl group which has a possibility of forming explosive compounds such as nitrobenzene as its degradation product.
5. Compatibility to a fuel reprocessing plant. No use of reagent such as hydrochloric acid and organic reagent with chlorine which causes corrosion of stainless steel. Increasing a possibility of using a waste treatment facility in the fuel reprocessing plant for the treatment of the wastes generated from partitioning.

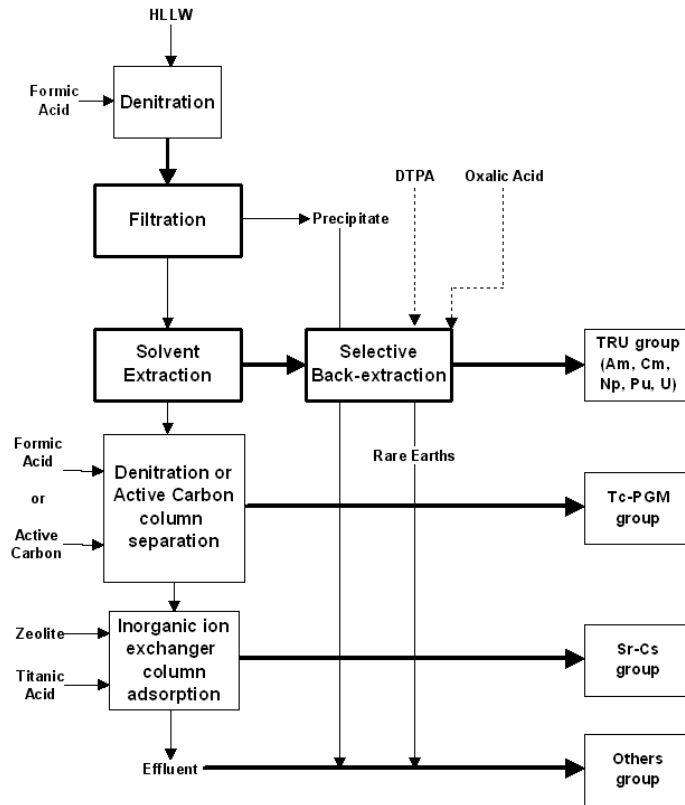
Four group partitioning process

Through the fundamental study, the four group partitioning process has been constructed as shown in Figures 1 and 2. Main characteristics of the four group partitioning process are as follows:

1. All TRU elements including pentavalent Np are extracted with DIDPA after the denitration of HLLW, reducing the nitric acid concentration from 2 M to 0.5 M.
2. Tc and PGM are separated by precipitation through denitration or by adsorption with an active carbon.
3. Sr and Cs are separated by adsorption with inorganic ion exchangers, titanate acid and zeolite, respectively.
4. The TRU elements extracted in the DIDPA solvent are sequentially back-extracted with 4 M nitric acid for Am, Cm and lanthanides, 0.8 M oxalic acid solution for Np and Pu, and 1.5M sodium carbonate solution for U.

- Back-extracted Am, Cm and lanthanides are extracted again with DIDPA, and then Am and Cm are preferentially back-extracted with 0.05 M diethyltriaminepentaacetic acid (DTPA) solution, leaving lanthanides in the DIDPA solvent.

Figure 1. **Four group partitioning process**



Effectiveness of the partitioning process

Separation efficiency obtained experimentally with mainly simulated HLLW and the estimated recovery through whole partitioning process are shown in Table 1 along with the target recovery, where the separation efficiency of the element means the recovery in the first chemical step for its separation and the target recovery of TRU elements was determined to make the potential radiotoxicity of a vitrified HLW after storage for 1000 years comparable to that for naturally occurring mineral containing 3wt% of U.

The separation efficiency and the estimated recovery of TRU elements are quite high and almost satisfied with the target recovery. The recoveries of Tc and PGM are around 90 to 95% which is lower than the target recovery. This lower recovery is not so important because of their little contribution to the potential radiotoxicity of HLW.

As for the separation of actinides, Am and Cm, from lanthanides, it is possible to reduce the lanthanide content less than 25wt% under the condition of 99.99% separation efficiency of actinides, which is fully satisfied with the purification suitable for nuclide transmutation.

The radiation durability of the DIDPA solvent is about 7 times higher than TBP and its degradation products give hardly drawback effects on the TRU extraction because most of the products are organophosphoric acid compound like DIDPA. Thus there is no frequent need to purify the DIDPA solvent prior to its recycle use, which greatly contributes to the reduction of a secondary waste generation.

Generation of solid materials after the partitioning and its positive effects on the management of HLW

Table 2 shows the volume of solid materials after partitioning of HLLW2. The volumes of the TRU group and the Tc-PGM group were estimated as oxide and metal respectively. The volume of the Sr-Cs group was estimated for the solid material generated by the direct calcination of the inorganic ion exchangers loaded with Sr and Cs, and the volume of the others group for the vitrified material containing 30wt% of oxides of fission and corrosion products. Cementation was considered for the secondary wastes such as CaHPO₄ and NaNO₃.

Table 2. Volume of solid materials after the four group partitioning for one ton of the spent fuel burned up to 33 GWd/t

Group	Main nuclides or elements	Solid form	Volume (L)
TRU	²³⁷ Np, ²⁴¹ Am	oxide	0.09
Tc-PGM	⁹⁹ Tc, Ru, Rh, Pd	metal	0.39
Sr-Cs	⁹⁰ Sr, ¹³⁷ Cs	calcined product	14
Others	Zr, Mo, Fe, rare earths	vitrified material	31
Total volume of high-level waste after the partitioning			~45
High-level waste volume without partitioning			~150
Secondary waste after the partitioning		cemented material	330

In relation to Table 2 positive effects of the partitioning on the management of HLW can be described as follows:

1. Most of nuclides with long-term radiotoxicity are collected in the TRU group whose volume is only 0.06% of a vitrified HLW without partitioning. The long-term radiotoxicity of HLW can be greatly reduced by the separation of the TRU group and its nuclide transmutation.
2. Most of nuclides contributing to the heat generation of HLW are collected in the Sr-Cs group whose volume is only 10% of the vitrified HLW. This means, from a view-point of volume only, a storing capacity for cooling of the vitrified HLW for 30 years can be used for the storage of the Sr-Cs group for 300 years, during which the activities of ⁹⁰Sr and ¹³⁷Cs with half-live of about 30 years are reduced by a factor of about 1000.

3. The solid materials obtained from a direct calcination of inorganic ion exchangers loaded with Sr and Cs over 1 000 C possess extremely higher thermal stability and lower leachability by a factor of about three orders of magnitude than the vitrified HLW.
4. In the vitrification of the others group, it is possible to increase an elemental concentration as compared with that in the vitrified HLW because of no presence of heat generating nuclides such as ⁹⁰Sr and ¹³⁷Cs, thus contributing to the volume reduction of the other group, about 20vol% of the vitrified HLW. For the others group it might be possible to dispose of directly into deep underground without any long-term cooling.
5. Total volume of the four groups is estimated to be 45 L for one ton of the spent fuel, which is smaller by a factor of 3.3 compared with that of the vitrified HLW. Extremely higher volume reduction of HLW might be expected by the four group partitioning.
6. Volume of the cemented waste is only about 20% of that generated in a reprocessing plant.

Moreover, an alpha activity concentration of the cemented waste becomes lower than 1 GBq/ton and its shallow land disposal might be expected.

Recent Study on the four group partitioning process

Prevention of colloid formation and removal of the colloid in the pre-treatment step for the partitioning

Studies on pre-treatment of HLLW for the DIDPA extraction in the four group partitioning process showed that colloid was formed at denitration step when a simulated HLLW was heated before denitration. The heating step was added to make the precipitate easy-to-filter, which is very important from the chemical engineering point of view. Since the colloid disturbs the extraction with DIDPA by forming emulsion, the prevention of the colloid formation and the removal of the colloid was studied using simulated HLLW.

The main component of the colloid was Zr, which remains in the pre-treated HLLW in a yield of about 50%. Modification of heating and denitration condition in the pre-treatment could not prevent the formation of either the colloid or the very fine particles which is very difficult to filtrate. Addition of phosphoric acid, which is one of the reagents for Zr precipitation, was found to be effective. To prevent the emulsification in the DIDPA extraction, amount ratio of phosphoric acid to the initial Zr should be more than 0.8.

As for the removal of the colloid formed in the denitrated HLLW addition of reagents for Zr precipitation also is the most effective among the various methods examined except very direct method of ultra filtration. Four reagents of phosphoric acid, ammonium para-molybdate, sodium ortho-molybdate and telluric acid were examined for the colloid removal and all the reagents could convert the colloid to precipitate by heating the solution after the addition. It was concluded that ammonium para-molybdate would be the best reagent among the four reagents because Mo is already included in HLLW, ammonium para-molybdate does not induce extra salts, it makes easiest-to-filter precipitate and it does not change the acid concentration.

Construction of optimum separation process for Tc-PGM Group by precipitation through denitration

For the purpose of constructing the optimum separation process for Tc and PGM by precipitation through denitration, the acid concentration of the denitrated solution and the precipitation ratio of elements were examined using simulated DIDPA raffinates at the various concentrations of elements and nitric acid and in the various heating conditions.

When the simulated DIDPA raffinate was heated strongly at the denitration, the several-times concentration of the raffinate was required for efficient separation of PGM. If the twice concentrated raffinate was denitrated by the addition of formic acid with the ratio of $[\text{HCOOH}] / [\text{HNO}_3] > 2.4$, or if the 4-times concentrated raffinate was denitrated with the ratio of $[\text{HCCOH}] / [\text{HNO}_3] > 2$, pH of the denitrated solution increased to neutral region and then PGM was separated as precipitates.

In case the denitration was performed without the concentration of the simulated DIDPA raffinate, the temperature rising rate of the solution was found to be an important parameter. In order to increase the pH of the denitrated solution to neutral region and to separate PGM as precipitates by the denitration at $[\text{HCOOH}] / [\text{HNO}_3] = 2.2$, the temperature rising rate should be slower than a threshold value and the solution temperature after the rising should be over 95 C.

Tc behaviour in the four group partitioning process

A small scale partitioning test on the four group partitioning was performed using simulated HLLW with addition of a macro amount of Tc as a total test that summarises the previous studies on Tc separation and as a final confirmation about Tc behaviour before the partitioning test with real HLLW at the Nuclear Fuel Cycle Safety Engineering Research Facility (NUCEF).

At the pre-treatment step including denitration step and newly-introduced colloid removal step by addition of Mo, Tc remained in the solution. Ratios of Tc found in the precipitates was 0.23% at the denitration and 0.21% at the colloid removal. The loss of Tc to the precipitate was negligible.

At the DIDPA extraction step, 99.93% of Tc transferred to the raffinate. Calculated distribution ratio was 0.013.

At the precipitation step by denitration of the raffinate after concentration, 98.2% of Tc were precipitated. It was confirmed that the Tc precipitates even at a macro amount.

At the dissolution step for Tc from the precipitate with hydrogen peroxide, 84.6% of Tc were recovered as a solution. By repeated dissolution, the recovery can be increased.

Back-extraction of actinides from organophosphoric acid with hydrazine carbonate

Back-extraction of actinides from organophosphoric acid solvent with hydrazine carbonate is an attractive method to separate actinide from other actinides and lanthanides from the standpoint of reducing secondary waste because it is so-called salt-free. The back-extraction from HDEHP (di(2-ethylhexyl)phosphoric acid) and DIDPA was studied to elucidate its behaviour of actinides and lanthanides.

In the case of HDEHP, the separation factor of Am(III) and Eu(III) was about three and Am might be separated from lanthanides in an appropriate hydrazine carbonate concentration from 0.6 M to 1.0 M.

Np(IV) and Pu(IV) were back-extracted with 0.6 M hydrazine carbonate solution from HDEHP with the distribution ratios of 0.11 and 0.47, respectively, whereas Am(III), Eu(III) and U(VI) were hardly back-extracted, whose distribution ratios were 2.3, 7.3 and 13.6 respectively.

Therefore, it is possible to separate actinides each other and to separate trivalent actinides from lanthanides by changing the hydrazine carbonate concentration.

Partitioning tests with simulated HLLW at NUCEF

Partitioning tests with simulated HLLW have been performed in the partitioning test facility at NUCEF which was constructed for the demonstration of the four group partitioning process with real HLLW. One of the purposes was to obtain the data on elemental behaviour to be compared with the results of the tests with real HLLW. Another purpose was to check the operability of the facility.

Table 3. Fractional distribution (%) of each element at the mixer-settler

Element	Raffinate	Back-extracted with 4M HNO ₃	Solvent
Y	< 0.002	5.6	94.4
La	< 0.06	> 99.93	< 0.01
Ce	< 0.01	97.9	2.1
Pr	< 0.02	99.85	< 0.13
Nd	< 0.01	98.7	1.3
Sm	< 0.008	96.5	3.5
Eu	< 0.006	96.3	3.7
Gd	< 0.04	97.5	2.5
Fe	4.64	0.52	94.84
Zr	< 0.3	< 3.1	> 96.6
Mo	> 95.4	4.1	< 0.5
Te	88.8	11.6	< 0.6
Ru	98.7	0.2	1.1
Rh	> 99.0	0.9	< 0.1
Pd	98.2	0.8	1.0
Sr	> 99.98	0.02	< 0.001
Ba	> 99.99	0.01	< 0.001
Rb	> 99.96	< 0.03	< 0.01
Cs	> 99.91	< 0.07	< 0.02

Phosphoric acid was added to the simulated HLLW before denitration in the pre-treatment step for the DIDPA extraction in order to remove completely Zr not only in ionic form but also in colloidal form, which sometimes disturbs the aqueous - organic phase separation in the DIDPA extraction. About 99.5% of Zr, 98% of Mo, 42% of Te, 20% of Fe and 5% of Ru were removed from the simulated HLLW as a precipitate in this pre-treatment step.

In the DIDPA extraction a 16 stages mixer-settler was used and 7 stages used for extraction of TRU, 4 stages for scrubbing and 5 stages for back-extraction of Am and Cm. The fractional distribution of each element in this DIDPA extraction steps is shown in Table 3. Lanthanides could be almost completely extracted with DIDPA and back-extracted with 4 M HNO₃. Further complete back-extraction of lanthanides might be easily accomplished by increasing the number of the back-extraction stage. Other elements except Fe, Zr and Y were not extracted and therefore Sr and Cs were well separated from lanthanides. About 99.8% of Fe, 80% of Zr and 0.5% of Y were back-extracted with the oxalic acid solution.

The raffinate of the DIDPA extraction was fed to the separation step for PGM and Tc by precipitation through denitration. More than 90% of PGM was precipitated and almost all Cs was remained in the solution, but 20-30% of Sr was coprecipitated. These results well agreed with the results of previous experiments in a small scale. Recovery of Sr from the precipitate should be studied.

Partitioning tests with real HLLW at NUCEF

As the first step of the four group partitioning test with real HLLW, semi-hot test with tracer level of real HLLW has been performed at NUCEF. In this test more than 99.99% extraction of Am with DIDPA was confirmed and 99.92% was back-extracted with 4 M nitric acid. Chemical behaviours of other elements were also almost consistent with those in the partitioning test with simulated HLLW.

Conclusion

The four group partitioning greatly contributes to the reduction of the high-level waste volume and the establishment of an advanced HLW management technology as well as the promotion of the transmutation of long-lived nuclides which contributes to the reduction of long-term burden of HLW into natural environment.

Demonstration of the four group partitioning process with real HLLW is now in progress, the effectiveness of the process will be verified and the process will be optimised for its practical utilisation.

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**ACTINIDES(III)-LANTHANIDES GROUP SEPARATION FROM NITRIC ACID USING
NEW AROMATIC DIORGANYLDITHIOPHOSPHINIC ACIDS**

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Abstract

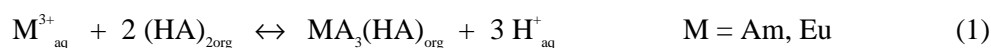
In this paper, extractants are presented which made it possible to separate actinides(III) and lanthanides from strong nitric acid solutions (0.05 - 1 mol/L). For this purpose, new aromatic dithiophosphinic acids were synthesised and characterised, and the distribution ratios of Am(III), Eu(III) and all relevant lanthanides were determined in batch extraction experiments. The extractant used was a mixture of aromatic dithiophosphinic acid + synergist in an aromatic solvent. In particular, the influence of the synergist and solvent is described. With the aid of a 12-step flowsheet it was also possible for the first time to continuously partition actinides/lanthanides at an acid concentration of 0.5 mol/L HNO₃.

Introduction

Isolation of the trivalent Am and Cm actinides from liquid high-level waste is the aim of various partitioning strategies. However, the desirable selective extraction from high-level nitric acid solutions produced by the PUREX process and containing over 30 fission products has not been possible to date. After U, Pu, Np and the majority of undesirable fission products have been separated, an actinide(III) fraction arises in all the partitioning processes so far known (e.g. TRUEX, TRPO, DIDPA and DIAMEX) [1]. The trivalent actinides are so far always accompanied by the trivalent lanthanides, which are abundantly present in HLLW, due to their comparable chemical and physical properties. Since they impair the transmutation of Am and Cm due to their high neutron absorption cross-sections, the two element groups should be partitioned again in a subsequent step. This actinide/lanthanide partitioning is still one of the most difficult operations in any partitioning process.

