Recent Activities on Aqueous Partitioning at JAEA

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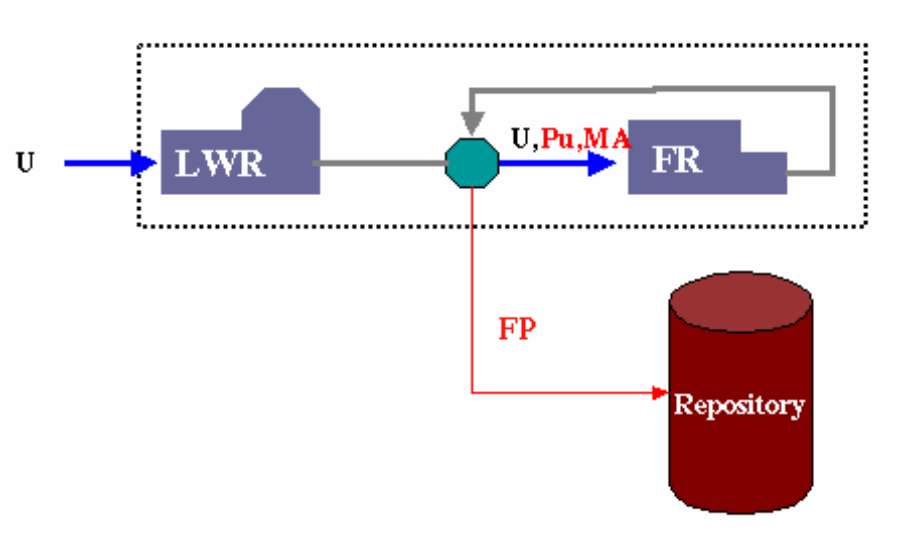
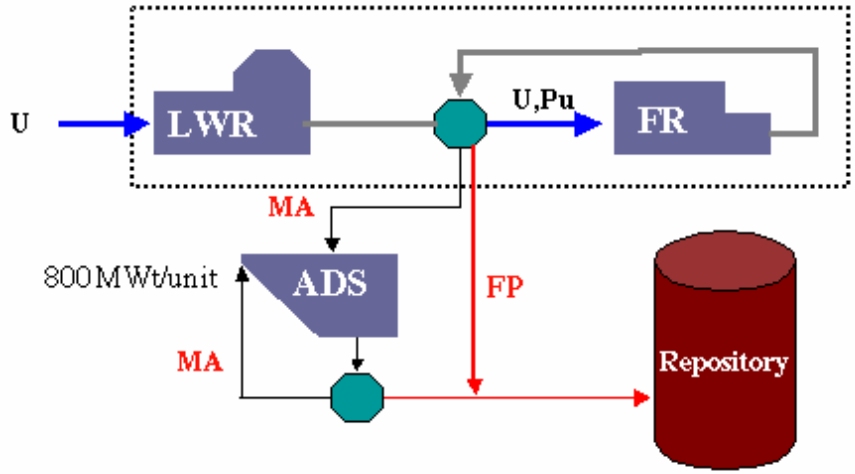
Two Types of P&T schemes

