OECD Nuclear Energy Agency
11th Information Exchange Meeting on
Actinide and Fission Product Partitioning and Transmutation
San Francisco, California, USA
1 - 5 November 2010

Development of Separation Process for Transuranium Elements and Some Fission Products Using New Extractants and Adsorbents

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Concept of the process development

- Separation process for transuranium elements (TRU=Am, Cm, Np and Pu) and some fission products (Sr, Cs and Mo) from high-level liquid waste (HLLW) after the recovery of U, Pu, (Np and Tc)

Purpose of the separation
- TRU separation for transmutation
- FP separation for reduction of volume and heat in HLW

- Using new innovative extractants and adsorbents [Phosphorus-free compounds consisting of carbon, hydrogen, oxygen and nitrogen (CHON principle)]

- Improvement in economy
- Reduction of secondary wastes
Extractants and adsorbents applied

**TDdDGA (Dodecyl-DGA) for TRU separation**

\(N,N,N'N''\)-tetradodecyldiglycolamide

**Oct.PDA for An(III)/RE separation**

\(N,N''\)-dioctyl-\(N,N''\)-diphenyl-pyridine-2,6-dicarboxyamide

**DtBuCH18C6 for Sr separation**

di-t-butylcyclohexano-18-crown-6

**Calix-crown R14 for Cs separation**

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

Fe oxide adsorbent for Mo separation

Detail of these extractants and adsorbent and the application to the separation process are explained later.
TDdDGA (Dodecyl-DGA) for TRU extraction

- Very high Distribution ratio (D) for An(III) and RE at high HNO₃ concentration
- Very low D of An(III) at low HNO₃ concentration
- Soluble in n-dodecane
- CHON extractant
- High extraction capacity without any additives
  0.033M Nd with 0.1M TDdDGA in n-dodecane ↔ 0.006M Nd with 0.1M TODGA (Octyl-DGA)
- Some complexing agents are required to reduce the extraction of Zr and Pd
  HEDTA was selected.
  HEDTA: Hydroxylethyl-ethylenediamine-triacetic acid
- To extract Np, it should be reduced to Np(IV).
  H₂O₂ was applied. H₂O₂ also reduces D of Zr.

Org. phase : 0.1M TDdDGA - n-dodecane
Aq. phase : 0.1M HEDTA - 0.5M H₂O₂ - HNO₃

Fig. Dependence of distribution ratio on the HNO₃ concentration in the presence of HEDTA and H₂O₂
Concept of the process with TDdDGA

Starting solution for the TRU extraction process
- High-level liquid waste, assumed to be the raffinate of the co-extraction step for U-Pu-Np separation in the NEXT Process.
  NEXT Process is an advanced reprocessing process being developed at JAEA for FBR fuel.
- It contains residual U, Pu and Np, and these three actinides should be controlled.

Process flow
- First, An(III) and An(IV) are extracted by reducing Np(V) to Np(IV).
  U(VI) is transferred to the raffinate.
- Next, An(III) is stripped with diluted HNO₃.
- Finally, An(IV) is stripped with a complexing agent.

Counter-current continuous extraction tests using mixer-settler units were performed with simulated HLLW containing 12 fission product elements and actinide tracers.

Conceptual flow of the process
High-level liquid waste (HNO₃:1-3M)

1) Am test
2) High loading test
No problem in the mixer-settler operation

Good phase separation, No third phase formation
Both Am and Nd are extracted and stripped in a very high yield, almost 100%.

Other RE were extracted in a high yield as Nd.

Decontamination factor (DF)
- Sr : >100
- Zr : 33
- Pd : 105

Results of Am Test (1) - Am and Nd behavior -

No difference in concentration profiles of Am and Nd.
→ Nd is a almost perfect substitute for Am in this system.
Sr : Very low concentration in the organic outlet stream in the first mixer-settler, but accumulation was observed and a steady state was not reached for Sr.

Pd : High recovery in the raffinate

Zr : Very small fraction in the organic phase.

Process condition should be modified to avoid the Sr accumulation.

Simulation calculation was performed for this purpose using PARC-MA.