In the recent past, several interesting extractants have been presented in the literature for actinide/lanthanide partitioning by liquid/liquid extraction. Of particular interest are studies by Chinese scientists [2] who achieved incredibly high Am/Eu separation factors > 5000 with purified Cyanex 301.

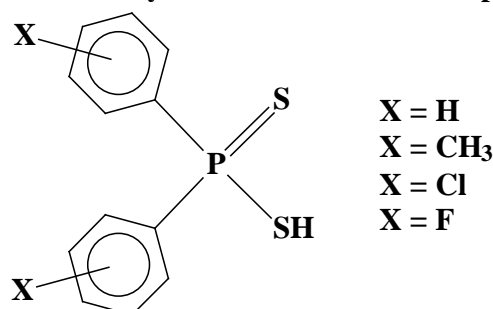
Since we have recently [3] confirmed the excellent results of Zhu et al., we considered that it would be interesting to extend our studies to the selective extraction of trivalent actinides from lanthanides using this class of sulphur-containing extractants. According to Zhu et al. the following extraction mechanism is proposed for the extraction of Am(III) and Eu(III) with Cyanex 301 (HA) where the subscripts aq and org refer to the aqueous and organic phases.



It can be seen from Equation 1 that the extraction equilibrium also depends on acid strength. Three protons are released during extraction. Since previous research on Cyanex 301 indicated that its acidity is too low and that it only becomes an effective extractant in the higher pH regions of aqueous solutions (i.e. pH > 3), it was necessary to attempt to increase the acidity of such ligands as R₂PSSHs by attaching electron-withdrawing substituents (R) so that they could extract in lower pH regions. The ideal acidity of the aqueous phase for the actinide(III) extraction should fall in the range below pH 2. Otherwise the pH value must be controlled or stabilised by a buffer during separation, especially if real waste solutions and Am(III) concentrations > 10⁻³ mol/L are involved.

Recently we have shown that aromatic dithiophosphinic acids (Figure 1) synthesised in our laboratory are more powerful extractants than Cyanex 301 and first results have already been published [4,5]. A detailed description of the synthesis and characterisation of the extractants and the experimental description of batch extraction studies are to be found in reference [6], where studies on the radiolytic stability of the new extractants are also reported, featuring high resistance to gamma radiation. The present paper describes the latest results on actinide/lanthanide partitioning with the aid of aromatic dithiophosphinic acids and, for the first time, also presents the promising results of a continuous extraction procedure.

Figure 1. Structure of the synthesised aromatic dithiophosphinic acids

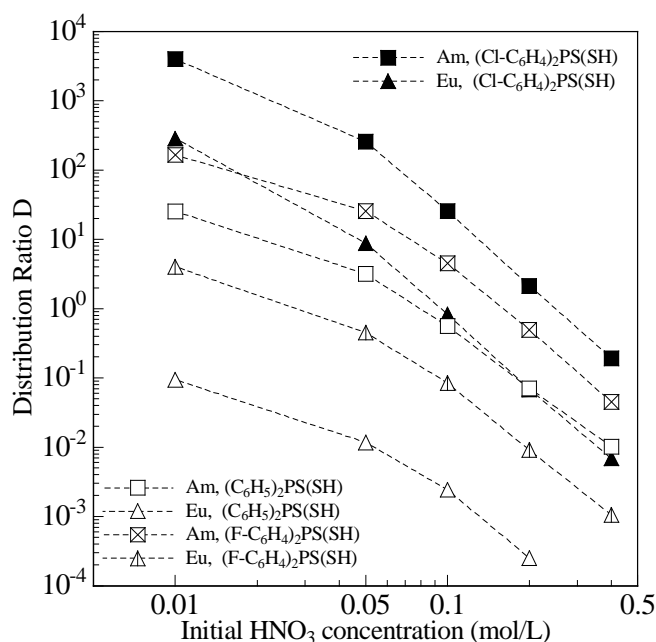


Results and discussion

Effect of the synergist

The extraction results with bisphenyl-, bis(chlorophenyl)- and bis(fluorophenyl)-dithiophosphinic acid using TBP as the synergist from 0.01 to 0.4 mol/L nitric acid are shown in Figure 2. It can be seen that the extraction ratios of Am(III) and also Eu(III) increase strongly in the order $(C_6H_5)_2PS(SH) < (F-C_6H_4)_2PS(SH) < (Cl-C_6H_4)_2PS(SH)$. However, the selectivity in the investigated acidity range decreases in the same order with Am/Eu separation factors of 230 - 280, 41 - 57 and 28 - 31. This suggests that the extraction can be improved by incorporating even stronger electron-attracting groups (such as NO_2 or two Cl groups), whereas selectivity decreases inversely. The influence of TBP and the extractant concentration on the extraction of Am and Eu has also been examined. The results of a slope analysis are reported in reference [6]. It was found that the optimum extractant concentration was 0.5 mol/L and that of the TBP synergist ranged between 0.1 and 0.25 mol/L. No extraction has been observed without TBP.

Figure 2. Extraction of Am(III) and Eu(III) with different 0.5 M dithiophosphinic acids + 0.25 M TBP in toluene from HNO_3



The influence of the synergist on the extraction of Am(III) and Eu(III) with the dithiophosphinic acid $(\text{Cl-C}_6\text{H}_4)_2\text{PS}(\text{SH})$ was studied. We tested various neutral triorganylphosphates and phosphine oxides. The results are shown in Table 1. For comparison, the data with TBP are listed in the first line of Table 1. Using mixtures of trimethyl- or triphenylphosphate + bis(chlorophenyl)dithiophosphinic acid, for example, no extraction of Am(III) and Eu(III) ($D_{\text{Am, Eu}} < 10^{-3}$) from 0.2 M HNO_3 was observed. On the other hand, we observed a selective extraction of Am(III) with a distribution ratio D_{Am} of 2 and a high Am/Eu separation factor of > 200 under the same conditions using trioctyl- or tris(2ethylhexyl)phosphate as the synergist.

Obviously, the selectivity is caused by steric hindrance. At the phase boundary, however, a white voluminous precipitate was observed, which made phase separation difficult and was presumably caused by co-extracted HNO_3 or H_2O . Therefore, no further investigations were carried out.

The best results so far have been achieved with the synergistic combination of bis(chlorophenyl)dithiophosphinic acid + trioctylphosphine oxide (TOPO). Similar results were obtained with tributylphosphine oxide (TBPO). As can be seen from Table 1, the Am(III) distribution ratios increase by approx. two orders of magnitude compared to TBP (e.g. $D_{\text{Am, TOPO}} = 152$ and $D_{\text{Am, TBP}} = 2$, respectively, for 0.2 M HNO_3) with comparable Am/Eu separation factors of approx. 30.

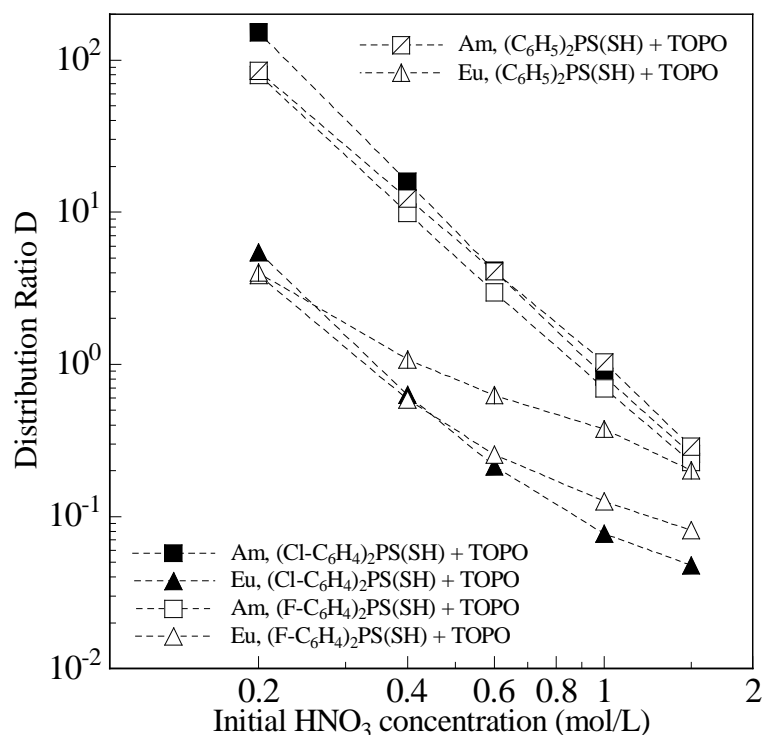
Table 1. The influence of the synergist on the extraction of Am(III) and Eu(III) with 0.5 M bis(chlorophenyl)dithiophosphinic acid + synergist in toluene from nitric acid

Synergist (0.25 mol/L)	0.2 mol/L HNO_3			0.4 mol/L HNO_3		
	D_{Am}	D_{Eu}	$\text{SF}_{\text{Am/Eu}}$	D_{Am}	D_{Eu}	$\text{SF}_{\text{Am/Eu}}$
Tributylphosphate	2.13	0.068	31.2	0.19	0.0068	28.1
Trimethylphosphate	0.0046	0.00037	12.3	0.0012	0.00056	2.3
Triphenylphosphate	0.0017	0.00022	8.1	0.00051	0.00026	2.0
Trihexylphosphate	25.54	21.25	1.2	3.25	3.31	0.9
Trioctylphosphate*	2.11	0.0088	237.9	0.165	0.0013	122.5
Tris(2-ethylhexyl)phosphate*	1.98	0.00165	1199.8	0.169	0.00072	235.1
Tributylphosphine oxide	121.07	5.89	20.5	11.54	0.588	19.6
Trioctylphosphine oxide	152.25	5.46	27.9	15.85	0.632	25.1
Cyanex 925	4.17	1.54	2.7	0.456	0.167	2.7

* precipitate formed after extraction

Figure 3 shows a comparison of the three dithiophosphinic acids + TOPO as the synergist. Surprisingly, a different pattern is found here compared to that with the synergist TBP (cf. Fig. 2). At an acid concentration of 0.2 mol/L HNO_3 the extraction results with different dithiophosphinic acids are even almost comparable to each other. This also applies to the Am distribution ratios at higher HNO_3 concentrations. However the Eu distribution ratios increase in the order $(\text{Cl-C}_6\text{H}_4)_2\text{PS}(\text{SH}) < (\text{F-C}_6\text{H}_4)_2\text{PS}(\text{SH}) < (\text{C}_6\text{H}_5)_2\text{PS}(\text{SH})$ with increasing acidity so that the selectivity also decreases in the same order (inversely for TBP).

Figure 3. Extraction of Am(III) and Eu(III) with different 0.5 M dithiophosphinic acids + 0.25 M TOPO in toluene from HNO₃



Influence of the diluent

In previous extraction studies toluene was used as the solvent because the aromatic dithiophosphinic acids are poorly soluble in nonpolar solvents such as n-dodecane. A disadvantage of toluene, however, is that it is very aggressive towards Plexiglas, the material of our mixer-settlers which will be used in the near future for the continuous counter-current tests, and therefore cannot be used.

For this reason, other aromatic hydrocarbons were tested, e.g. Plexiglas is very resistant to tert.-butyl benzene. Surprisingly, the extraction properties also changed when changing the solvent. The results are compiled in Table 2.

It can be seen that the distribution ratio D_{Am} increases with rising molecular magnitude of the solvent and that the Am/Eu separation factors also increase in the order toluene < xylene < tert.-butyl benzene < tri-isopropylbenzene. With tri-isopropylbenzene, for example, a $D_{Am} = 4.75$ and a separation factor of 30 is obtained for HNO₃ = 1 mol/L. Increasing the size and number of substituent on the benzenic ring seems to decrease the interaction between the diluent and the extractants, and consequently, let the extractant exert a more direct interaction with the M(III) ions.

Table 2. The influence of the diluent on the extraction of traces of Am(III) and Eu(III) with 0.5 M bis(chlorophenyl)dithiophosphinic acid + 0.25 M TOPO from nitric acid (without macro concentrations of lanthanides)

Diluent	HNO ₃ (mol/L)	D _{Am}	D _{Eu}	SF _{Am/Eu}
Toluene	0.5	7.19	0.306	23.5
	1.0	0.794	0.0732	10.8
	2.0	0.113	0.0329	3.4
	3.0	0.0263	0.0158	1.7
Xylene	0.5	8.83	0.385	22.9
	1.0	0.927	0.0805	11.5
	2.0	–	–	–
	3.0	–	–	–
Tert.-butylbenzene	0.5	19.18	0.615	31.2
	1.0	1.768	0.0988	17.9
	2.0	0.193	0.0393	4.9
	3.0	0.0476	0.0219	2.2
Tri-isopropylbenzene	0.5	55.8	1.23	45.6
	1.0	4.76	0.159	29.8
	2.0	0.416	0.0570	7.3
	3.0	0.106	0.0461	2.3

Distribution ratios of ²⁴¹Am and all relevant Lanthanides

Prior to the continuous counter-current experiments, the distribution ratios of all relevant lanthanides present in the feed of an An(III)/Ln(III) fraction from the DIAMEX process had to be determined. Table 3 shows the compositions of the four simulated feed solutions with different HNO₃, which were used in the subsequent extraction studies. Table 4 show the results of the extraction of ²⁴¹Am and ¹⁵²Eu and of the other Ln(III) (determined by ICP-MS) with 0.5 M bis(chlorophenyl)dithiophosphinic acid + 0.25 M TOPO in tert.-butyl benzene. The results with tert.-butyl benzene as the solvent show that the planned counter-current tests can be carried out at a HNO₃ feed concentration of about 0.5 - 1 mol/L. However, it can also be seen that the distribution ratios D_{Am} and D_{Eu} are smaller by a factor of 2 in comparison to those determined from pure HNO₃ (cf. Table 2).

Table 3. Composition of the simulated An(III)/Ln(III) feed solutions generated from DIAMEX process for the extraction tests

	HNO ₃			
	0.50 mol/L	0.99 mol/L	2.06 mol/L	3.09 mol/L
Element	Concentration in g/L determined by ICP-MS ¹⁾			
Y	0.2372	0.2345	0.2380	0.2261
La	0.7446	0.7200	0.7409	0.7064
Ce	1.4595	1.3830	1.4470	1.4070
Pr	0.6832	0.5993	0.6715	0.6447
Nd	2.4823	2.4550	2.4948	2.4045
Sm	0.4806	0.4685	0.4796	0.4603
Eu	0.0939	0.0878	0.0907	0.0900
Gd	0.0751	0.0765	0.0813	0.750

¹⁾ rel. Error ± (4-10)%

Table 4. Extraction of Am(III) and lanthanides(III) with 0.5 M bis(chlorophenyl)dithiophosphinic acid + 0.25 M TOPO in tert.-butylbenzene from simulated An/Ln feed solution.

	HNO ₃							
	0.5 mol/L		1.0 mol/L		2.0 mol/L		3.0 mol/L	
Element	D _{M(III)}	SF _{Am/Ln}	D _{M(III)}	SF _{Am/Ln}	D _{M(III)}	SF _{Am/Ln}	D _{M(III)}	SF _{Am/Ln}
Y	0.325	36.7	0.0384	43.6	<0.0005	-	<0.0004	-
La	0.254	46.9	0.0353	47.4	0.0053	33.8	0.0015	29.2
Ce	0.551	21.6	0.0741	22.6	0.0060	29.8	0.0025	17.0
Pr	0.527	22.6	0.0844	19.9	0.0135	13.3	0.0044	9.8
Nd	0.296	40.3	0.0527	31.8	0.0099	18.1	0.0031	14.2
Sm	0.373	31.9	0.0672	24.9	0.0099	18.0	0.0039	11.2
Gd	0.303	39.4	0.0515	32.5	0.0082	21.8	0.0026	16.3
Eu	0.357	33.4	0.0688	24.4	0.0122	14.8	0.0066	6.6
¹⁵² Eu	0.352	33.8	0.0931	18.0	0.0377	4.8	0.0216	2.0
²⁴¹ Am	11.926		1.677		0.180		0.0436	

Determination of the M(III) Transfer Kinetic

In order to obtain information about the transfer kinetics of the dithiophosphinic acid/TOPO/tert.-butyl benzene and An(III)/Ln(III) feed simulate extraction system, the dependence on the mixing time (0.5 - 12 min) was determined. After mixing, both phases were immediately separated by centrifugation at 4200 rpm (1 min), aliquots were sampled and analysed by γ -spectrometry. Table 5 shows the results of the simple kinetics studies. It can be seen that the equilibrium state is only obtained after 10 min mixing time.

