Recent Activities on Aqueous Partitioning at JAEA

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Two Types of P&T schemes

- **Homogeneous recycling** with commercialized FR
  - MA-MOX fuel with aqueous reprocessing
  - MA-bearing metal fuel with pyrochemical reprocessing
- **Double-strata concept** with accelerator driven system
  - MA-bearing nitride fuel with pyrochemical reprocessing

**Homogeneous recycling**

- LWR → U, Pu, MA → FR → Repository

**Double strata concept**

- LWR → U, Pu → FR → ADS → MA → FP → Repository
Aqueous partitioning technologies

• Advanced aqueous process (NEXT process)
  - Crystallization of U
  - Co-recovery of U-Pu-Np
  - MA recovery

• 4-Group Partitioning Process

• Alternative technologies (Innovative extractants & adsorbents)
  - Selective extraction of U
  - Total recovery of TRU
  - Separation of MA/rare earths
  - Separation of Sr-Cs
  etc.
Overview of the NEXT process

- NEXT (New Extraction System for TRU Recovery) process is expected to have some advantages over the conventional process based on the PUREX:
  - The relative simplicity for remote operation
  - Volume reduction of organic solvent in the extraction process
  - Reduction in the cost for the equipments and the hot cell volume
  - Reducing waste volume
  - Enhancement of nuclear proliferation resistance

Schematic Flow of the NEXT Process
Principle of the crystallization

- Recovery of ~70% of U in dissolver solution as uranyl nitrate hexahydrate (UNH) crystal by cooling the dissolver solution
  - Decrease of temp. from $T_1$ to $T_2$
    - Decrease of U solubility from $a_1$ to $a_2$

- Plutonium, MA, FP in dissolver solution
  - Effect on the purity of UNH crystal (decontamination factor (DF) of these elements to UNH crystal)

- Study on the behavior of Pu and FP during crystallization using U-Pu-HNO₃ solution & real dissolver solution is important
Pu and FP behavior in the crystallization process

- **U pre-recovery as UNH crystal by cooling dissolver solution**
  - Pu behavior: Depends on its valence
    - Pu(VI): Co-crystallized with U
    - Pu(IV): Remained in mother solution
  - FP behavior: Possibility of crystallization for some FP, e.g., Cs

  Required to control the behavior of these elements

<table>
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<tr>
<th>Pu ratio in U crystal</th>
<th>Crystallization product</th>
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<tbody>
<tr>
<td>Pu(IV), Pu(VI) ratio in solution</td>
<td>Appearance</td>
</tr>
<tr>
<td>Run1</td>
<td>Pu(IV): 100% Pu(VI): 0%</td>
</tr>
<tr>
<td>Run2</td>
<td>Pu(IV): 0% Pu(VI): 100%</td>
</tr>
<tr>
<td>Run3</td>
<td>Pu(IV): 62% Pu(VI): 38%</td>
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Uranium crystal obtained in U-Pu(IV)-Cs-HNO₃ (after washing).
**Mini centrifugal contactors**
- Rotor diameter: 30mm
- Rotation speed: 2,500 – 3,500rpm
- Maximum capacity: 5.5 l/h
- Hold-up: 25ml/stage
- 16 stages / bank

Single Cycle Co-extraction Process for U-Pu-Np Co-recovery

- Feed
- Scrub
- Strip
- Raffinate
- HNO₃
- Extraction - Scrubbing
- U-Np-Pu co-stripping

Mini Centrifugal contactors for U-Pu-Np co-recovery
Single Cycle Co-extraction Flowsheet for U-Pu-Np Co-recovery

U-Pu-Np co-recovery flowsheet trial at CPF

Results

・ DF of Total gamma was about $10^4$.
・ Pu and U were not detected in HA raffinate and solvent
  (U < 0.03g/L, Pu < 0.2g/L)
・ Most of Np was detected in U-Np-Pu product, but a little Np leaked to HA raffinate (about 2%)
MA recovery (SETFICS: Solvent Extraction for Trivalent f-elements Intra-group Separation in CMPO-complexant System)

Experimental flowsheet of the SETFICS process using mixer-settlers for high loading and application of hydroxylamine nitrate.