- **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



Double strata concept

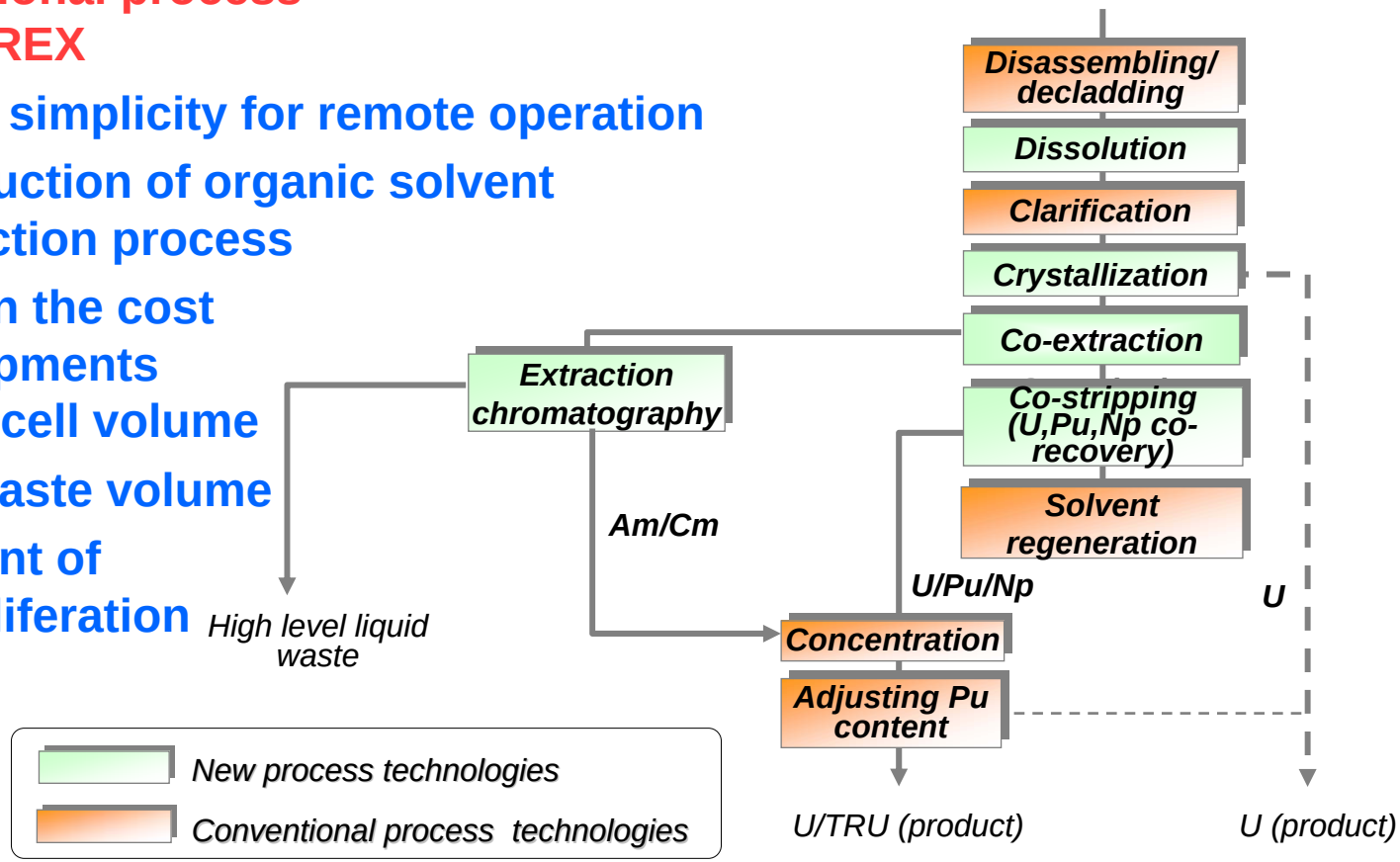
Aqueous partitioning technologies

- **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.