Table 5. Am(III) and Eu(III) extraction kinetics for 0.5 M bis(chlorophenyl)dithiophosphinic acid + 0.25 M TOPO in tert.-butylbenzene from simulated An(III)/Ln(III) feed solution (0.5 M HNO₃)

Contact time (min)	D _{Am}	D _{Eu}	SF _{Am/Eu}
0.5	0.795	0.184	4.3
1	1.55	0.263	5.8
2	1.64	0.316	5.2
5	4.31	0.357	12.1
6	7.21	0.352	20.2
10	9.66	0.380	25.4
12	9.18	0.392	23.4

Continuous An(III)/Ln(III) Separation with the aid of Centrifugal Extractors

An 8-stage miniature centrifugal extractor battery (two batteries with four stages each) of the same design as installed at ITU, Karlsruhe, was acquired from INET Beijing, China. A first continuous extraction test was carried out for An(III)/Ln(III) separation at 0.5 mol/L HNO₃. The aim of this experiment was to determine in the first place the efficiency and hydraulic properties of the centrifugal extractors. At the same time, however, we expected that the extraction kinetics, especially of Am(III) (see Table 5), would exert a great influence on the process parameters initially determined empirically. On the basis of the results so far obtained, a flowsheet was proposed by P. Baron, CEA, France, which is shown in Figure 4.

Figure 4. Flowsheet of the counter-current test with centrifugal-contactors for the An(III)/Ln(III) separation

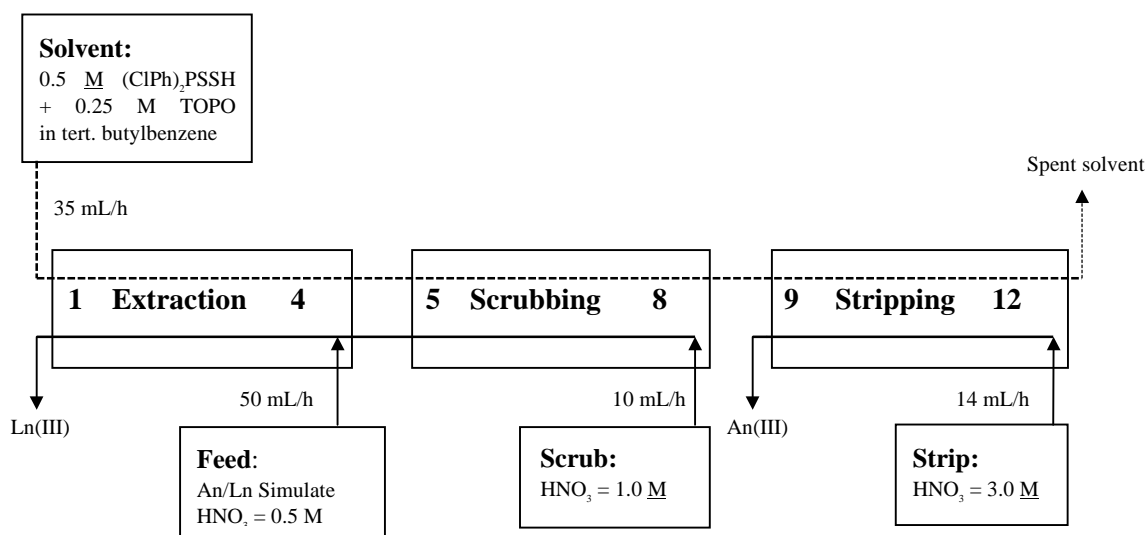


Table 6 shows the composition of the feed solution. The extraction scheme contains eight stages for extraction + scrubbing and four stages for stripping. Since only eight stages were available, however, the loaded organic phase coming from stage 8 was collected and stripping was carried out with four steps in a subsequent second test after previous cleaning of the extraction battery. The attainment of the steady state (after approx. 3 h) was checked by sampling at the outlets (raffinate stage 1, product stage 8). Subsequently, the samples were taken, the organic phase was separated from the aqueous phase by centrifuging, and aliquots were first measured with the aid of gamma spectrometry.

Table 6. Composition of the simulated An(III)/Ln(III) feed solutions generated from DIAMEX process. The HNO₃ concentration was 0.5 Mol/L

Element	Concentration (g/L)	Activity (Bq/mL)	γ-Activity (Cps/mL)
Am		²⁴¹ Am, 1850	148.912
Cm		²⁴⁴ Cm, 500	
Y	0.235		
La	0.787		
Ce	1.535	¹³⁹ Ce, 2500	75.719
Pr	0.722		
Nd	2.627		
Sm	0.517		
Eu	0.0975	¹⁵² Eu, 1850	81.638
Gd	0.0725	¹⁵³ Gd, 1850	46.377

The following main results were obtained and are summarised in Table 7. The mass balances for ²⁴¹Am, ¹⁵²Eu, ¹⁵³Gd and ¹³⁹Ce were good for the extraction and scrubbing part (100 - 103 %), less satisfactory for the stripping part (67 - 81 %). The decontamination factor DF(Am)_{raf/feed} was 28.2. In the case of Am(III)/Ln(III) separation the DFs in column 6 of Table 3 were obtained, which increase in the order Ce < Eu < Gd. As was to be expected, the extraction efficiency obtained with the aid of the centrifugal extractors was not good. The distribution ratios of ²⁴¹Am determined in stages 1 and 8, for example, were clearly (by a factor of 3 - 4) below those obtained in batch experiments. This reflects the influence of the slow extraction kinetics of Am(III). In contrast, the extraction kinetics of the lanthanides is clearly better.

The concentration profiles of the γ-active radionuclides ²⁴¹Am, ¹⁵²Eu, ¹⁵³Gd and ¹³⁹Ce are shown in Figures 5 and 6. The experiment remains to be complemented by the α-analyses for the determination of the Cm concentration profiles and the ICP-MS analyses for quantifying the inactive lanthanides. Moreover, the H⁺ concentration profile remains to be determined. Based on the results obtained here, further experiments are planned for An(III)/Ln(III) separation in the centrifugal extractors.

Table 7. Distribution ratios, mass balance and decontamination factors in the extraction-scrubbing stages obtained in the counter-current test

Element	D _{M(III)} stage1	D _{M(III)} stage 8	Extract (%) stage 8	Raffinat (%) stage 1	DF (Am/Ln)	DF (Am) raf /feed
Am	2.88	2.153	99.35	3.55		28.18
Ce	0.293	0.144	4.20	96.27	33.76	
Eu	0.208	0.134	2.32	101.20	61.24	
Gd	0.164	0.119	1.49	101.85	94.69	

Figure 5. Concentration profile of ^{241}Am , ^{152}Eu , ^{153}Gd and ^{139}Ce in the extraction-scrubbing bank

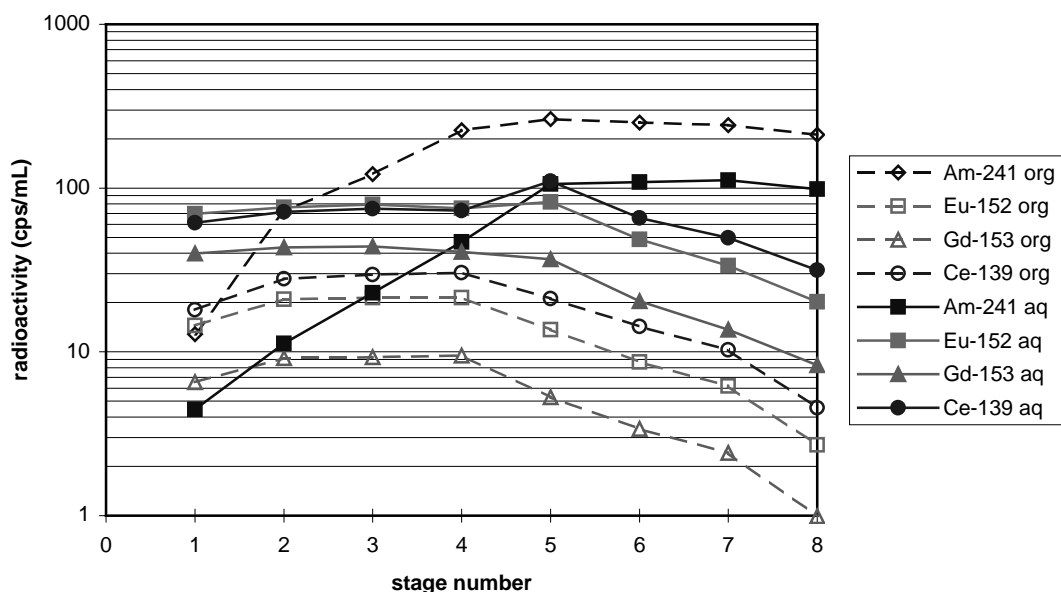
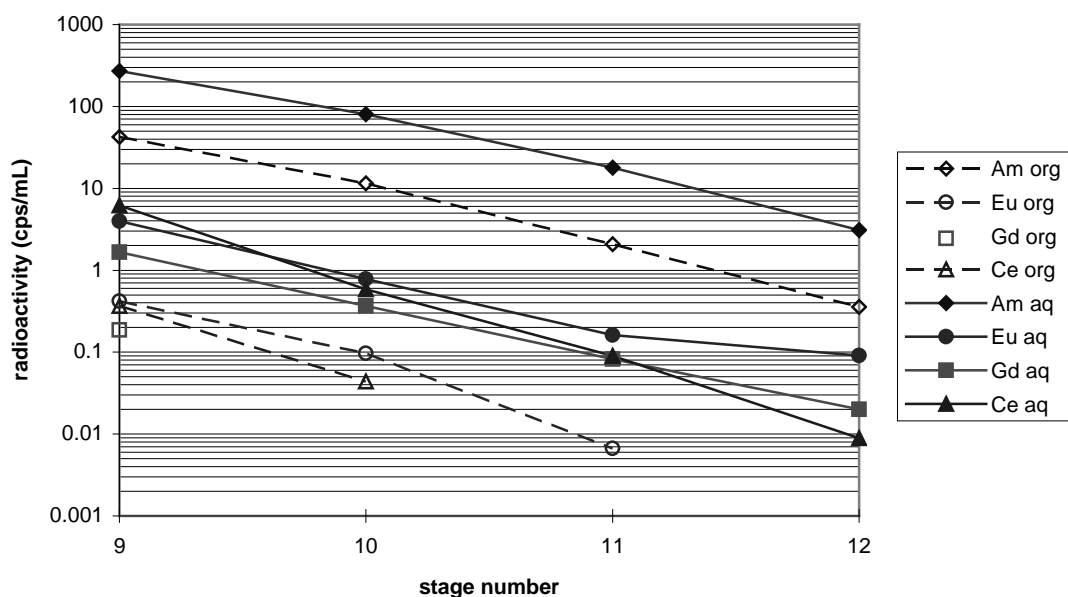


Figure 6. Concentration profile of ^{241}Am , ^{152}Eu , ^{153}Gd and ^{139}Ce in the stripping bank



Conclusions

The results of this study show that actinide(III)/lanthanide(III) partitioning is possible with high efficiency using the newly developed S-containing extractants. By variation of the synergist and solvent it is now possible to carry out group separation at 1.0 mol/L HNO_3 with Am(III) distribution ratios > 1 and Am(III)/Ln(III) separation factors > 20 . The results of the continuous test clearly show that it will be possible in future to successfully reprocess real An(III)/Ln(III)-containing process solutions arising from HLLW partitioning.

Acknowledgements

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INACTIVE DIAMEX TEST WITH THE OPTIMIZED EXTRACTION AGENT DMDOHEMA

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Abstract

In the frame of the development of the DIAMEX process, first studies including counter-current hot tests were performed, with the DiMethyl-DiButylTetraDecylMAlonamide as reference extractant. In parallel, the diamide formula has been optimised so that a new extractant was proposed: the DiMethylDiOctylHexylEthoxyMAlonamide. This new reference extractant was used in two inactive flowsheets. The performances obtained were satisfying and confirmed the choice of DMDOHEMA as the new reference extractant for the DIAMEX process

Introduction

As part of the SPIN program, the CEA has undertaken the development of the DIAMEX process, which uses diamide extractants to separate minor actinides from fission products in High Level Liquid Waste. DIAMEX is the first step of the strategy adopted and leads to the coextraction of actinides(III) and lanthanides(III). Actinide/lanthanide separation will be achieved by another specific process.

Preliminary counter-current hot tests had confirmed the feasibility of the concept with the DMDBTDMA (DiMethyl-DiButyl-TetraDecyl-MalonAmide) [1].

Then, two routes have been studied to prevent from zirconium and molybdenum extraction ; two inactive flowsheets were performed with DMDBTDMA as extractant and finally oxalic scrubbing was preferred [2].

In parallel, studies have then been undertaken to optimise the diamide formula, so that performances would be improved. Distribution coefficients of actinides and lanthanides(III) have been enhanced, third phase boundary occurs at higher acidities and metal concentrations and degradation products are shorter and then easier to manage. Two inactive tests using mixer-settlers were carried out in order to qualify the DIAMEX reference flow-sheet with the new proposed DiMethyl-DiOctyl-HexaEthoxy-MalonAmide molecule (DMDOHEMA).

The objectives of the first test were to check :

- The quantitative extraction of lanthanides (simulating actinides).
- The high values of the decontamination factors towards Zr and Mo.
- The high value of the decontamination factor towards Fe.

The objective of the second test was to study the behaviour of Ruthenium.

Flow-sheet elaboration

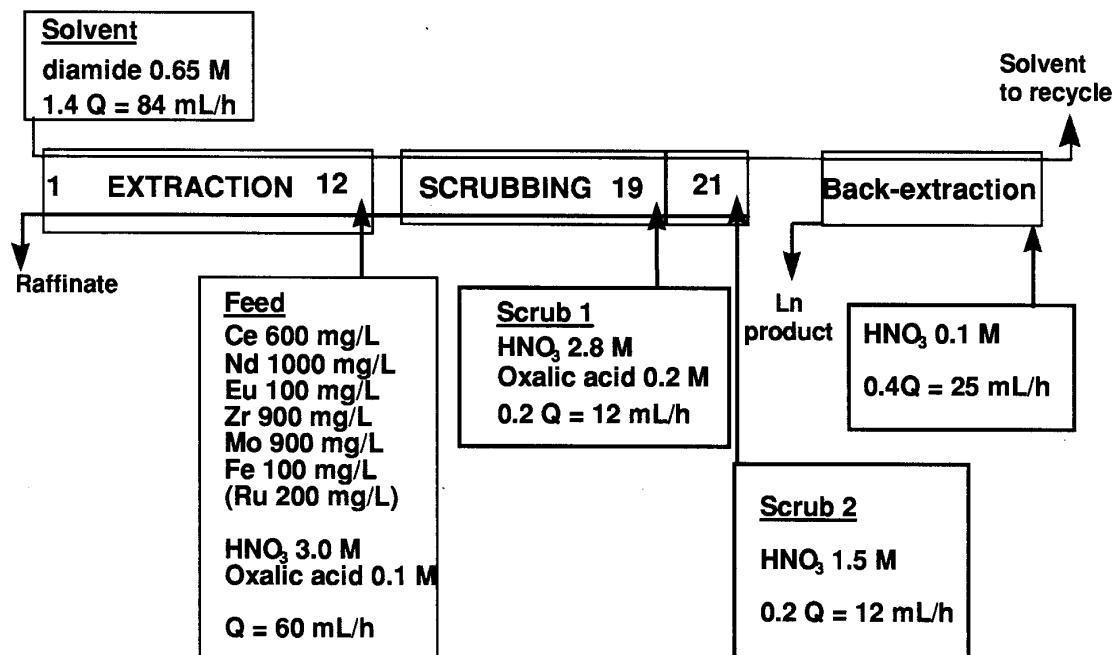
The “reference flow-sheet” was adapted to the new organic solvent, thanks to the PAREX code. The possible improvements of the “reference” flow-sheet using the DMDBTDMA were related to the better affinity of DMDOHEMA towards An(III) and Ln(III) :

- Decrease of nitric acidity in extraction and scrubbing sections (3 mol/L instead of 3.5 mol/L), to prevent from iron extraction.
- Decrease of the organic/aqueous flowrate ratio, so that solvent consumption was reduced.

In addition, concerning the stripping section, aqueous flowrate has been optimised (reduced), so that “An, Ln product” is recovered more concentrated.

The flow-sheet tested is presented in figure 1.

Figure 1 New DIAMEX flow-sheet designed for the inactive runs with DMDOHEMA



Experimental

The runs were conducted in mixer-settlers, composed of 21 stages for the “extraction-scrubbing” section and 8 stages for the back-extraction.

Hydraulic behaviour of the solvent in the mixer-settlers was satisfying for both runs.

Though, a black precipitate (probably RuO₂) occurred at the feed introduction stage, during the second run with Ruthenium. Nevertheless, this precipitate did not perturb the hydraulic behaviour of the mixer-settlers batteries.

Results of the cold runs

Both flowsheets which were similar, except the presence of ruthenium in the second one, achieved good and similar performances :

- Lanthanides extraction :
More than 98.5 % of Eu and more than 99.8 % of Nd and Ce were extracted.
- Disturbing fission products removal :
More than 99.7% of Zr and Mo were eliminated.
More than 98.1 % of Fe was eliminated.
Ru was eliminated at 79 %.
- Lanthanides pollution :
Less than 0.05 % of Zr.
0.11 % of Mo.
0.45 % of Fe.
3.4% of Ru.