Decontamination factor obtained in the counter-current experiment
(0.2 M CMPO–1.4 M TBP in n-dodecane)

<table>
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<tr>
<th>Nuclides</th>
<th>Loss (%)</th>
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<tr>
<td>Am-241</td>
<td>0.16</td>
</tr>
<tr>
<td>Cm-242</td>
<td>0.39</td>
</tr>
<tr>
<td>Cm-244</td>
<td>0.33</td>
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MA recovery (Extraction chromatography)

- SiO$_2$-P: porous SiO$_2$ covered by SDB polymer
- Resin: extractants (CMPO, TODGA, BTP, etc) immobilized in SiO$_2$-P

The CMPO/SiO$_2$-P resin

Cross section of the porous SiO$_2$

Separation tests for simulated HLLW by CMPO/SiO$_2$-P resin
(Column 10 mm $\phi$ x 50 mm h, Flow rate 0.76 m/h, Temp. 323K)
Aqueous partitioning technologies

- Advanced Aqueous Process (NEXT process)
  - Crystallization of U
  - Co-recovery of U-Pu-Np
  - MA recovery

- 4-Group Partitioning Process

- Alternative technologies (Innovative extractants & adsorbents)
  - Selective extraction of U
  - Total recovery of TRU
  - Separation of MA/rare earths
  - Separation of Sr-Cs
  etc.
The 4-Group Partitioning Process was tested with concentrated real HLLW. Objective elements, Am, Cm, Np, PGM, Sr, Cs, were separated as expected. Am, Cm: >99.998% extracted, >99.98% stripped. Pu: >99.99% extracted, >99.98% stripped. Np: 98.2% extracted, >99.93% stripped (>99.95% at optimum condition). PGM: 99% precipitated. Tc: 96.2% at semi-hot test. Sr, Cs: DF > 10^4. No major problem in operation. No difference in separation behaviors of elements between simulated and real HLLW. Process performance, the separated fraction and secondary wastes were evaluated.
Development of innovative extractants & adsorbents

- Although the main steps of the 4-group partitioning process have been verified, it is also necessary to improve the partitioning process from viewpoints of the economy and the reduction of secondary wastes.

- The R&D effort on the partitioning is presently concentrated on development and improvement of innovative extractants and adsorbents as alternative technologies. Selective extraction of U, Total recovery of TRU, Separation of MA/rare earths and Separation of Sr-Cs.

- Molecular modeling, quantum chemistry, radiation chemistry, structural studies on extractants and f-element complexes have also been investigated for the R&D of new extracting molecules.
Selective separation of U (1/2)

**Extraction of U(VI) by BAMA**

We have synthesized several Branched Alkyl Monoamide (BAMA) to obtain higher selectivity for U(VI) versus Pu(IV).

![Chemical structures of BAMA](image)

- N,N-di-(2-ethyl)hexyl-3-methyl-butanimide (D2EH MBA)
- N,N-di-(2-ethyl)hexyl-2-methyl-propanamide (D2EHMPA)
- N,N-di-(2-ethyl)hexyl-2,2-dimethylpropanamide (D2EHDMPA)
- N,N-di-(2-ethyl)hexyl-(2-ethyl)hexanamide (D2EH2EHA)

**SF:** $D_{U}/D_{Pu} = 3.6$ 79.4 182 71.3
Selective separation of U (2/2)

BAMA for selective separation of U(VI)
- D2EHDMPA is one of BAMA which have steric hindrance on the coordination with An ions.
- D2EHDMPA can separate U(VI) from Pu, MA and FP without the reduction of Pu(IV).

1.5 M D2EHDMPA (3.0 M HNO$_3$)

1. 0.5 M U(VI) · · · · · · · · · · D$_U$ = 1.5
2. 50 mM Pu(IV) · · · · · · · · · · D$_{Pu}$ = 0.04
3. FP (Sr,Zr,Ru,Rh,Pd,Ba,Nd,Mo,Ce,Tc) · · · · · · · · · · D$_{FP}$ ≤ 0.1
4. 0.5 M U(VI)-Tc(VII) · · · · · · · · · · D$_{Tc}$ = 0.4

N,N-di(2-ethyl)hexyl-2,2-dimethyl-propanamide (D2EHDMPA)
JAEA developed a novel extractant, N,N,N’,N’-tetraoctyldiglycolamide (TODGA) for the recovery of actinide ions.