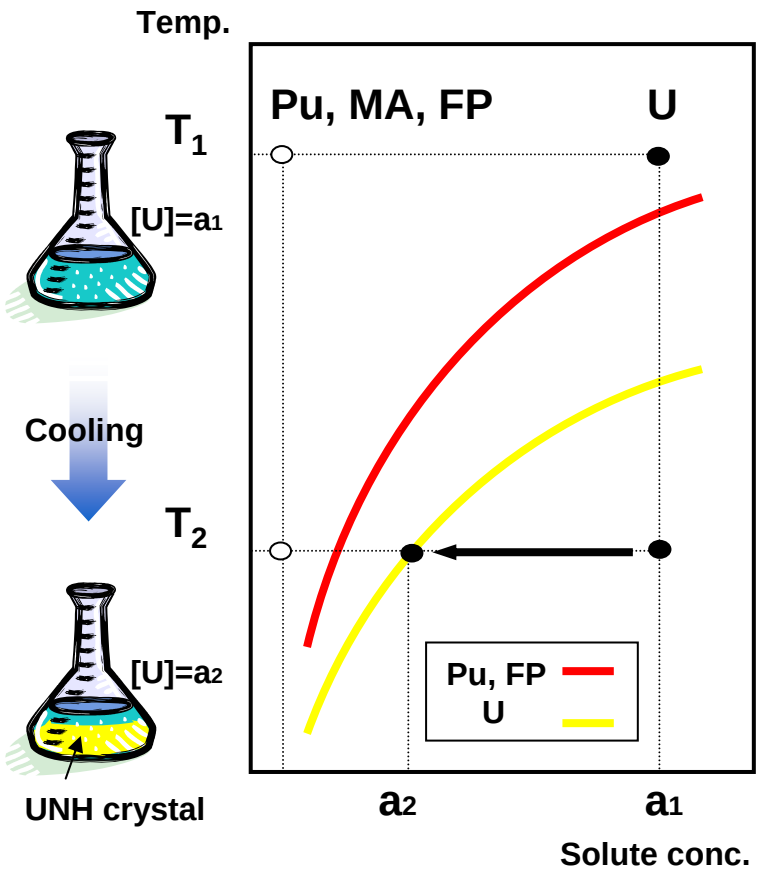
Overview of the NEXT process

- **NEXT (New Extraction System for TRU Recovery) process is excepted 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



Solubility curve

➢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

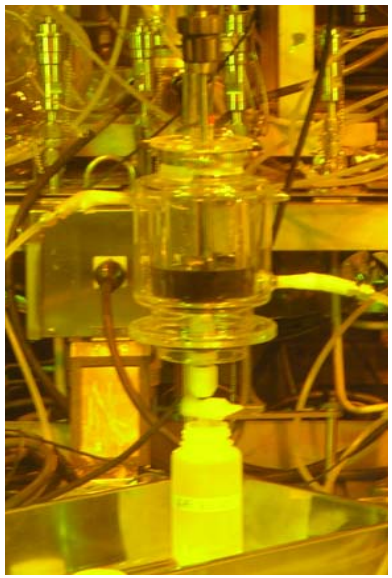
- Effect on the purity of UNH crystal (decontamination factor (DF) of these elements to UNH crystal)

◆Study on the behavior of Pu and FP during crystallization using U-Pu-HNO_3 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