Besides, experimentally measured metal ion concentration profiles were in good agreement with the calculated ones, except for iron and ruthenium, as it can be seen on figures 2 to 7 :

Figure 2 Comparison between the Experimental and Calculated Nitric acid Profiles in the Extraction-Scrubbing Section (Test 2)

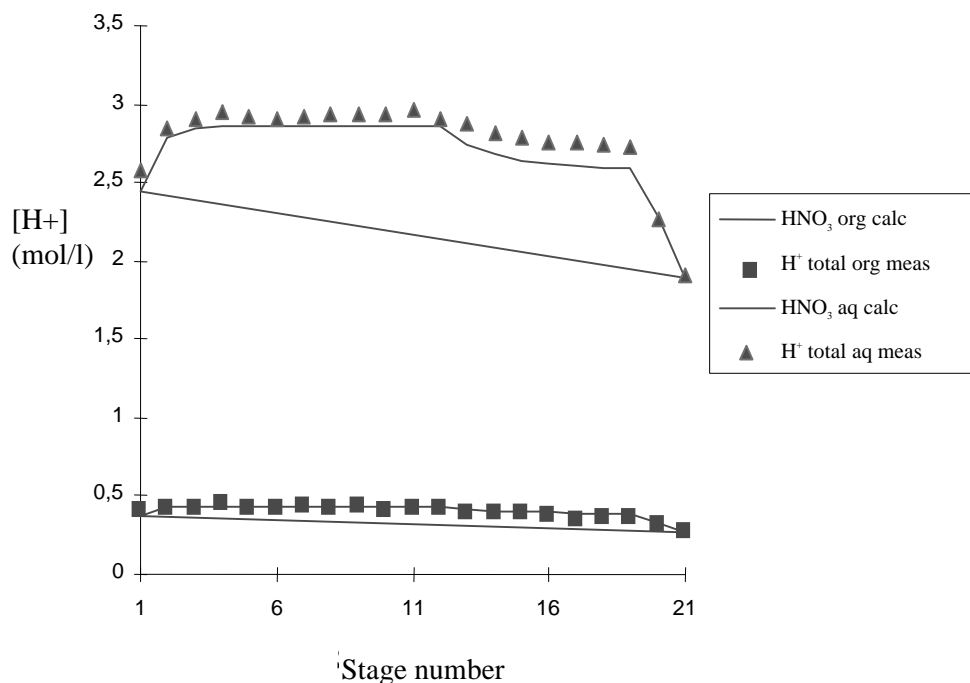


Figure 3 Comparison between the Experimental and Calculated Neodymium Profiles in the Extraction-Scrubbing Section (Test 2)

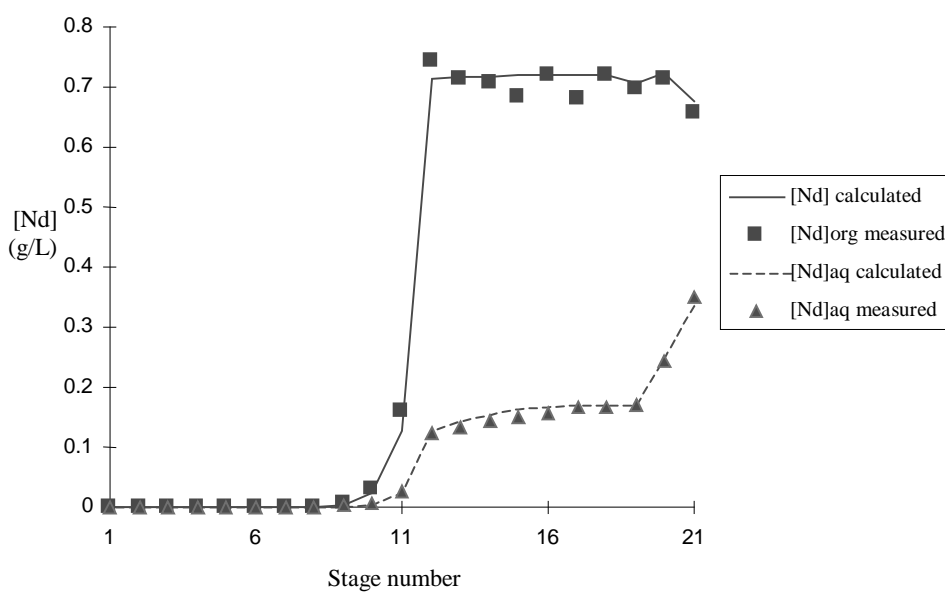


Figure 4 Comparison between the Experimental and Calculated Zirconium Profiles in the Extraction-Scrubbing Section (Test 2)

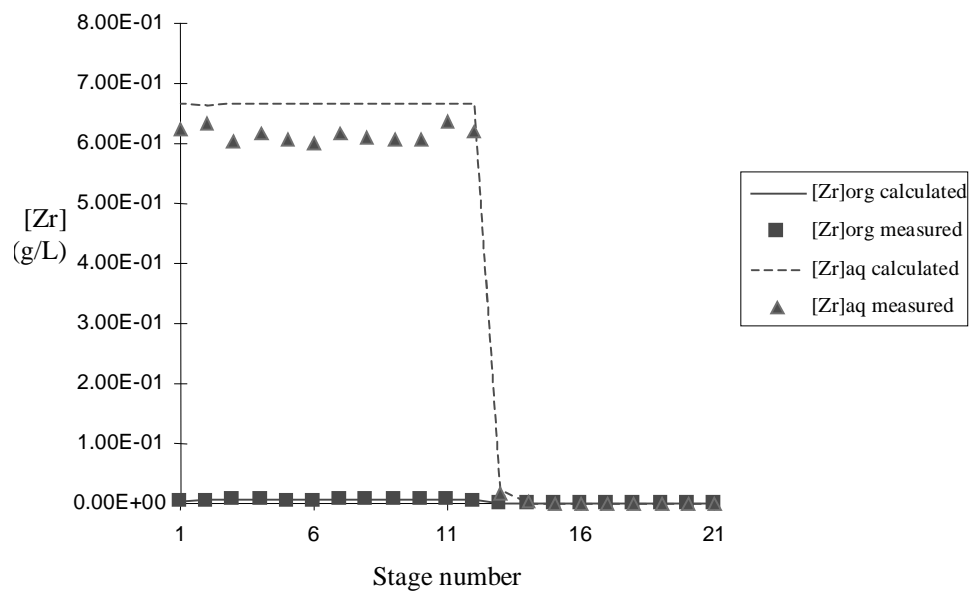


Figure 5 Comparison between the Experimental and Calculated Molybdenum Profiles in the Extraction-Scrubbing Section (Test 2)

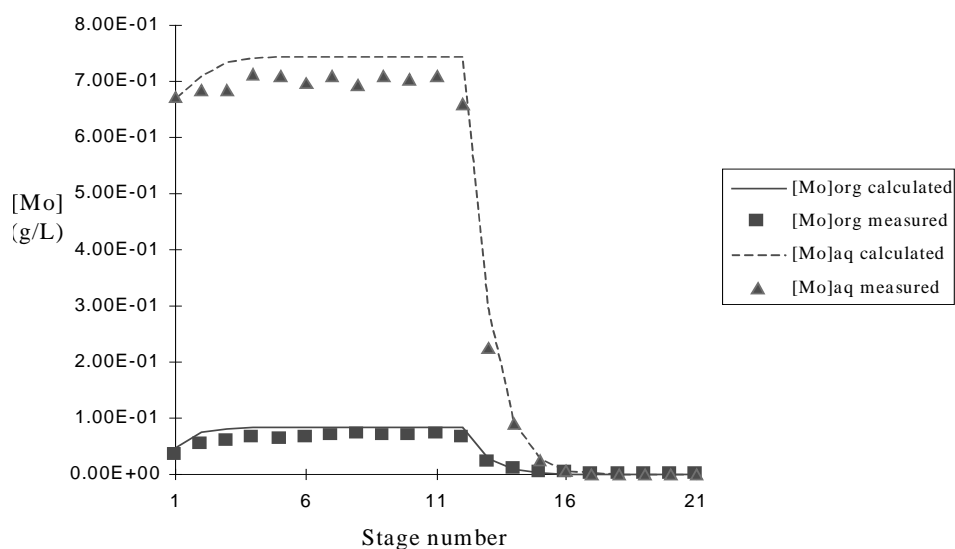


Figure 6 Comparison between the Experimental and Calculated Iron Profiles in the Extraction-Scrubbing Section (Test 2)

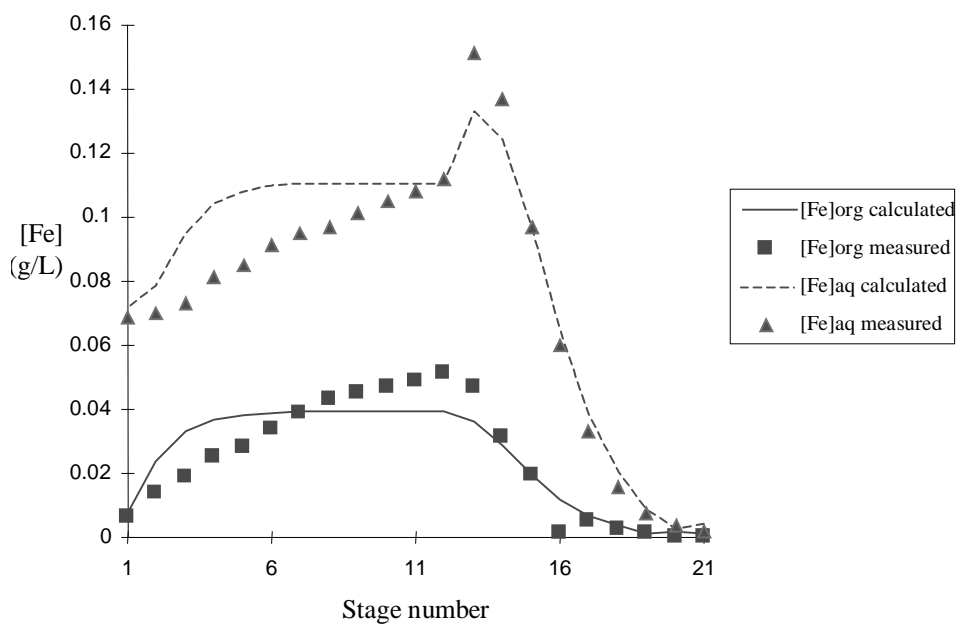
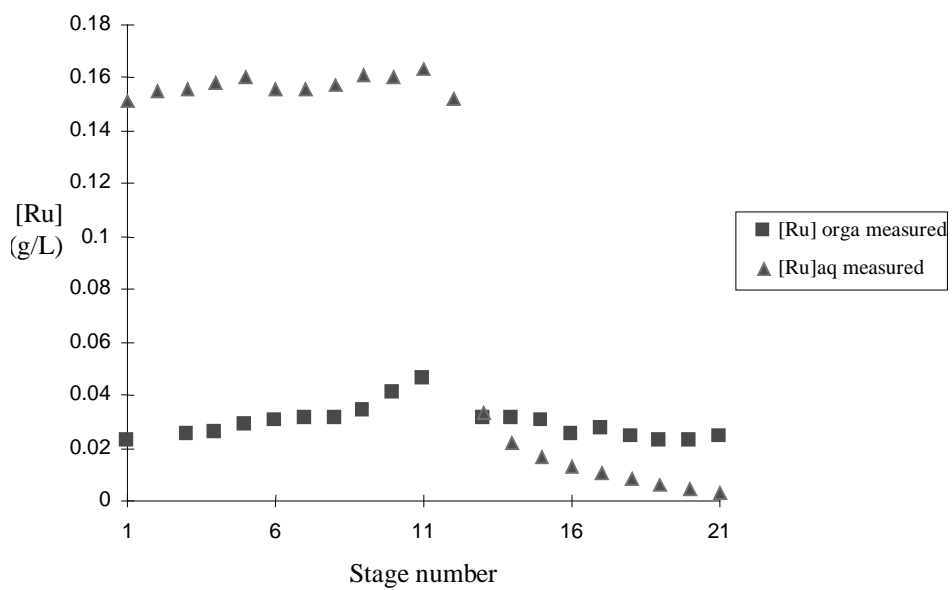


Figure 7 Experimental Ruthenium Profiles in the Extraction-Scrubbing Section (Test 2)



Conclusion

The inactive runs enabled us to confirm the choice of DMDOHEMA as a new extracting agent for the DIAMEX process, because :

- The hydrolytic behaviour was correct,
- The performances regarding lanthanides extraction were excellent and as good as those obtained with DMDBTDMA.
- The elimination of Zirconium was quantitative as with DMDBTDMA.
- The elimination of both Molybdenum and Iron was improved :
 - 99.7 % for Molybdenum (to be compared to 95 % for DMDBTDMA)
 - 98.1 % for Iron (to be compared to 27 % for DMDBTDMA)
- The efficiency to remove ruthenium was encouraging ; it is better than in the case of the run performed in the CYRANO hot cell (50 % of Ru only were eliminated in the CYRANO run, whereas 79 % of Ru were eliminated in these runs).

Nevertheless, these runs have also shown that the chemistry of Iron, and most of all that of Ruthenium, still had to be investigated and our knowledge deepened, because a good simulation of their chemical behaviour was not yet obtained for synthetic solutions.

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DEVELOPMENT OF THE SESAME PROCESS

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Abstract

The main goal of the SPIN program developed by CEA is to improve the management of high activity waste containing minor actinides and long-lived fission products. In that field, americium has been pointed out as the main hazardous element to be firstly recovered. With the aim to extract more than 99% of the americium contained in high level liquid waste (HLLW), the SESAME process, which consists in the selective extraction of oxidised Am, is foreseen as a promising way to succeed in Am management. Dealing with the americium selective recovery from HLLW, many studies concerning the electrochemical oxidation of Am to its hexavalent state in the presence of lacunary polyanionic ligands (LHPA) have been carried out. The main results of several laboratory scale tests of the SESAME process are presented and the further process development is discussed.

Introduction

As a part of the SPIN program launched by CEA, ACTINEX program is more precisely devoted to the definition of new processes for minor actinides and long-lived fission products recovery from HLLW. Among minor actinides, americium has been defined as the prior element to recover. In that field, SESAME process has been proposed to remove selectively americium from high activity liquid effluents. This process is based on the electrochemical oxidation of Am(III) to oxidation state (IV) or (VI) followed by the selective extraction of oxidised Am [1]. This process is especially interesting as it is not concerned with the actinide(III) to lanthanide(III) group separation.

Three possibilities exist to apply SESAME at the backend of the PUREX process. The simpler is the solution to treat, the easier the SESAME process is to implement. Thus, when going from SESAME A to SESAME C, the difficulty to remove Am from the solution increases. When dealing with SESAME C, many interfering elements have to be managed and Ru, Mo, Zr, Cs are the most troublesome ones for Am oxidation in the presence of LHPA.

If americium is coming from the stripping solution of DIAMEX process, many interfering elements have been removed and Am oxidation is easy to achieve.

This way corresponding to SESAME B, has been selected as the reference scheme and has been recently described². The main steps of that scheme are listed below:

- Concentration of the DIAMEX stripping solution to increase the acidity of the solution to ca $[\text{HNO}_3] = 5 \text{ M}$.
- Electrochemical oxidation of Ce(III) to Ce(IV) and extraction of Ce(IV) with TBP.
- Electrolysis of the solution after adjustment of the LHPA and AgNO_3 concentrations.
- Extraction of Am(VI) by TBP using a solvent extraction technique (centrifugal contactors).
- Recovery of the silver mediator using an electrodeposition technique (H_2O_2 is used as an antinitrite agent).

This paper is essentially focused on the R&D studies concerning the Am(III) to Am(VI) electrochemical oxidation mechanism and results dealing with the solvent extraction of Am(VI).

Electrochemical oxidation of Am(III) to Am(VI)

The electrochemical oxidation of Am(III) in nitric media is well known and has been described in several papers [1,5]. The quantitative oxidation can be carry out using complexants such as lacunary heteropolyanions which are specific for tetravalent species.

The stability constants of Am(III) and Am(IV) complexes with the relevant LHPA have been described by [6,8] and presented in Table 1.

Table 1. **Apparent stabilities of constants of 1:1 and 1:2 Am(III)/LHPA and Am(IV)/LHPA complexes in 1M nitric media**

Am + LHPA	$\log \beta_1$	$\log \beta_2$	$\log k_2 = \log \beta_2 - \log \beta_1$
Am(III) + $\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}^{10-}$	2.7±0.1	4.8*	2.1
Am(IV) + $\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}^{10-}$	19.3±0.2	22.9±0.2	3.6
Am(III) + $\alpha\text{-SiW}_{11}\text{O}_{39}^{8-}$	4.4±0.4	6.7±0.4	2.3
Am(IV) + $\alpha\text{-SiW}_{11}\text{O}_{39}^{8-}$	21.3±0.3	26.1±0.4	4.8

* extrapolate using estimated values in acid nitric concentration 2M from [4]

Those results show that Am(IV) is strongly complexed by LHPA, especially compared to Am(III). Another important result is that tungstosilicate is a stronger complexing agent towards Am than tungstophosphate. It is also of interest to note that the stability constants β_1 are much higher than constants k_2 . This fact can be explained taking into account electrostatic interactions which are important in such complexes. Indeed, constant β_1 characterises the interaction of one cation and one anion which is favourable, whereas constant k_2 characterises the interaction between two anions.