Condition of “High loading test” was obtained, where distribution ratio of Sr in each stage of the first mixer-settler was reduced by increasing the concentration of RE in the organic phase.
High loading test with Am and Np

Table: Composition of the feed solution

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (mM)</th>
<th>Element</th>
<th>Concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>2.48</td>
<td>Pd</td>
<td>11.56</td>
</tr>
<tr>
<td>Y</td>
<td>1.39</td>
<td>Cs</td>
<td>14.07</td>
</tr>
<tr>
<td>Zr</td>
<td>14.39</td>
<td>Ba</td>
<td>5.87</td>
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<tr>
<td>Mo</td>
<td>9.87</td>
<td>La</td>
<td>11.7</td>
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<tr>
<td>Ru</td>
<td>14.78</td>
<td>Nd</td>
<td>20.75</td>
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<tr>
<td>Rh</td>
<td>4.41</td>
<td>Eu</td>
<td>4.57</td>
</tr>
<tr>
<td>HNO₃</td>
<td>3.0 M</td>
<td>Am, Np</td>
<td>7~8×10³</td>
</tr>
</tbody>
</table>

Solvent loading:
17.1mM RE
2.1 times higher than the Am test

Operation time was extended.

TEDGA: N,N,N’-tetraethyldiglycolamide
Results of High loading Test - Am, Np -

Am extraction: > 99.99%
Np extraction: 62%
A few % of Np was found in Am fraction.
Sr, Pd, Zr were separated from An.

The observed concentration profiles of RE agreed well with profiles calculated by the simulation code.

Fig. Concentration profiles of Am and Np in the first and second mixer-settler in the High loading test.
Comparison of concentration profiles

Fig. Concentration profiles of Sr and RE in the High loading test.

Fig. Concentration profiles of Sr and RE at a transient state calculated by simulation code, PARC-MA.
Results of TRU extraction step development

Process simulation by PARC-MA revealed that most of La (and a part of lighter Ln) can be transferred to the raffinate at a steady state, keeping the high extraction yield of Nd (TRU).

Optimized process condition can be given by the calculation with the simulation code.

Element behavior in the TRU extraction step

High-level liquid waste ( [HNO$_3$]=2~3M )

- TRU Extraction → La, a part of lighter Ln, other FP, U(VI)
- An(III) Strip → Am, Cm, heavier Ln, Small part of An(IV) and Y
- An(IV) Strip → Large part of An(IV)(Np, Pu) and Y

Fig. Concentration profiles of Sr and RE calculated by simulation code, PARC-MA at a steady state.
Hetero-donor type extractant, pyridine-dicarboxyamide

- Very stable in HNO₃ media
- Separation factor is not so high, particularly in extraction with \( n \)-dodecane solution

**Applied to extraction chromatography**

Distribution coefficient at 5M HNO₃
Am:22.8, Nd:4.8, Eu:7.8, Gd:8.4 (cm³/g)
Separation factor Am/Nd:4.8, Am/Gd:2.7
Oct-PDA was successfully impregnated into Amberlite XAD-4 resin.

Sufficient separation of Am(III) from Eu(III) in 5 M HNO₃ was achieved by Oct-PDA/XAD-4 column.

Effluent: 5 M HNO₃  
Flow rate: 0.1 ml/min.  
Column size: 5 mmφ x 20 cm

Np(IV) and Pu(IV) can be eluted with H₂C₂O₄.

Fig. Separation of Am and Eu by extraction chromatography using Oct.PDA/XAD-4

Am(III) product in TRU extraction step  
0.1~0.3M HNO₃  
Am, Cm, Nd, heavier Ln  
part of Np, Pu, Y

Concentration and acidity adjustment  
5M HNO₃

Extraction chromatography

Lanthanides  
Am, Cm, part of Y  
Part of Np, Pu
**Concept of Sr-Cs separation process development**

- Sr-Cs separation from nitric acid solution of higher concentration
- Some extractants can be applied to the separation but cannot be used with aliphatic hydrocarbon diluent. → Extraction chromatography

Porous silica particles coated with copolymer of formylstyrene and divinylbenzene (SiO₂-P) was used to support the extractant.