Crystallizer

Pu ratio in U crystal

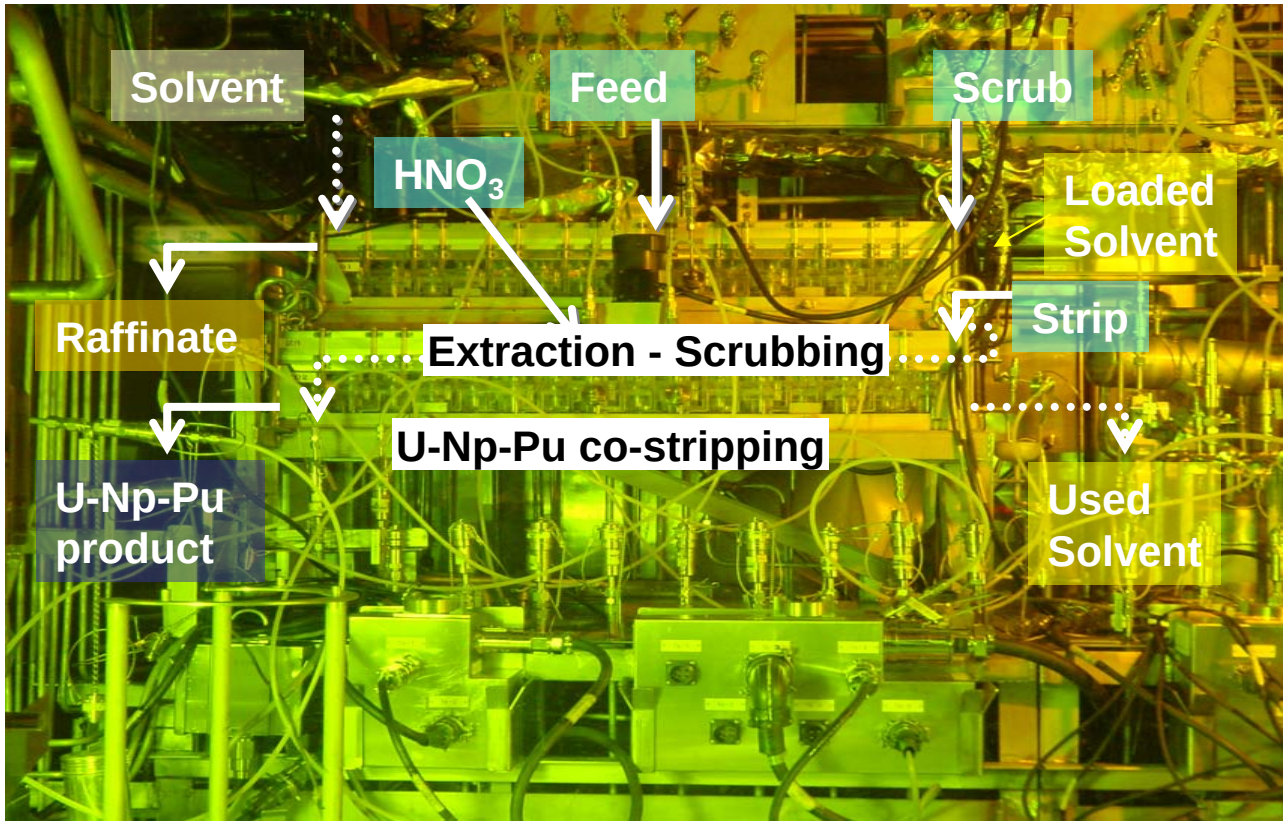
Pu(IV), Pu(VI) ratio in solution	Crystallization product Appearance	Pu ratio
Run1 Pu(IV) : 100% Pu(VI) : 0%		100 : 0.3 (U) (Pu)
Run2 Pu(IV) : 0% Pu(VI) : 100%		100 : 5 (U) (Pu)
Run3 Pu(IV) : 62% Pu(VI) : 38%		100 : 1.5 (U) (Pu)

Uranium crystal obtained in U-Pu(IV)-Cs-HNO_3 (after washing).

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

○**Mini centrifugal contactors**

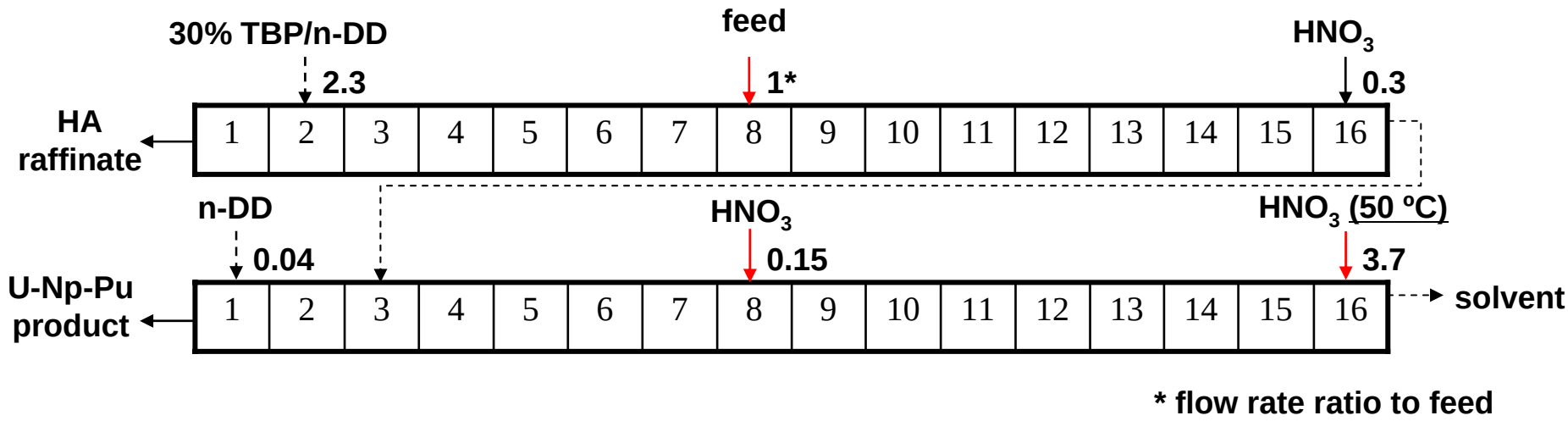
- **Rotor diameter : 30mm**
- **Rotation speed :**
  2,500 – 3,500rpm
- **Maximum capacity : 5.5 l/h**
- **Hold-up :**
  25ml/stage
- **16 stages / bank**