The determination of the formation constant of the complexes has permitted to determine the variation of standard conditional potential of Am pair involved as function of logarithm of LHPA concentration. According to the Nernst formula, in the case of same total concentration for both Am(IV) and Am(III), the equilibrium potential of the solution is expressed by the Eq. 1):

$$E_{eq}^{IV/III} = 2.62 + \frac{2.3.R.T}{F} \log \left(\frac{1 + \beta_1^{III} [LHPA] + \beta_2^{III} [LHPA]^2}{1 + \beta_1^{IV} [LHPA] + \beta_2^{IV} [LHPA]^2} \right) \quad (1)$$

For the Am(VI)/Am(IV) pair, same formula can be written as Eq (2):

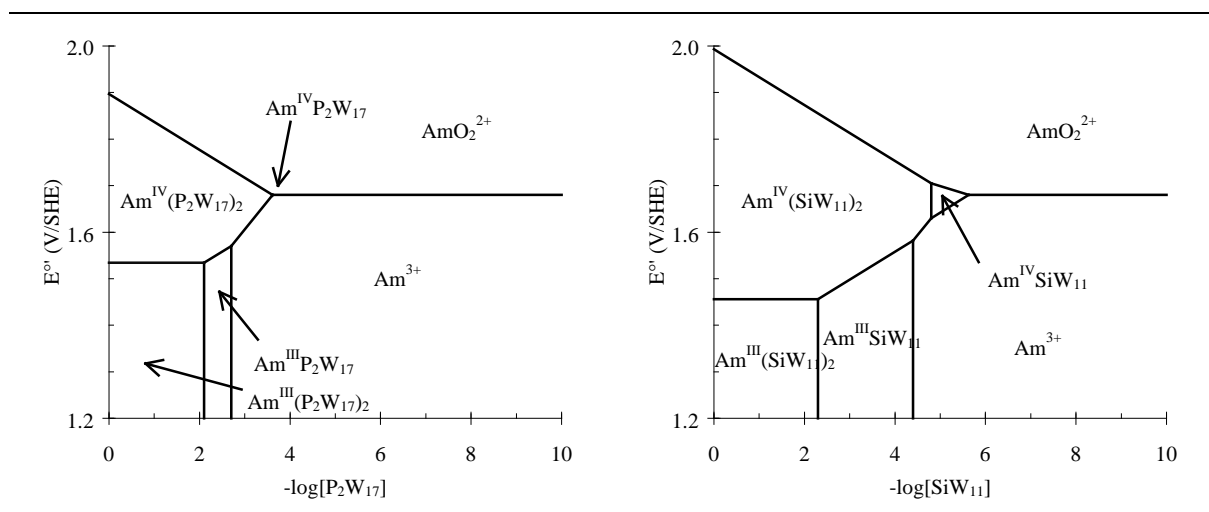
$$E_{eq}^{VI/IV} = 1.21 + \frac{2.3 RT}{2 F} \log \left(\frac{1 + \beta_1^{IV} [LHPA] + \beta_2^{IV} [LHPA]^2}{1} \right) \quad (2)$$

The potential diagram shows that the potential of Am(LHPA)₂/AmO₂⁺ pair with P₂W₁₇O₆₁¹⁰⁻ is lower than in the presence of SiW₁₁O₃₉⁸⁻ and explains that in the case of SiW₁₁O₃₉⁸⁻ it is impossible to get Am(VI) for polyanion/Am ratio higher than two. As it has been observed, the final oxidation state of Am depends on the [LHPA(total)]/[Am] ratio and on the oxidation potential.

If this ratio exceeds two, quantitative and rapid oxidation of Am(III) to Am^{IV}(LHPA)₂ is observed and, as those complexes don't get oxidised at an anode potential of less than 2.2 V/SHE, no Am(VI) is observed. For ratios below two, the final oxidation products are Am(VI) and Am^{IV}(LHPA)₂; such oxidation was obtained with a ratio R of 0.5. The evolution of the UV-visible spectrum of the solution during the oxidation process was recorded and used to estimate the evolution of Am oxidation. From these data and the balance and equilibrium equations, it was then possible to compute the speciation of Am throughout the oxidation process as shown on Figure 3.

Initial rapid oxidation of Am(III) to Am(IV)-LHPA complexes occurs, and then Am(VI) is generated. The calculated transient formation of 1:1 Am(IV) complexes was confirmed by a small peak at 560 nm in the UV-visible spectra [6]. The slow oxidation rate can be explained by the great structural change between complexed Am(IV) and the americium ion.

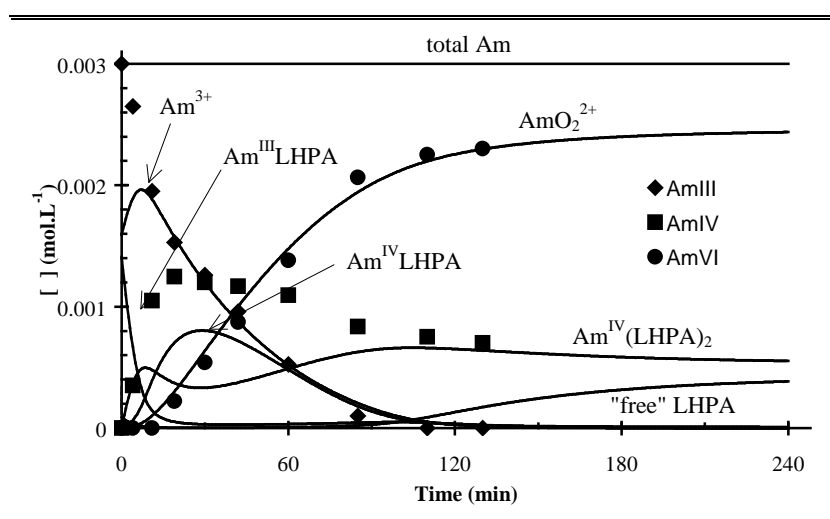
Figure 1. E-pL diagram of the standard conditional potential of Am as function of -log(LHPA) with the two LHPA : $P_2W_{17}O_{61}^{10-}$ and $SiW_{11}O_{39}^{8-}$ in 1M nitric acid



As a conclusion, quantitative Am(VI) generation is possible with both polyanions. Nevertheless, it is easier to obtain Am(IV) with the tungstosilicate and easier to reach Am(VI) with tungstophosphate.

Figure 2. Evolution of Am species during electrochemical oxidation of Am(III) with tungstosilicate and silver nitrate. ■ experimental data, — computed data.

conditions: $[Am] = 3 \times 10^{-3}$ M, $[SiW_{11}O_{39}^{8-}]/[Am] = 0.5$, $[HNO_3] = 1$ M, $j = 0.38$ mA.cm⁻², $E = 1.92$ V/SHE, $[AgNO_3] = 0.01$ M,



Solvent extraction of Am(VI)

As the process to develop is supposed to work in a continuous way, oxidised Am will essentially be recovered using a solvent extraction technique. Among the two Am oxidation states suitable for that process (Am(IV) or Am(VI)), Am(VI) is of first interest as it exists in the aqueous phase as the AmO_2^{2+} species which is not complexed with LHPA ligand in the operating conditions. So, in the case of Am(VI) recovery, a selective extraction actually occurs. Concerning Am(IV) extraction, Am has to be extracted in the form of the $\text{Am}^{\text{IV}}(\text{LHPA})_2$ complex which requires a further Am / LHPA separation steps.

To check the possibility to recover oxidised Am from fission products solution, extraction tests using a chromatographic extraction technique have been run on simulated mixtures of Am, Cm and lanthanides. The possibility to selectively recover Am(VI) from solutions with acidity ranging from 1 M to 3 M, has been validated with columns packed with silica gel loaded with HD(DiBM)P (27% wt). The treated solution was previously electrolysed in the presence of the $\text{P}_2\text{W}_{17}\text{O}_{61}^{10-}$ polyanion and silver nitrate.

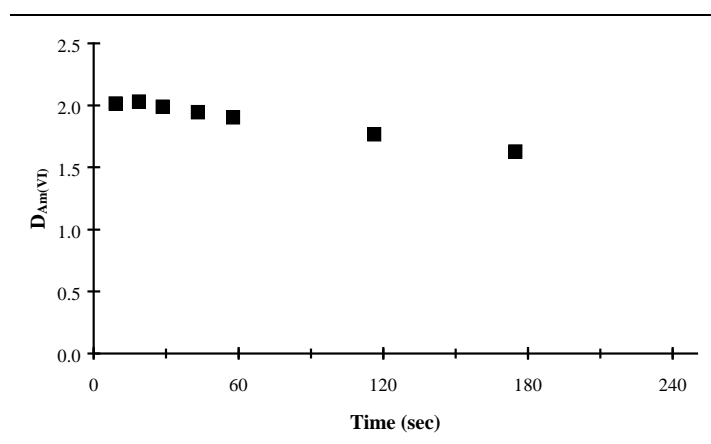
As satisfactory results have been obtained, R&D studies on Am(VI) solvent extraction have been launched.

Batch tests experiments

As our main purpose is to develop the reference process described above, Am has to be extracted from highly acidic solutions ($[\text{HNO}_3] \sim 5 \text{ M}$). In that field TBP is the most suitable molecule for the extraction of hexavalent species. In addition it is an industrially used extractant showing good stability towards radiolysis and acidic hydrolysis.

Figure 3. Kinetics of extraction of Am(VI) by TBP in 5M nitric acid

conditions: $[\text{Am}] = 3 \times 10^{-3} \text{ M}$, $[\text{HNO}_3] = 5 \text{ M}$, 30% TBP in Dodecane, $[\text{AgNO}_3] = 0.01 \text{ M}$, room temperature

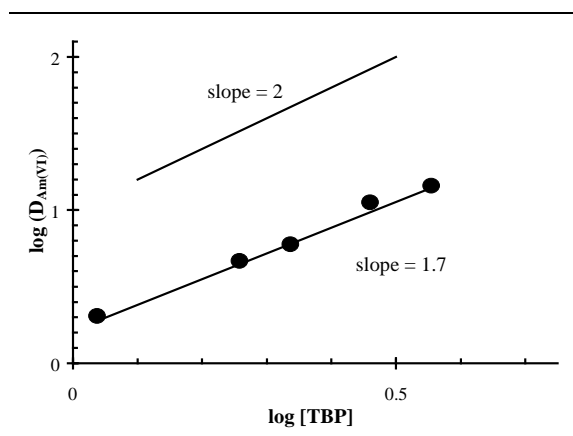


Distribution coefficients of Am(VI) have been determined in 5 M nitric acid solution for different contacting time. As shown on Figure 3, the equilibrium time is reached quickly but after 30 sec decreases slowly. This decrease is not only due to the self reduction of Am(VI) but due to the direct reduction with the solvent. These results have been confirmed during the measurement of distribution coefficient as function of TBP concentration. The logarithm representation: $\log(D_{\text{Am(VI)}}) = f(\log([\text{TBP}]))$, gives a slope of 1.7 compared to the expected slope 2 as shown on Figure 4.

The mechanism extraction of trivalent lanthanides involves three molecules of TBP per molecule of lanthanides. Therefore, as the TBP concentration increases, a diminution of the separation factor between Am and Ln(III) occurs. Thus, for the further continuous experiments a 30% v/v of TBP concentration has been chosen.

Figure 4. **Influence on the TBP concentration on distribution coefficient of Am(VI) in 5M nitric acid.**

conditions: $[Am] = 3 \times 10^{-3}$ M, $[HNO_3] = 5$ M, $[AgNO_3] = 0.01$ M, contacting time = 30 sec, room temperature



Extraction using centrifugal contactors

To confirm the possibility to extract selectively oxidised americium, a hot test has been run on a simulated Am-Cm-Ln mixture representative of a DIAMEX stripping solution [9]. During that test called SESAME 3, Am was oxidised in an electrolysis cell (both LHPA : PW and SiW have been tested) which was connected to a set of two centrifugal contactors. Once Am(III) is quantitatively oxidised to Am(VI), the solution is contacted with the organic phase (HD(DiBM)P 0.5 M or TBP 30% vol in dodecane). After two extraction stages, the aqueous phase was sent back to the electrolysis cell (the electrolysis current is not switched off during the extraction). This test was mainly performed to check the Am(VI) extraction with a liquid organic phase, so no scrubbing and stripping stages were added to the experimental set-up.

During these experimentations, the influence of the following parameters has been studied; nature of LHPA, americium concentration, nature of the extracting molecule, organic to aqueous ratio (O/A).

These tests have proved the possibility to produce Am(VI) using either PW or SiW polyanions whatever is the starting solution. Concerning the use of SiW, the oxidation kinetics of Am(III) to Am(VI) is generally slower than in the presence of PW. This confirms previous laboratory scale experiments. If americium concentration is increased (about ten times), a quantitative oxidation is still obtained. This corresponds to the treatment of a DIAMEX solution which has been concentrated as proposed in the SESAME reference scheme.

Extraction tests have demonstrated that Am(VI) extraction can be done with both selected extractants. With HD(DiBM)P the extraction kinetics of Am(VI) is much slower than with TBP, however, better separations factors between Am and Cm and trivalent lanthanides are obtained.

Concerning TBP, americium recovery yields close to 90% were reached, but due to the configuration of the set-up (no scrubbing of organic phase) an important amount of Cm(III) and Ln(III) (about 20% of initial amount) has been co-extracted with Am. This configuration of the extracting device has also brought some drawbacks such as the solubilization of organic species in the electrolyzer which prevents the americium oxidation.

Figure 5. **Extraction of Am(VI) with TBP**

conditions: *oxidation* : $[Am] = 2.6 \times 10^{-3} M$, $[HNO_3] = 4 M$, $[Ag] = 5 \times 10^{-3} M$,
 $[PW]_{free}/[Am] = 0.5T = 305 K$, $V = 250 ml$, $I = 0.5 A$, $S = 12.5 cm^2$ Pt anode (10% Ir).
extraction : TBP (30 %) / dodecane, $O = 0.8 l/h$, $A = 0.3 l/h$, $I = 2 A$ during extraction

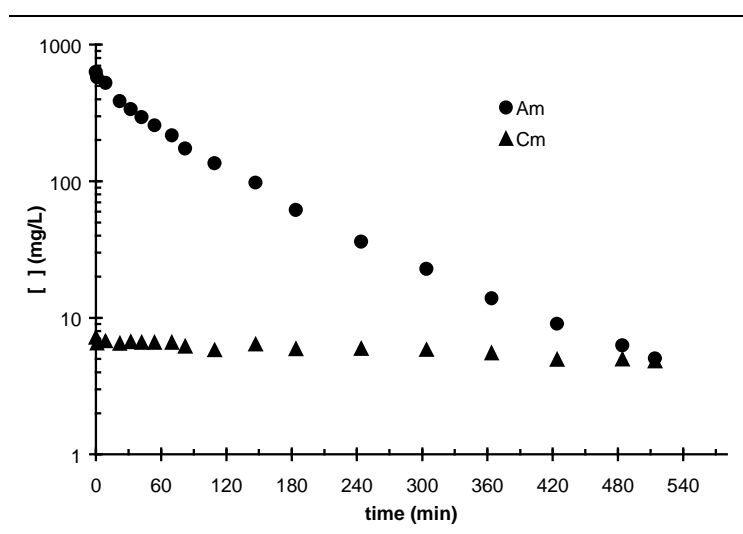


Figure 5 shows the variations of americium and curium concentrations versus time during an extraction test with TBP run on a concentrated americium solution. Am is gradually extracted from aqueous solution but the overall processing time is quite long.

Preliminary tests have confirmed the improvement of americium decontamination factor towards Cm and Ln when the loaded organic phase is scrubbed with nitric acid solution containing AgO. It was also checked that Am(VI) stripping with a reducing solution ($HNO_3 + H_2O_2$) was quite easy to achieve. Through the SESAME 3 test, the solvent extraction of Am(VI) from acidic nitric acid solutions was validated. However the tested experimental set-up did not permit to achieve the required americium recovery yields (greater than 99%). Further tests including scrubbing stages of organic and aqueous phases are planned to improve recovery yields and decontamination factors of Am. The diluent scrubbing of the aqueous phase which removes solubilized organic species coming from extraction stages is necessary to build a multistage scheme including several consecutive extraction and oxidation steps.

Further R&D Studies

Following these demonstration tests of SESAME process, more basic studies are still underway. They concern americium oxidation and extraction, LHPA removal and recycling, oxidised Am and LHPA on-line measurement, degradation and recycling of extracting molecules, recovery of silver from Am extraction raffinates. The extraction of Ce(IV) by TBP using centrifugal contactors has also been defined and successfully tested.