- High solubility in n-dodecane
- Strong extractability for An(III) and An(IV) from higher HNO₃ solution

D(An) > 1000
Recent progress

-The limit of metal concentration (LOC)

12 mM for Nd(III), 13 mM for Pu(IV) in 0.2 M TODGA/3 M HNO₃

LOC can be improved by modifying its alkyl groups attached to amidic nitrogen atoms.

- Back extraction of An(III) and An(IV) by using new water-soluble ligand TEDGA(N,N,N’,N’-tetraetyldiglycolamide)
N-type donor extractant for An(III)/RE(III) separation

Separation in acidic solution and chemical stability were problem.

NO-type hybrid donor extractant for An(III)/RE(III) separation

Electronic structure of PDA molecule (calculated by Gaussian98)

Molecular design is required to improve the SF(Am/Lns)
Effective and selective MA(III) separation from rare earths using PDA is in progress by modifying its alkyl groups attached to amidic nitrogen atoms.

e.g., $R_1=\text{Ph}$, $R_2=\text{CH}_3$

$R_1=\text{Ph}$, $R_2=C_n\text{H}_{2n+1}$  
(n=4, 8, …)

Organic phase:
0.1M PDA + Chloroform
Selective adsorbent of Sr-Cs under high nitric acid concentration

**Novel inorganic adsorbent (cation exchanger) of Cs**
- Sodium-silicon-tantalum and sodium-titanium-tantalum mixed oxides
- Prepared by hydrothermal synthesis from alkoxides (Si, Ti, Ta)
- Highly Cs selective against H⁺
- Stable in nitric acid

- **Na-Si-Ta-O**
  - Nature
    - Si:Ta = 0.7-1.1
    - Amorphous
  - Kd of Cs from 3 M HNO₃
    - 3300 ml g⁻¹ (equilibrium, 4 days)
    - 2320 ml g⁻¹ (24 h)
  - No decrease of exchange capacity after leaching by 3M HNO₃ at 90 °C for 2 days

- **Na-Ti-Ta-O**
  - Nature
    - Ti:Ta = 0.26
    - Crystalline, pyrochlore
  - Kd of Cs from 3 M HNO₃
    - 650 ml g⁻¹ (equilibrium, 2 weeks)
    - 100 ml g⁻¹ (24 h)
  - No decrease of exchange capacity after leaching by 3M HNO₃ at 90 °C for 2 days
Separation of Sr-Cs (2/2)

Novel selective adsorbents (organic-inorganic composite) of Sr or Cs

- Inpreganating selective extractants
  - Crown ether (example 1), for Sr
  - Calix-crown (example 2) for Cs

- Porous-silica-based (composite with macro reticular type polymer) material (SiO$_2$-P) as a non-conventional support

![SiO$_2$-P support](image)

(1) di-t-butylcyclohexano-18-crown-6 (DtBuCH18C6)

(2) 1,3-[(2,4-diethyl-heptylethoxy)oxy]-2,4-crown-6-calix[4]arene (calix-crown R14)

- Studies are undergoing.
  - Preparation (selection of extractants / modifiers)
  - Leaching of extractants into HNO$_3$
  - Kd (Sr, Cs, FP, U, TRU)

Note: The studies are performed in cooperation with IRI (Institute of Research and Innovation).
JAEA considers that the NEXT process is the most suitable technology for partitioning of the FR fuel, however, JAEA also proposes alternative technologies that are expected to be the options for the NEXT process, considering reduction of the risks for development and future improvement of performance.
ARTIST
(Amide-based Radio-resources Treatment with Interim Storage of Transuranics)

Topics:
1) Selective separation of U
2) Recovery of TRU by TODGA
3) Sr and Cs separation
4) An/Ln separation

spent fuel

\[ \text{UO}_2 \]

BAMA process

\[ \text{PuO}_2 \]

TODGA process

Sr, Cs separation

Sr, Cs separation

FP

disposal

interim storage

\[ \text{Np, Pu, Am, Cm, Ln Oxide} \]

N-donor process

\[ (\text{Pu}), \text{Np, Am, Cm} \]

transmutation

\[ \text{Ln} \]