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



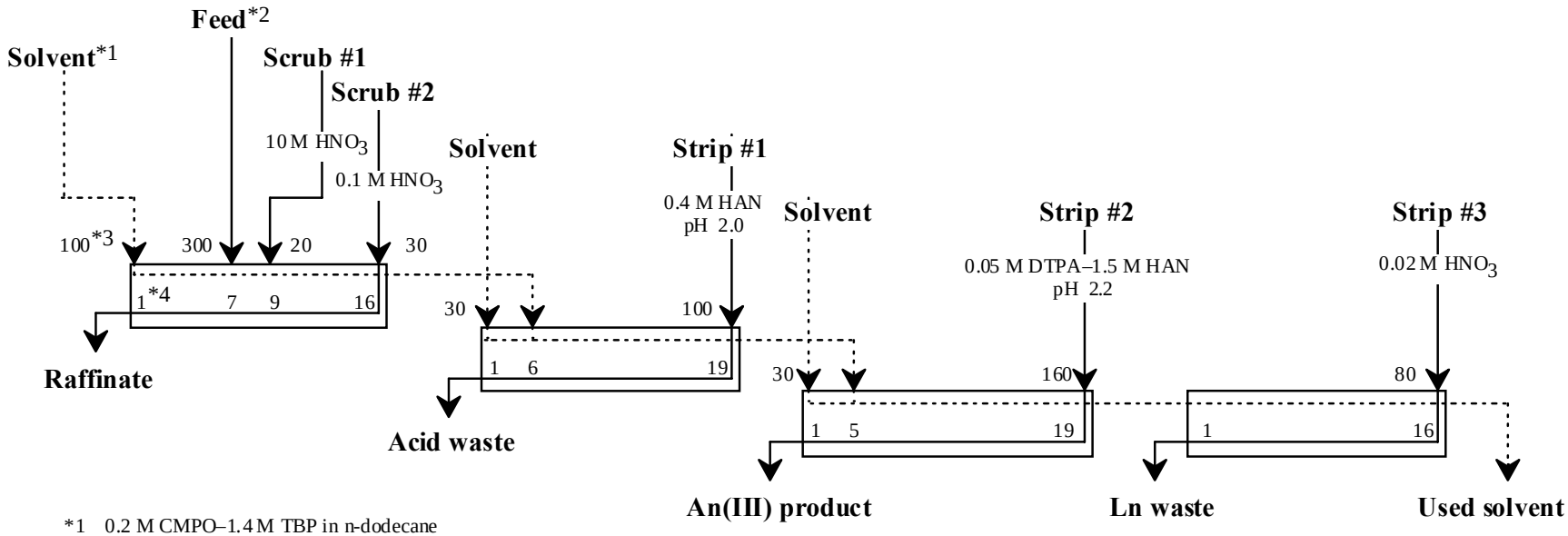
Results

- 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.