A new hot cell experiment using benches of centrifugal contactors is planned in the beginning of next year. It consists in the test of separation scheme including extraction, scrubbing and stripping steps. A diluent scrubbing of the raffinate will be added to enhance the electrochemical oxidation efficiency of further stages. Results of these experiments will allow to implement the separation flowsheet achieving the required performances.

Conclusion

The feasibility demonstration of SESAME principle is now achieved. Much attention is still to be paid on the extraction of Am(VI) which needs to be improved. Next hot tests should involve a more complete separation scheme as proposed in the reference scheme and take into account the main observations of SESAME 3 test. Especially, no extraction loop is expected to be used. Other studies concerning the alternative route (extraction of Am(IV)) are also underway but to a lesser extent.

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**ESTIMATION OF MATERIAL BALANCE IN PYROMETALLURGICAL
PARTITIONING PROCESS FOR TRUs FROM HLLW**

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Abstract

A pyrometallurgical partitioning process has been proposed and studied by CRIEPI. In this process, more than 98% of alkali metals were separated in a denitration step. Almost all of the another elements were converted to chlorides from oxides in a chlorination step. Separation experiments by means of multiple batch extraction was also carried out in the LiCl-KCl/Bi system, and more than 99% of each TRU was recovered. The material balance of solutes and solvents in the partitioning process was estimated from the experimental results of each step in the process. The refining salt, Cd, Bi, and Pb as solvent, Li as reductant, and generated chlorine gas can be recycled to the process. This process is, therefore, expected to generate less secondary radioactive waste in comparison with an aqueous process and should require relatively compact facilities.

Introduction

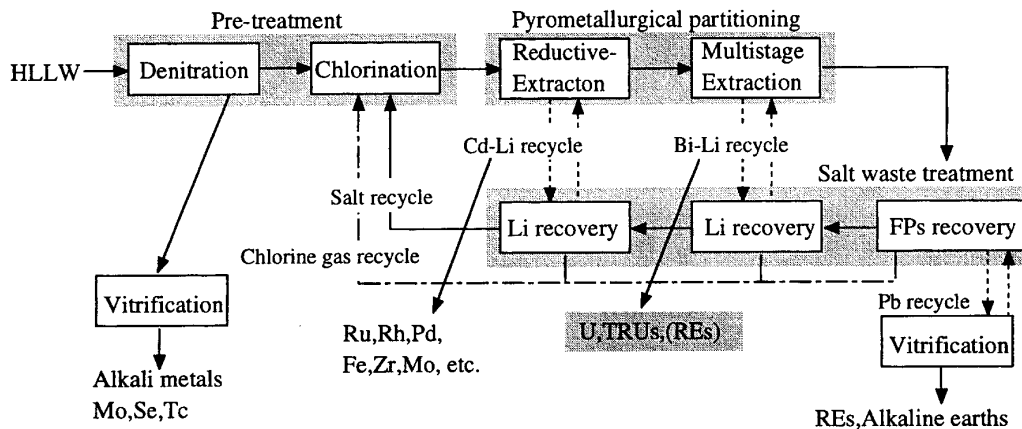
High level liquid waste (HLLW) from a reprocessing of light water reactor spent fuels contains a small amount of long-lived nuclides consisting mainly of transuranic elements (TRUs), such as Np, Pu, Am, and Cm. A pyrometallurgical partitioning process for TRUs from HLLW is expected to generate less amount of secondary radioactive waste in comparison with conventional aqueous process, and should require relatively compact facilities [1]. U and TRUs recovered from the HLLW will be blended in metallic fuels and transmuted in a fast breeder reactor.

Table 1 Composition of elements in the HLLW calculated by ORIGEN-II code with burn-up of 48 CWd/t-U in PWR and cooling time of 4 years (99.5% of U and dPu are recovered by reprocessing)

element		mol	wt.(g)	wt.%		mol	wt.(g)	wt.%		mol	wt.(g)	wt.%
uranium	U	19.73	4694	7.44								
TRUs	Np	3.02	715.5	1.13	Am	2.41	583.6	0.93				
	Pu	0.22	52.10	0.08	Cm	0.41	100.1	0.16				
fission products (FP)	Rb	5.48	473.7	0.75	Nd	39.81	5770	9.15	Ru	32.78	3346	5.31
	Cs	27.01	3646	5.78	Pm	0.32	46.27	0.07	Rh	5.59	575.3	0.91
	Sr	12.56	1119	1.77	Sm	7.78	1163	1.84	Pd	22.45	2376	3.77
	Ba	17.25	2370	3.76	Eu	1.51	231.0	0.37	Ag	1.08	117.5	0.19
	Y	6.94	617.7	0.98	Gd	1.57	244.5	0.39	Cd	1.82	202.9	0.32
	La	12.49	1736	2.75	Zr	53.34	4976	7.89	Sn	1.13	137.0	0.22
	Ce	24.08	3393	5.38	Mo	49.13	4795	7.60	Se	0.98	78.88	0.13
	Pr	11.20	1579	2.50	Tc	10.61	1050	1.67	Te	5.53	715.8	1.14
corrosion product	Fe	62.67	3500	5.55								
solvent cleaning	Na	550.24	12650	20.06								

The composition of the HLLW shown in Table 1 were based on ORIGEN-II calculations with burn up of 48 GWd/t-U in PWR and cooling of 4 years [2]. Because of the chemical similarity to TRUs and rare earth elements (REs), the separation of TRUs from REs is considered to be difficult. The target of the pyrometallurgical partitioning process is to recover more than 99% of each actinide contained in HLLW in a product where the weight ratio of TRUs to REs is more than one [1]. The flow diagram of the pyrometallurgical partitioning process is illustrated in Figure 1. It consists of denitration, chlorination, reductive-extraction, countercurrent extraction, and salt waste treatment process.

Figure 1. Pyrometallurgical partitioning process



The objective of this paper is to propose the pyrometallurgical partitioning process with estimated material balance of solutes and solvents. The material balance is estimated by use of the distribution coefficient of each element measured in the LiCl-KCl/Cd, Bi, and Pb system [3,4,5,6] and the amount of solvents in each process decided by the previous experiments.

Concept and experimental results for the partitioning process

Denitration process

The elements except for alkali metals in the HLLW are converted from nitrates to oxides with generating H₂O and NO_x gas at 773K at the denitration process. The experimental result for denitration used non-radioactive elements is shown in Figure 2 [7]. More than 98% of each alkali metal were separated by water rinse method because alkali nitrates which were soluble in water did not convert to oxides at 773K. Rb and Cs are FPs, and Na is originated from solvent cleaning materials. About 3% of Sr and 1% of Ba also remained as nitrates and were separated in this process. More than 60% of Mo, 80% of Se, and 98% of Re which substituted for Tc, were converted water-soluble complex oxide with alkali metals and were also separated from other oxide elements in this process.

Figure 2. Mass balance in denitration

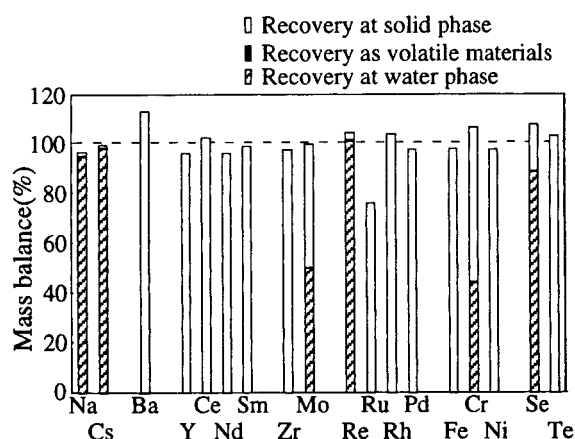
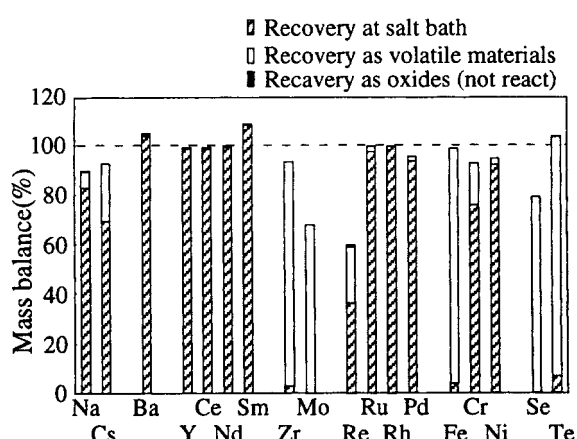


Figure 3. Mass balance in chlorination



Chlorination process

The oxides generated at the denitration process are mixed into LiCl-KCl salt and are converted to chlorides under Cl₂ gas flow at 973K at the chlorination step. The experimental result for chlorination used non-radioactive elements is shown in Figure 3 [8]. More than 99% of REs, alkaline earths, and Rh, and 97% of Ru and Pd were converted to chloride at this process. More than 95% of Fe, Zr, Mo, Te, and Se, however, evaporated at this process. They were captured into a LiCl-KCl molten salt bath maintained the temperature at 700K. The experimental result for Fe, Zr, and Mo is presented in Table 2 [9]. The salt bath with captured chlorides will be returned to the reductive-extraction process.

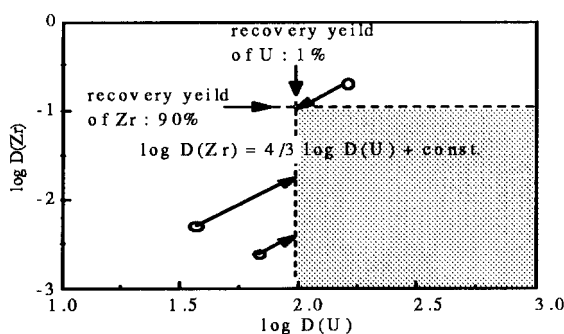
Table 2. Recovery yield of volatile chloride at molten salt trap

	MoC15	ZrC14	FeC13
Initial amount (mg): A	195	198	206
Amount remained as oxide (mg): B	67	192	142
Recovery at molten salt trap (mg): C	133	50	53
Recovery behind molten salt trap (mg): D	0.6	0.1	0.3
Recovery yield (%): C/(C+D)	99.6	99.8	99.5
Mass balance (%): (B+C+D)/A	103	123	95

Reductive-extraction process

The FPs which are more noble than U are extracted into Cd phase by use of Li as reductant in LiCl-KCl/Cd system at 773K to 823K [10]. The purpose of this process is to remove as much of these FPs as possible from the salt while carrying less than 0.1% of each TRU into the Cd. Fe, a corrosion product, is also extracted into Cd. These elements are expected to separate from U easily from the estimation by use of free energies of formation in LiCl-KCl. Some part of U was, nevertheless, extracted into Cd when some part of Zr and Fe still remains in the salt phase in previous tests [10]. It assumed that the solubility of U in Cd decreased and U formed intermetallic compound in Cd with Fe and Zr. Figure 4 shows the experimental results of distribution of U and Zr between LiCl-KCl and Cd. This figure shows more than 90% of Zr and less than 1% of U can be extracted into Cd on the assumption that Zr is tetravalent and U is trivalent chloride in the salt.

Figure 4. Relationship between distribution coefficients of U and those of Zr at reductive-extraction process (O : experimental data in LiCl-K Cl/Cd at 723 K)



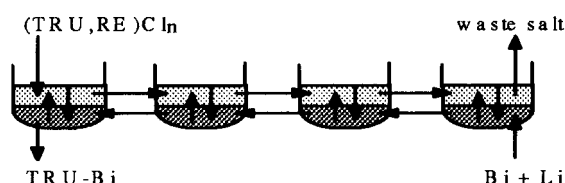
The elements extracted into the Cd are recovered as metal form waste by means of a distillation of the Cd. The Cd is collected and reused in this process. The salt phase which includes U, TRUs, REs, alkaline earth elements, and some part of Zr are processed in the countercurrent extraction process.

Countercurrent extraction process

U and TRUs are extracted into Bi phase and are separated from FPs by the difference between the distribution coefficients of actinides and that of FPs in molten LiCl-KCl and liquid Bi system at 773 K. For greater than 99% of TRUs to be recovered in a single step reductive-extraction, most of

the REs would accompany the TRUs. This separation criteria, therefore, are expected to be achieved by means of a countercurrent extraction. The concept of a countercurrent extraction process shows in Figure 5. The salt contained TRUs and REs is put into the first stage as salt phase. Liquid Bi-Li alloy is put into the last stage as metal phase. The salt phase and the metal phase are transferred to the next stage after equilibrium condition attained.

Figure 5. Concept of counter current extraction system



It is assumed for this estimation that each element can be treated as the dilute solution in salt phases and doesn't form intermetallic compounds in Bi phases. The separation factor (SF) measured between LiCl-KCl eutectic salt and liquid Bi at dilute concentration can be used for the simulation study under the above condition. SF of metal "M" is defined as follows:

$$SF_M = D_M / D_{Nd} = [X(M) / Y(M)] / [X(Nd) / Y(Nd)] \quad (1)$$

In this equation, D_M means distribution coefficient of M, and $X(M)$ and $Y(M)$ mean mole fraction of MCl_n in the salt and that of M in Bi phase, respectively. The separation factors are shown in Table 3 [3, 4]. Figure 6(a) and Figure 6(b) shows the calculated recovery yield of U and TRUs and that of REs, respectively, in case that 99% of Am were recovered in 2 to 5 stages countercurrent extraction. Figure 7 shows the weight ratio of recovered TRUs to REs calculated in case that 99.9% of Am was recovered is 3.08, which fully satisfied the requirement for the fabrication of metallic fuel.

Table 3. Separation factor of U TRUs, and REs to Nd measured in LiCl-KCl/Bi system at 773 K

	ref.(4)	ref.(3)
U	0.00065	0.0011
Np	0.0051	0.012
Pu	0.0076	-
Am	0.015	-
Nd	1.0	1.0
Pr	-	0.99
Ce	-	0.89
La	-	2.7
Gd	-	11
Y	-	630

The recovered TRUs are separated from Bi and will be transmuted in a metallic fuelled FBR. Bi is reused in this process and the salt contained REs and alkaline earth elements are processed in a salt waste treatment process.

Figure 6. Recovery of (a) U and TRUs (b) REs calculated in case of 99.9% of Am recovered using counter current extraction in LiCl-KCl/Bi system at 723 K

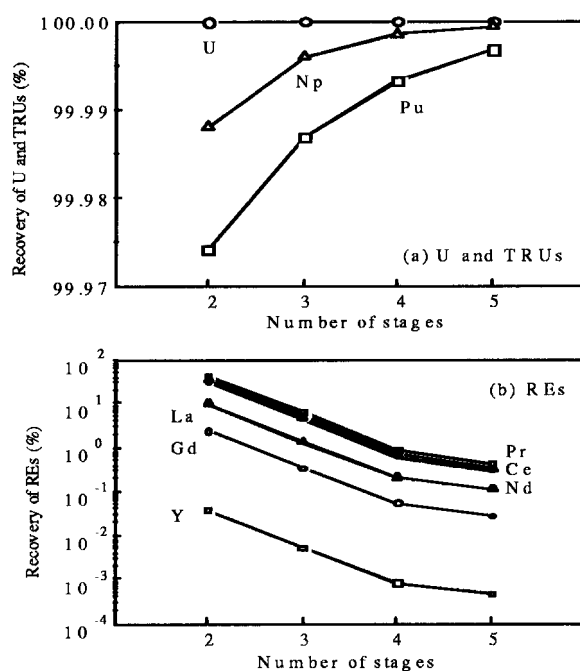
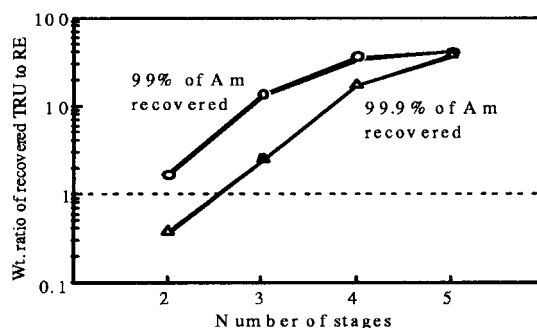


Figure 7. TRUs/REs wt. ratio calculated in case of 99% or 99.9% of Am recovered using counter current extraction in LiCl-KCl/Bi system at 723 K



Salt waste treatment process

The salt with FPs is treated at salt waste treatment process to minimise the amount of disposal LiCl-KCl solvent as waste. REs, alkaline earths and alkali elements included in the salt from the countercurrent extraction process are extracted into Pb anode by electrolysis in this process. The separation between Li and FPs is considered difficult, because the free energy of formation of Li chloride is close to that of alkali and alkaline earth FPs. Separation factors of FPs to Li in LiCl-KCl/Pb system at 723K are shown in Table 4 [5]. The amount of Li accompanied FPs increases with an increase in the amount of FPs recovered into Pb anode. Some part of alkali and alkaline earth FPs are, therefore, expected to recycle with LiCl-KCl in order to minimise the amount of disposal Li as waste. The metals recovered into Pb anode are converted to oxides at 1073 K with B₂O₃ under air flow condition and then are vitrified. Pb metal does not convert to oxides in this treatment [11] and is reused in this process.