DtBuCH18C₆ for Sr separation

DtHexCH18C₆ for Sr separation

Calix-crown R14 for Cs separation

Modifier is required to adsorb Sr and Cs.

Modifier: 1-Octanol, 1-Dodecanol, 1-Hexadecanol

- Selection of modifier
- Optimum molar ratio of the modifier to the extractant
Column adsorption test for Cs separation

Cs separation with Cs adsorbent column

Extractant : Calix-crown R14
Modifier : 1-Hexadecanol
Modifier/Extractant = 4.17
Column : 10mmφ×240mmH
Flow rate : 1cm³/min
Feed : 4M HNO₃

Cs was separated from other elements as almost isolated fraction.

Another experiments on repeated adsorption and elution with simulated solution showed that Calix-crown R14 adsorbent is very stable against extractant elution. We found almost no change in adsorption capacity after 60-cycle repetition.
Column adsorption test for Sr separation

Sr separation with Sr adsorbent column

Extractant: DtBuCH18C6
Modifier: 1-Hexadecanole
Modifier/Extractant=1.25
Column: 10mmφ×280mmH
Flow rate: 1cm³/min
Feed: 2M HNO₃

Sr was eluted finally with water.

Cs should be separated before Sr separation.

The adsorbent for Sr was less stable compared with the adsorbent for Cs because of the elution of the extractant.
Cs-Sr separation test with a genuine HLLW

Feed: HLLW (2cm³)  Scrub: 3M HNO₃(2cm³)  Eluent: H₂O

Almost no change in element behavior
Sequential adsorption test

Raffinate of the TRU extraction step
(Test with simulated HLLW)

- Cs Adsorption
  - Ru, Pd: DF=85
  - Sr, Zr, Mo, Rh, Ba: DF>100
- Eluent (Cs free)
  - Cs: DF>100
- Sr Adsorption
  - Ba: DF=2.2
  - Ru: DF=77
  - Zr, Mo, Rh, Pd: DF>100
- Eluent (Sr, Ba free)
  - Sr: DF>100

Mo Adsorption

Almost the same elements behavior. Complexing agent, HEDTA, showed no effects on the adsorption of Cs-Sr (favorable effect on Pd).
Adsorbent for Mo separation

Various metal oxide adsorbents were examined for Mo separation; Fe-Pd oxide, Fe oxide, Mn oxide, Al oxide, Co oxide, amorphous Zr oxide. Hematite type iron oxide (Fe adsorbent) had high Mo adsorption ability even in 3M nitric acid solution and low solubility in nitric acid.

Granulation of Fe oxide adsorbent
Fe oxide powder obtained by calcination can be granulated, which allows column adsorption.

Before granulation (Powder of Fe oxide)  Granulated Fe oxide adsorbent Grain size: (a) 1.7mm, (b) 0.6mm

Column of the Fe adsorbent used in Mo separation tests
Almost no adsorption of FP except Mo.
Mo can be eluted with oxalic acid.
Mo can be separated from other fission products.

Adsorption test with the effluent from the Sr adsorption (mentioned before) showed no difference in element behavior.
Summary

Separation process shown in the figure was developed at JAEA. All the separation steps were tested using simulated solutions with and without some radioactive isotopes and the Cs and Sr separation steps were verified with a genuine HLLW, and the element behavior was examined.

Extraction process for TRU with TDdDGA should be tested with a genuine HLLW as the next study. Further research and development would be required on extraction chromatography from an engineering point of view.
Acknowledgement

The authors would like to express their grateful acknowledgement to
Dr. Y. Sasaki, Dr. Y. Kitatsuji, Dr. Y. Sugo,
Dr. M. Watanabe, Dr. M. Arisaka, Dr. T. Asakura,
Dr. T. Kikuchi, Dr. H. Hoshi, Mr. S. Ichimura,
Mr. M. Sato, Mr. H. Hagiya (JAEA)

Prof. T. Fujita, Dr. G. Dodbiba (The University of Tokyo)

Present study includes the result of “Development of separation technology of transuranium elements and fission products by using new extractants and adsorbents” entrusted to Japan Atomic Energy Agency by the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).

Thank you very much for your attention