

**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.

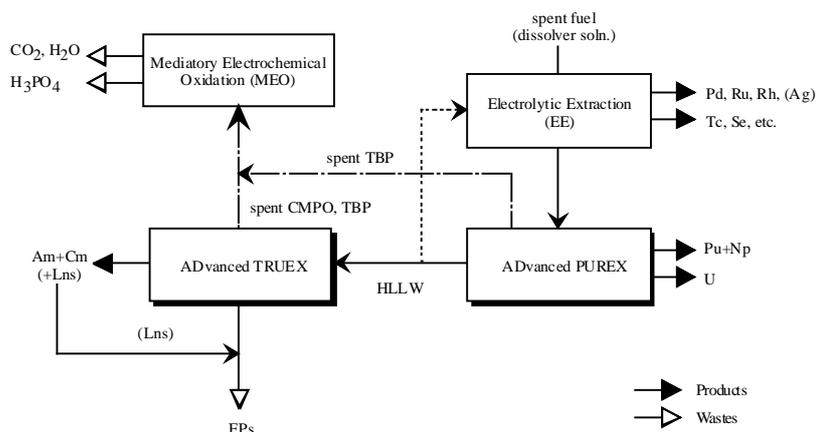
Long-lived nuclides separation system

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-live 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 $O\phi D[IB]CMPO$ (hereafter CMPO: Octyl[phenyl]-N, N-diisobutylcarbamoylmethyl phosphine oxide) has been parametrically studied in the presence of Ag^{+2+} , 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

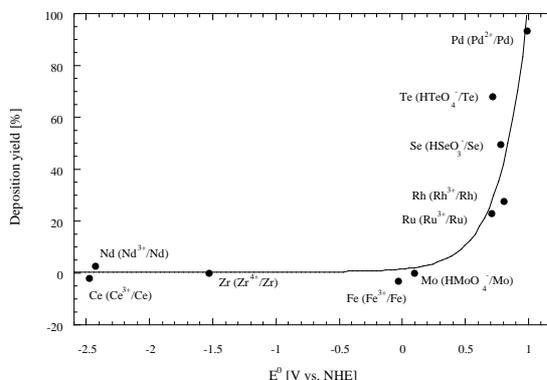
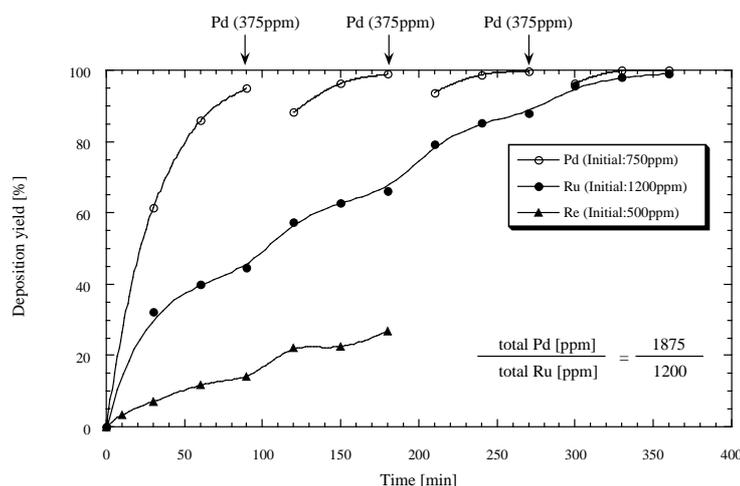


Figure 3. Time dependency of Ru and Re deposition yields with addition of Pd^{2+} ion in 2.5N HNO_3 Pd/Ru mixture or Pd/Re mixture solution



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

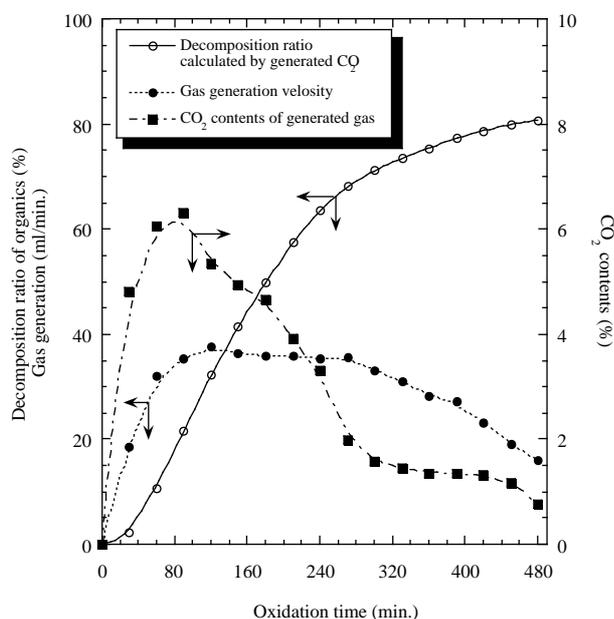


Figure 4 shows the typical example of the off-gas behaviour during the MEO of TRUEX solvent (0.2M CMPO/1M TBP/n-dodecane) dispersed in the anolyte with 3M nitric acid. The MEO condition was that anodic current density: 500 mA/cm^2 , temp: 50°C , Pt-Ti anode, Ag^+ : 0.5M, devoted TRUEX solvent: 0.447 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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