Table 4. Relationship between distribution coefficient of alkali metals and divalent elements and that of Li measured in LiCl-KCl/Cd, Bi, or Pb system

$$\log D(M) = a \log D(Li) + b$$

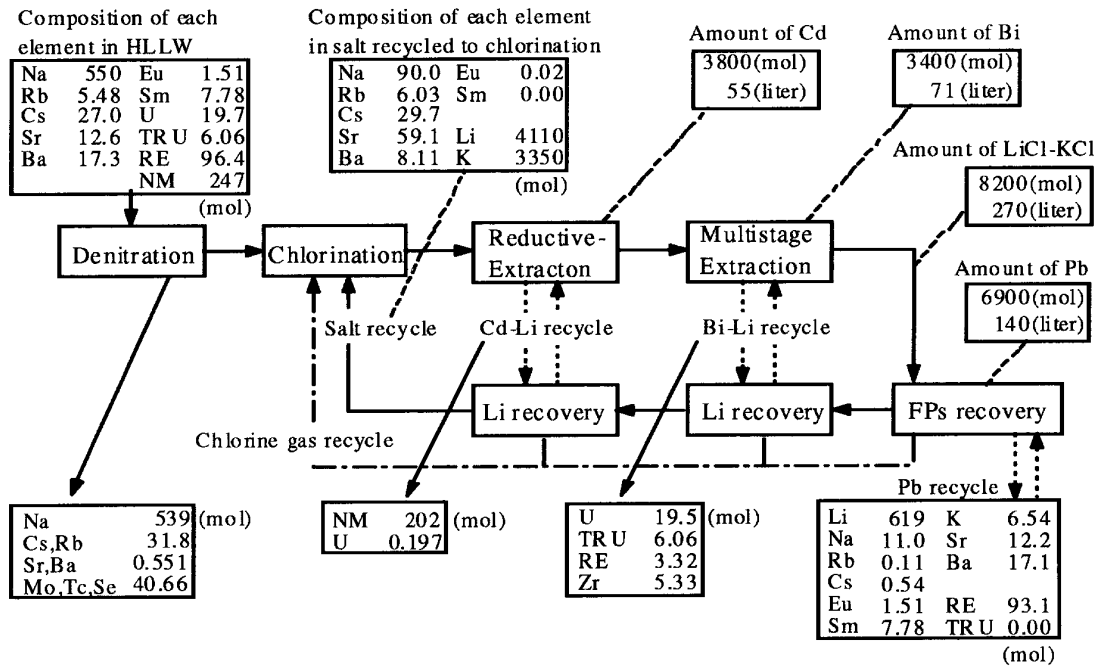
	LiCl-KCl/Cd (773K)			LiCl-KCl/Bi (773K)			LiCl-KCl/Pb (723K)		
	b	a	ref.	b	a	ref.	b	a	ref.
Sm	-2.57	1.88	(3)	-3.60	1.96	(3)	-3.14	2	(5)
Eu	-2.16	1.99	(3)	-2.76	1.96	(3)	-2.48	2	(5)
Ba	-0.93	2.07	(3)	-2.28	1.91	(3)	-1.74	2	(5)
Sr	-0.45	1.93	(3)	-1.07	1.87	(3)	-0.90	2	(5)
Na	0.72	1	(11)	-	-		0.10	1	(5)
K	3.57	1	(11)	0.80	1	(11)	1.88	1	(5)
Cs	-	-		-	-		0.91	1	(5)

Reductant Li for the reductive-extraction process and for the countercurrent extraction process is also recovered by electrolysis into Cd anode and Bi anode, respectively. Alkali and alkaline earth FPs also recovered into Cd or Bi with Li in accordance with their separation factor shown in Table 4. Chlorine gas and LiCl-KCl refined with small part of alkali and alkaline earth elements generated in this process are recycled to the chlorination process.

Estimation of material balance

The process flow with material balance is shown in Figure 8. The values of amount for each element in this figure are estimated in case that about 500 litre of the HLLW generated from PUREX process for 1 ton-U of PWR fuel is treated as 1 batch in the pyrometallurgical partitioning process which is reached the steady condition.

Figure 8. Material balance in pyrometallurgical partitioning process



Material balance of products and wastes

The product is recovered at countercurrent extraction process and the wastes are generated from denitration, reductive-extraction, and salt waste treatment process. The recovery yield of each element in each step is shown in Table 5. It is assumed that all of oxides are converted chlorides at the chlorination process and vaporised chlorides are recovered completely and transferred to the reductive-extraction process.

Table 5. Experimental recovery yield of each element at each process in pyrometallurgical partitioning

	Ru, Mo Rh, Pd	Se (Tc)	Re (Tc)	Fe (Tc)	Zr	Te	Cd	U TRU	RE	Ba, Na, Sr Rb, Cs
Separation at denitration		60	85	98						<3 >98
Volatile at chlorination	(2)	(40)	(15)	(95)	(97)	(100)	(40)			(<1) (<1)
Separation at reductive-extraction	100	40	15	2	100	>90	100	<1		
Recovery from multistage extraction						<10		>99 >99	<10	
Separation at salt waste treatment								<1	>90 >97	<2

It is expected that more than 99.9% of U and TRUs are separated from FPs by 3 stages' countercurrent extraction. The weight ratio of recovered TRUs to REs is 3.08 in case that 99.9% of Am was recovered, which fully satisfied the requirement for the fabrication of metallic fuel. It was assumed that 10% of Zr remained in salt phase in the reductive-extraction process and it is recovered into Bi with U and TRUs.

The waste from denitration process contains alkali nitrates, complex oxides of Tc, Mo, Se with alkali metals, and small part of alkaline earth nitrates, which are vitrified after oxidation. The waste from reductive-extraction process consists of 1% of U, 90% of Zr and the all of metals more noble than Zr, which are disposed of as metallic form waste, or are oxidised and vitrified. The another waste with REs, alkaline earths, and alkali metals in Pb alloy from salt waste treatment process are oxidised, separated from Pb, and vitrified.

Amount of salt and metal solvents

Amount of LiCl-KCl in the pyrometallurgical partitioning is estimated about 450 kg, 270 litre in order that the total concentration of U, TRUs, and REs is less than 1.5 mol% in the salt phase of the 1st stage in the countercurrent extraction process. In this condition, the concentration of each element of U, TRUs, and REs is less than 0.5 mol%, which is similar condition of previous separation test [4] and is low concentration enough for the simulation by use of the distribution coefficients measured in dilute system [12]. The total concentration of all solutes is about 7.1 mol% in the salt phase after the chlorination in this case. The concentration of the solutes affects the volume of the salt phase and the size of the facility. For the operation at higher concentration of the solutes, melting point and viscosity of the salt and distribution coefficients of each element in the system have to be obtained.

Amount of Pb in the salt treatment process is estimated about 1 400 kg, 140 liter in order that the concentration of REs and alkaline earth metals extracted into Pb by electrolysis is less than 10 mol% which is attained in previous study [11]. To decrease the amount of Pb causes to make the facility compact, but requires to extract REs and other FPs into Pb with higher concentration by electrolysis. It is assumed that 100% of Pb can be reused in this process after removal of FPs in this estimation.

Amount of Cd in the reductive-extraction process is estimated about 430 kg, 55 liter in order that the concentration of noble FPs, such as noble metals, Mo, Fe, Zr and so on, extracted into Cd is less than 5 mol%. The concentration of FPs in the reductive-extraction process affects that of reductant extracted into Cd by electrolysis. The concentration of the reductant in Cd is about 14.6 mol% in the case of the concentration of FPs is 5 mol% in Cd. This is expected to obtain because Cd-Li alloy including 20 mol% of Li could be made in previous study [13]. It is assumed that 100% of Cd can be reused in this process after distillation in this estimation.

Amount of Bi in the countercurrent extraction process is estimated about 710 kg, 71 liter in order that the concentration of U, TRUs, and REs in Bi is less than 1 mol%. It is expected that no intermetallic compounds are found in Bi phase for steady operation of the countercurrent extraction process. The solubility of REs in Bi at the multi-elements system become significantly smaller than those in the binary system [12]. When the total concentration of them is less than 1 mol%, intermetallic compounds seemed not to be formed [12]. The concentration of reductant extracted into Bi by electrolysis is less than 3 mol% in this case. It is assumed that 100% of Bi can be reused in this process after separation of U and TRUs in this estimation.

Amount of chlorine gas generated from three different electrolysis in salt waste treatment process is estimated about 12.8 m³ which is reused in chlorination process.

Amount of FPs in the recycled salt

The salt solvent is recycled in the pyrometallurgical partitioning process to reduce the secondary waste. The concentration of each alkali and alkaline earth FP in the recycled salt decreases with an increase in the amount of Li extracted into Pb with FPs, but the excess amount of Li to be fed vitrification becomes the secondary waste. Some part of alkali and alkaline earth FPs is, therefore, remained in the recycled salt to minimise the amount of disposal LiCl-KCl solvent as waste. A typical vitrified product of HLLW contains 3 wt.% of Li₂O and 10 wt.% of FPs oxides [14]. It can be considered that no Li is generated from the partitioning process as a secondary waste, in the case that the amount of Li extracted into Pb is less than 3/10 by weight of amount of FPs. In this estimation, 12.8% of Li is extracted into Pb with other FPs and same amount of Li is added as LiCl.

Summary

The material balance in pyrometallurgical partitioning of TRUs from HLLW was estimated by use of distribution coefficients measured in LiCl-KCl/ Cd, Bi or Pb. When 99.9% of Am was recovered, the weight ratio of recovered TRUs to REs was estimated 3.08 at 3 stages' countercurrent extraction between LiCl-KCl and Bi, which was enough for metallic fuel fabrication. The waste generated as three different forms. There were alkali nitrate and complex oxide of Tc, Mo, and Se with alkali from denitration process, noble metals from reductive-extraction process, and REs and alkaline earth as Pb alloy from countercurrent extraction process.

Amount of solvents were estimated by using previous experimental conditions. 270 liter of LiCl-KCl eutectic salt, 55 liter of Cd, 71 liter of Bi, and 140 liter of Pb are used in the pyrometallurgical partitioning process. It was found that almost all of them including chlorine gas and reductant could be recycled, and Li disposed at salt treatment process becomes one of the matrix composition of glass form. Less secondary waste, therefore, will be generated in comparison with aqueous process and should require relatively compact facilities.

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MOLTEN SALT REACTOR TECHNOLOGY FOR PARTITIONING & TRANSMUTATION AND HARMONISATION OF THE FUTURE NUCLEAR FUEL CYCLE

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Abstract

The most important developments regarding the available options to reduce actinide inventory will be discussed.

The relation between necessary single cycle transmuted fraction, fuel cycle processing losses and total losses to waste will be defined. An attempt is made to arrange the possible systems on order performance with regard to their potential to reduce the actinide inventory and actinide losses to wastes.

The objective of this paper is to illustrate clearly the potential advantages of molten salt fluoride based reactor technology integrated with innovative processing methods including reductive extraction, electro-refining and electro-deposition relative to traditional ones.

Also, this contribution aims to review the status of molten salt reactor technology, (including Russian experience), to evaluate the importance of remaining uncertainties and to identify the additional work needed.

Introduction

It is evident that the successful solution of the separation & transmutation (S&T) problems may be reached in the most natural way if the fuel is in the molten or gaseous phases for the on-line combination of the reactor and fuel processing plants. These systems could be used to consume TRU with high burnup and minimum handling, without need to repeatedly separate, purify and prefabricate TRU. Operating only at safe location with minimum TRU shipments they would function as near ideal sink for TRU which, once added, could not be easily, removed from the system. In other words it is the entrance door for solving difficult problems of spent fuel and weapon grade Pu.

As a foundation for closing of fuel cycle for all actinides we propose to use molten salt - burner reactors (MS-BR) suitable for integration with waste treatment processes in order to provide a low losses to wastes and extremely high burnup. Same time, differ from other fluid fuel reactor concepts, MS-BR is based on proven technology and has good potential to satisfy future safety requirements, operating as a burner.

These technologies allow to make utilisation of all actinides economic and energy efficient which does not leave them unrequired by power industry, but makes them practically inaccessible for terrorists and criminals.

Fuel cycles , losses to wastes and possible waste treatment

Figure 1 simply demonstrates recycling options for multicomponent Nuclear Power System (NPS) [1-2].The right upper part illustrates the activity for fast reactor cycle and the right lower part indicate the operations needed in a case a MS-BR option. In this context the following facts are important:

- The primary output of the reprocessing/separation process is material for new fuel.
- Reprocessing/separation process always have some losses of actinides to waste stream as a secondary output for direct disposal or further input to a separate treatment process.
- After number of cycles primary output could be moved from one separate S&T cycle to another due to technical limitations or economical reasons.

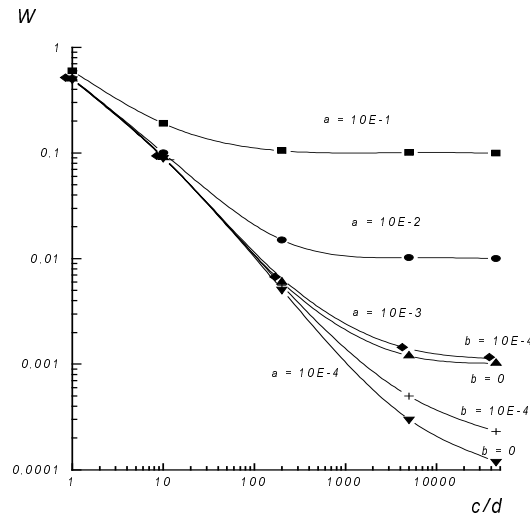
The total fraction of any nuclide which lost to waste stream - W , could be given by:

$$W = a + (1-a) \left[b \sum_{n=0}^{\infty} (1-b)^n (1-d)^n \left\{ \prod_{m=0}^n (1-c_m) \right\} + d \sum_{n=1}^{\infty} (1-b)^n (1-d)^n \left\{ \prod_{m=0}^n (1-c_m) \right\} \right]$$

where a, b and d are the single cycle fractions of element lost to wastes in normal reprocessing, fabrication and separate processing steps, c_m is the fraction transmuted in recycle pass m ($c_0 = 0$).

Using this equation it is possible to analyse various S&T cycles with regard to their ability to reach actinide reduction goals with reasonable losses. It is important that losses in normal reprocessing occur only once in the equation. This term in optimal case should be balanced with other part of the equation. Simple demonstration of the fact that extremely high ratios of c/d in each recycle where ($c = c_m = \text{const.}$) could provide reasonable total losses is given on Figure 1.

Figure 1. Relation between total losses to waste and ratio c/d of fraction transmuted per cycle to fraction lost to waste per cycle



For example, if $a = 10^{-4}$, to reach the total losses to waste W about 10^{-3} will be possible for options, with, $c/d=10^3$ (e.g. MS-BRs with $c = 0.5$, $d = 5 \cdot 10^{-4}$ and $b = 0$).

The following developments will be the most important regarding the available options to reduce actinide inventory:

- High neutron flux and short external recycle time interval to provide required balance of neutrons available for transmutation.
- Fuels suitable for high burnup and for separation processes.
- Reprocessing and separation technology with smaller actinide losses to wastes.
- Fuel cycles with less wastes for discharge and disposal.

Evaluating various advanced waste treatment technologies it has been found that several non-aqueous separation processes could be more suitable for this application than traditional aqueous one (see Table 1).

Table 1. Comparison between different fluid actinide fuelled systems

	Compactness	Radiation stability	Chemical stability	Vapor pressure	Solubility of actinides	Corrosion resistance
Aqueous	-	+/-	+/-	-	+/-	+
Molten chlorides	+	+	+/-	+/-	+	-
Molten fluorides	+	+	+	+	+	+
Liquid metals	+	+	+/-	+/-	+	-

The following features of these processes are important:

- The processing media is extremely radiation resistant.
- The working mechanisms are relatively simple and short cooling time is accepted.
- The actinides (An) and lanthanides (Ln) are separated good between groups but poorly within groups.
- Only a few reagents are needed which are mostly used to substitute carrier components.
- The materials are recycled to avoid waste disposal charges.

Some forms of engineering implementation of these processes are partially successful in Oak-Ridge National Laboratory (ORNL) [3], Argonne National Laboratory (ANL) [4], Los-Alamos National Laboratory (LANL) [5], Russian Research Center - Kurchatov Institute (RRC-KI), Institute of High Temperature Electrochemistry (IVTEX) [6] and Russian Institute of Atomic Reactors (RIAR) [7]. The basic processes include reductive extraction, electro-deposition and electro-refining. The carrier and processing media are liquid metals (e.g. Bi) and molten salts (chlorides, fluorides).

Important parameters for reductive extraction and electro-refining are electrochemical potential/free energy of formation $\Delta G_f^\circ(T)$ of chlorides (fluorides) and separation factors of elements between molten salt and liquid metal θ [8]. These separation factors for different elements with the same valency could be given by:

$$\ln\theta = \{ \Delta G_f^\circ(\text{Ln}, T) - \Delta G_f^\circ(\text{An}, T) \} / (RT),$$

where T - temperature (K), R - molar gas constant ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$).