*1 0.2 M CMPO–1.4 M TBP in n-dodecane

*2 Simulated waste solution; 2.6 M HNO_3, 0.03 M $H_2C_2O_4$, FP, CP

*3 Flow rate, mL/h

*4 Stage number

Decontamination factor obtained in the counter-current experiment

(0.2 M CMPO–1.4 M TBP in n-dodecane)

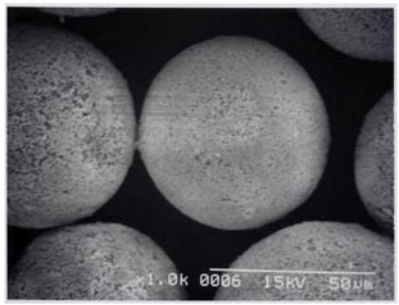
Cs	Pr	Nd	Sm
> 3100	> 10	1.8	1.9

The loss of Am and Cm obtained in the counter-current experiment

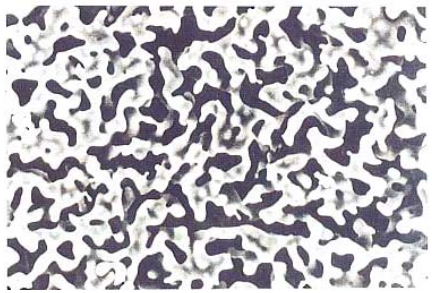
Nuclides	Loss (%)
Am-241	0.16
Cm-242	0.39
Cm-244	0.33

MA recovery (Extraction chromatography)

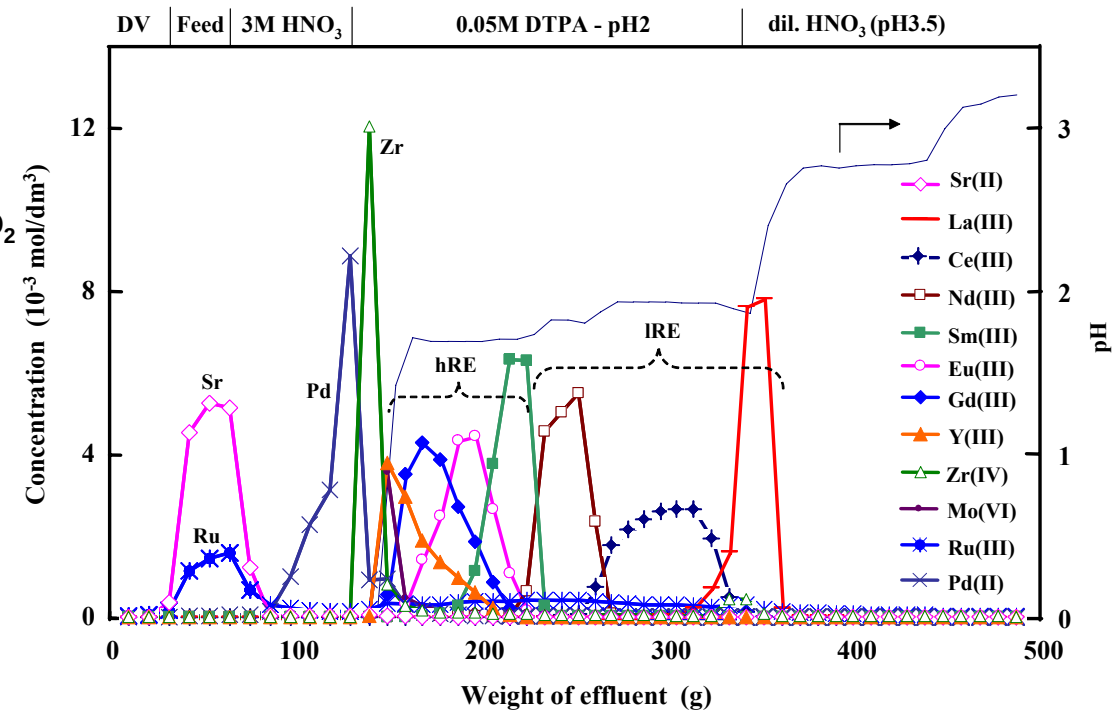
○SiO_2-P: porous SiO_2 covered by SDB polymer
○Resin: extactants（CMPO、TODGA、BTP, etc）immobilized in SiO_2-P



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 mmϕ 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.