Thermodynamic consideration predicts to need more efforts for separating Am and Cm from Ce and La in chloride system in comparison with fluoride one (see Table 2). The calculated separation factors of various elements in fluoride and chloride systems suggest for fluorides a better separation ability between actinides and lanthanides groups but poorly within groups.

Bi-Li reductive extraction flowsheet developed in ORNL [3] for $\text{LiF} - \text{BeF}_2$ solvent system could provide negligible losses of TRU ($d \approx 10^{-4}$) by use of several counter current stages. For fluoride based systems alongside with this method other method of TRU/lanthanides separation could be considered. This is electrochemical deposition of elements as metals on liquid or solid electrodes in electrochemical cells, filled with fuel salt and bismuth or lead. It is found that the recovery of 99.9% of TRU could be attained by combination of electro-refining and counter current extraction in the LiCl-KCl/Bi system by using Li as reductant with satisfying the separation ratio between TRU and rare earths of over 1.0 [9].

The applicability of the given method for fluoride based systems is defined by that the fuel salt at temperature 800-1100K is good electrolyte, the conductivity of which is comparable to conductivity of liquid electrolytes. In fluoride systems based on $\text{LiF} - \text{BeF}_2$ and LiF-NaF-KF the potentials of decomposition for components are higher than that for An and Ln trifluorides.

As on account (see Table 2) the difference of potentials of deposition Am and Ce in fluoride systems reaches 0.2V, it is possible to assert, that at electrolysis of fuel salt there will be the selective separation of these elements. The degree of separation will depends on value of an over-voltage on

electrodes. As shows experience of industrial production of a number of alkaline and alkaline-earth elements by electrolysis, at a difference of potentials of deposition of elements more than 0.1V, a degree of their separation is more than 100 (at nominal currents about 1A/cm²). Thus it is possible to expect for a degree of separation of actinides and lanthanides more than 100, and at several stages of electrochemical clean-up the contents of actinides in lanthanides can be reduced up to 10⁴ times. Further investigations have to be necessitated to make sure the using fluoride system and efficiency of the electro-winning and electro-refining.

Table 2. **Partial molar Gibbs energy of some trivalent halides, $\Delta G_f^o(T)$, kcal/mol**

Nuclide	Chloride[9] (T=800 K)	Fluoride[10] (T=1000 K)
U	164	305
Np	174	310
Pu	187	320
Am	195-200**	325
Ce	205	345
La	209	348

Outline of the Future Fuel Cycle

Basing on the status of fluid fuel reactor technology more attractive in future multicomponent NPS we consider processes concerned with the final uses of the recycled fuels as fluorides, in the molten salt reactors (MSR):

- Discharged fuel goes through reprocessing plant, actinides are extracted from waste.
- Uranium after isotope correction and plutonium and, possibly part of Np are recycled as a fuel in thermal and fast solid fuel reactors. Purex reprocessing of spent MOX fuel becomes more difficult, as the content in PuO₂ increases.
- Part of the plutonium together with minor actinides (MA) and if need some FPs are incinerated in a molten salt-burner reactor. Stable and short-lived FPs are removed from the burner reactor by the separation systems. These problems can be solved by chemical and physical methods in batch or on-line modes.
- Enhanced Purex, electrochemical and/or gas-fluoride volatility process should be investigated for considered above recycling options.
- The stable and short-lived FPs are directed to an interim storage facility from where they are sent to final disposal.

The advantages of the MSR as a burner reactor follow not only from a possibility for its effective combination with the pyrometallurgical or gas-fluoride technique of fuel reprocessing/separation, which is low-cost and produces a small volumes of wastes, but also from its capability to use fuel of any nuclide composition.

The MSRs have the flexibility to utilise any fissile fuel in continuous operation with no special modification of the core as demonstrated during MSRE operation for ^{233,235}U and Pu. Also, a good neutron balance allows use MAs largely contaminated by lanthanides. This simplify the lanthanide/MAs separation process and drastically could decrease the MAs losses to wastes [3].

The MS-BRs further require a minimum of special fuel preparation and can tolerate denaturing and dilution of the fuel.

In addition, there is a possibility to eliminate reactivity accidents in the reactor, providing it is operated at subcritical mode with acceptable, economical external neutron source. The subcritical mode could be important for the MS-BR because of the decrease of the delayed neutrons down to 0.1% due to composition of the fuel and its circulation through the core, as well as use of various fuel compositions.

The proposed strategy of Nuclear Power development is not an alternative to fossil-fired power, but represents its essential supplement. Different types of reactors do not compete with, but complement, each other allowing the best manifestation of the advantages of every type of plant designs. In this case accelerators are considered as neutron sources required to ensure the safe conditions for the functioning of Nuclear Power and to arrange more flexible fuel cycles for large scale Nuclear Power as well as to reduce and then to incinerate the equilibrium quantities of TRU and FPs at the stage of termination of Nuclear Power, if required, when more efficient and acceptable sources of energy appear or when the human kind's way of life and demands change.

Conclusion

MSR technology has been proved by multi-years international efforts. The MSR-Program performed in Russia, mainly at RRC - Kurchatov Institute, covered a wide range of theoretical and experimental studies. The main finding of experimental studies is that neither physical nor technical obstacles on a way to implement MSR and related fuel cycle technologies in the future Nuclear Power System were observed.

There is a good basis for the construction of MSR-based DEMO-facility in Russia. As the first step, the ISTC Project #698 devoted to the molten salt test facility construction could provide key data on the way toward the practical implementation of the accelerator-based transmutation and waste management technology.

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**AN EXPERIENCE ON DRY NUCLEAR FUEL REPROCESSING
IN THE CZECH REPUBLIC**

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Abstract

Experience of Czech research and industrial organisations in the development and realisation of pilot-plant technological line FREGAT-2 for dry reprocessing of fast reactor spent fuel is presented. The FREGAT-2 line is based on the fluoride volatility method. The possibility of using this experience of Czech organisations for developing technologies for selected areas of the transmutation process and the first results of technological research in this field in the Czech Republic are discussed.

Introduction

The development of dry reprocessing methods for spent fuel was motivated in the past by the assumed commercial utilisation of fast breeder reactors. Their application in the power industry can be economically efficient only in the case of a closed fuel cycle. However, reprocessing of fast reactor spent fuel brings about a number of specific difficulties in comparison to the reprocessing of spent fuel from thermal reactors. They are caused, for example, by higher burn-up, shorter cooling time resulting in a higher amount of energy released by the fuel, higher concentration and amount of plutonium, different cladding material, presence of metallic sodium, different fission products composition etc. Therefore, countries which were planning the introduction of fast reactors also were attempting to develop suitable methods for reprocessing, because the hydrometallurgical PUREX process was not suited to the fast reactor spent fuel.

One of the alternative processes, also being developed in the former Czechoslovakia in the 1970s and 1980s was the fluoride volatility process based on the separation of uranium and plutonium in the form of volatile hexafluorides from fission products, the majority of which form non-volatile fluorides. The process was developed in Czechoslovakia in co-operation with the former Soviet Union.

Fluoride reprocessing technology line FREGAT-2

The fluoride reprocessing consists of the following main operations:

- 1) Fuel elements decladding.
- 2) Transformation of the fuel to a powder.
- 3) Fluorination of the fuel.
- 4) Separation of uranium and plutonium fluorides.
- 5) Purification of the products obtained.

According to the agreement between the former Czechoslovak Atomic Energy Commission (now State Office for Nuclear Safety) and State Commission for Atomic Energy of the USSR it was agreed that the Soviet organisations will develop the technology and apparatus for items 1 and 2 and the Czechoslovak organisations for items 3 and 4. Item 5 will be worked out together, the purification of uranium on the Czechoslovak side and the purification of plutonium on the Soviet side.

The Nuclear Research Institute Rez was the contractor for the Czechoslovak side.

The Nuclear Research Institute Rez had a good qualification for the development of the fluoride reprocessing. It was at that time the only institution in the former Eastern bloc, except for the Soviet Union, where the fluorine gas production by anhydrous hydrogen fluoride electrolysis from potassium hydrogenfluoride melt had been managed.

Basic research in the field of volatile fluorides – for example of niobium, ruthenium, molybdenum, plutonium and wolfram, was the main subject studied in the Fluorine Chemistry Department of the Nuclear Research Institute Rez in the 1960s and early 1970s.

In the second half of the 1970s, the work on development and realisation of the pilot-plant technological line called FREGAT-2 was started. This line was intended for the fluoride technology verification by the way of experimental reprocessing of spent fuel from the Russian research fast reactor BOR 60.

The development and realisation of FREGAT 2 line was carried out in co-operation of the Nuclear Research Institute Rez with a number of Czechoslovak research and industrial organisations.

The most significant of them were:

- Chemoprojekt, Praha – design and engineering organisation which worked out the project of the entire technology including the measurement and control of the process.
- Institute of Nuclear Fuels, Zbraslav – design of special measuring and control instrumentation (manometers, pressure-vacuum gauges, flowmeters, closing and control valves). These instruments were designed for the fluorine, fluorides and hydrogen fluoride containing media.
- Research Institute of Chemical Equipment, Brno - design of all technological apparatuses and auxiliary equipment and manufacture of some of the apparatuses. Most of the apparatuses of the FREGAT-2 line which were in contact with fluorine, were made from nickel or Monel metal.
- Kovohute, Rokycany – production of nickel and Monel metal materials for the production of apparatuses.

Most of the technological apparatuses were manufactured in the engineering shop of the Nuclear Research Institute Rez. The work with nickel and its alloys as well as the necessary flaw detection methods were to be mastered in order to make products of required quality.

Spent fuel reprocessing in the FREGAT-2 line was based on the following principles.

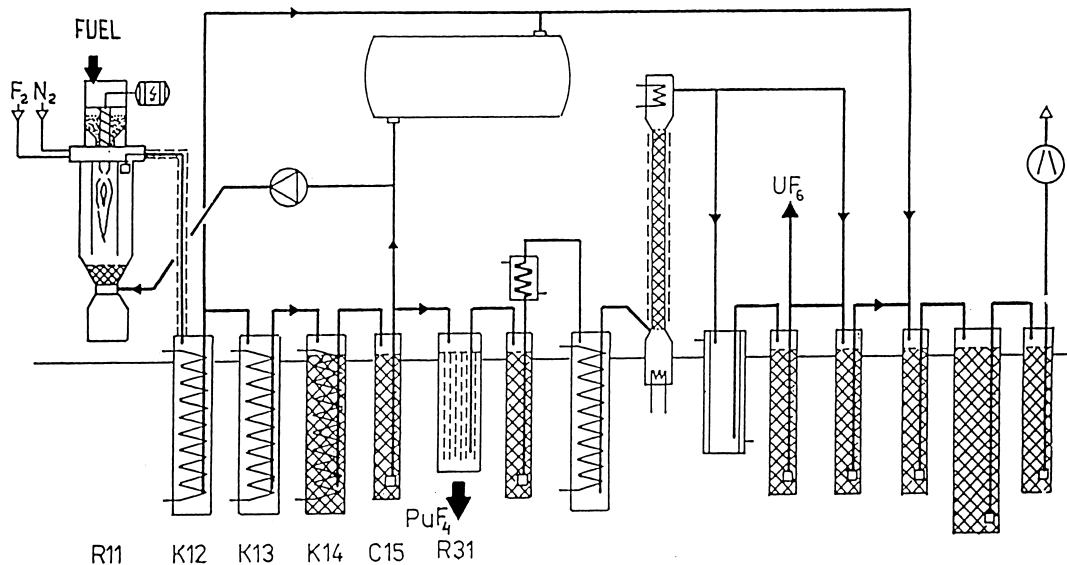
Powdered ceramic spent fuel is dosed in the nitrogen atmosphere by a worm doser into the preheated reactor R11 – fluorinator and at the same time fluorine gas also is fed. A reaction takes place in the flame, during which the uranium oxides react to form gaseous UF_6 , mostly plutonium to gaseous PuF_6 , a great majority of fission products form solid fluorides dropping to the fluorinator bottom and only a small part of fission products (Nb, Ru, Tc, Mo, I) reacts with fluorine under gaseous fluorides formation and will accompany uranium and plutonium together with rare gases.

Three condensers are situated after the fluorinator. The first one, K12, is intended for uptaking niobium and ruthenium. Uranium and plutonium fluorides should condensate in condensers K13 and K14 at -60 and -80 °C. It was assumed that a complete fluorination of Pu will not take place. Therefore, secondary fluorination of fuel in the reactor R11 was introduced by the way of fluorine circulation in a part of the apparatus by means of a circulating pump.

After the K13 and K14 condensers are filled with uranium and plutonium hexafluorides, the condensers are heated and the evaporated fluorides are introduced into the reactor R31, where thermal decomposition of PuF_6 to solid PuF_4 is taking place, whereas volatile UF_6 passes through the reactor. In this way, uranium is separated from plutonium.

UF_6 is then purified by column distillation to remove molybdenum, iodine and technetium fluorides.

Figure 1. Technological diagram of FREGAT-2 line



Czech industrial enterprises and research institutions produced in the 1980s the following main technological apparatuses and instrumentation:

- Worm and vibrating dosers for powdered spent fuel with a capacity of 1-3 kg fuel/hour.
- Flame fluorination reactors.
- Condensers for condensation and evaporation of fluorides.
- Sorption columns.
- Distillation columns for the distillation of a UF_6 - MoF_6 - IF_5 mixture.
- Closing and regulation valves for fluorine and fluoride media.
- Flowmeters for fluorine and fluorides for the flow rates of 0-600 l/hr and 0-4 000 l/hr.
- Pressure-vacuum gauge for the range of 10-200 kPa.
- Differential manometers for the range of ± 1 kPa.
- Auxiliary equipment for the hot cell.

This equipment, individual apparatuses and then the complete assemblies were subjected to functional and technological tests in the Nuclear Research Institute Rez. Depleted U_3O_8 was used as a fuel in these tests. A few tens of kg of U_3O_8 were used in these experiments. After completion of the tests the entire technology was transported to the RIAR Dimitrovgrad in the Soviet Union to make experiments in hot cells.

Because the ideas about an early application of fast reactors in the nuclear power industry were re-evaluated in the second half of the 1980s and also due to the Chernobyl accident, the experimental work on the FREGAT-2 line was discontinued in 1998 and all the apparatuses and equipment, which was the property of the Czechoslovak side were returned after decontamination to the Nuclear Research Institute Rez.

However, we succeeded in the meantime to test the function of most of the apparatuses by using experiments with depleted uranium and of most of the measuring and regulating circuits, too [1,2].

Although the experimental programme on the FREGAT-2 line was discontinued in 1998, the functionality of the majority of apparatuses and equipment and of the remote control was demonstrated and the soundness of most of the technological operations was confirmed. Czech research and industrial organisations acquired during the execution of the project FREGAT-2 good experience in the field of a complex development of a special radiochemical technology.

Fluoride technology for the transmutation programme

At present, Czech research and industrial organisations intend to use the above experience in the planned national programme of transmutation technology development. Study of various aspects of the ADTT and a research and development programme in this field is being carried out in the Czech Republic for 3 years already, most of all within the scope of the national programme of deep geological repository development. This programme is financially subsidised by the State and development of transmutation technologies within this programme represents to some extent the support of an alternative technology.

Some of the Czech research and industrial organisations take part in the preparation of the fully independent national programme of transmutation technologies development. First of all, it is the Nuclear Research Institute Rez plc, SKODA – Nuclear Machinery, Czech Power Company, Institute of Nuclear Physics of the Czech Academy of Sciences and other organisations that were participating in the development of the FREGAT-2 fluoride reprocessing technology.

Establishment of an experimental laboratory for research and development in the field of transmutation technologies is assumed within the Nuclear Research Institute Rez plc. Experimental studies of a limited extent on the determination of physico-chemical properties of melts of selected fluoride salts mixtures were carried out at this place. At present, assembly of the first experimental loop filled with a fluoride salt melt is carried out together with the SKODA - Nuclear Machinery company. Three of such loops are planned to be realised. They will be used, first of all, for the material and design studies of the transmutation technology. The laboratory experiments in the field of suitable fluoride melt preparation and its behaviour has been started and technological experiments of the first main separation steps of the spent fuel before transmutation are planned and prepared. Selected parts of FREGAT-2 equipment will be used for this investigation.

Conclusion

The Czech Republic as a country operating and constructing nuclear power plants and treating problems of spent nuclear fuel is interested in the international co-operation in the field of transmutation technologies development. A co-operation already exists at the level of individual institutions and is directed to the information exchange between the Czech organisations mentioned and research institutes in the U. S. A., France, Sweden, Italy, Russia, Korea and others.

Development and realisation of transmutation technology can be considered practicable at present within the scope of a wide international co-operation. It cannot be figured that the Czech Republic, as a relatively small country, could participate financially to a deciding extent on this research. However, within the international co-operation at the level of government and research institutions the tasks could be allocated in a way that each of the participants will take part on the investigation of some selected problems. Czech research and industrial organisations are prepared to participate in such a co-operation. Experience from the fluoride reprocessing technology development is a good basis for this co-operation.

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