4-Group Partitioning Process

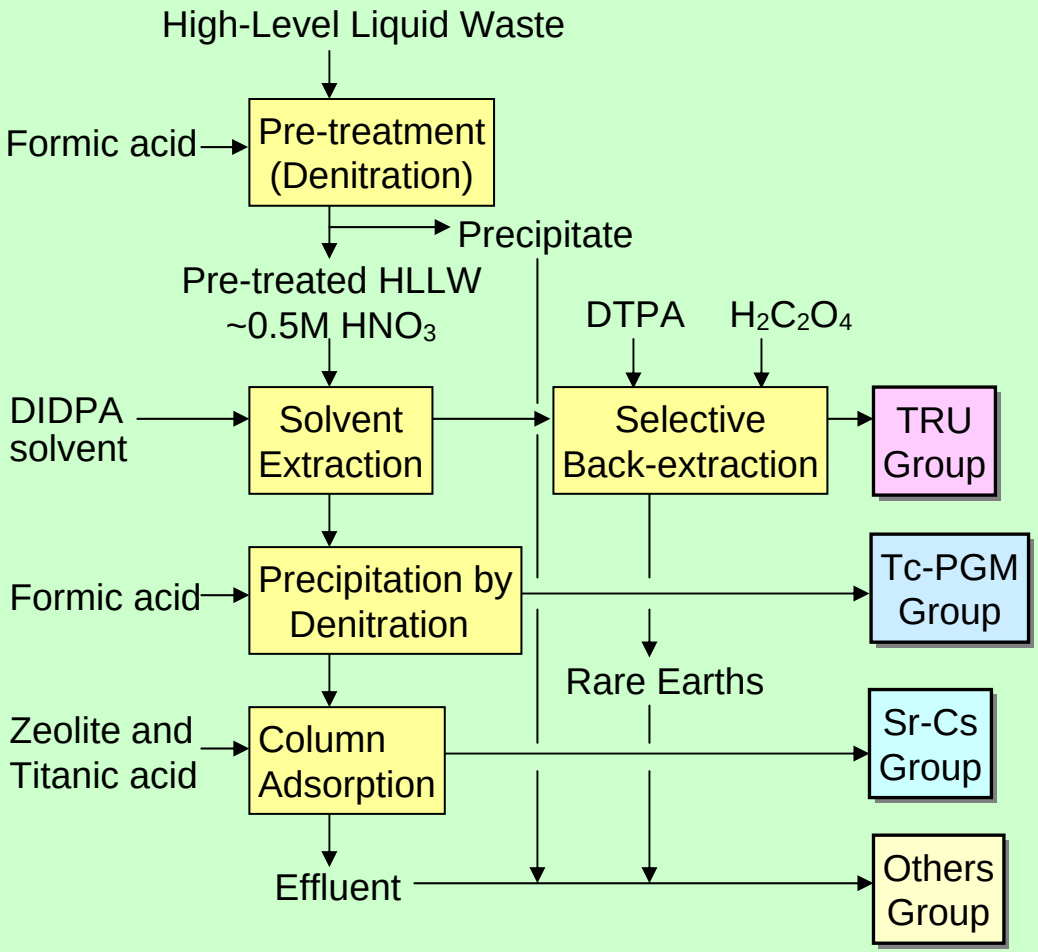


Fig. Flow Sheet of 4-Group Partitioning Process

- ✓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.

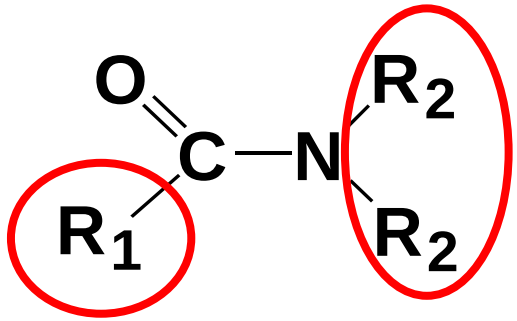
Selective extraction of U, Total recovery of TRU, Separation of MA/rare earths and Separation of Sr-Cs.

- 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.

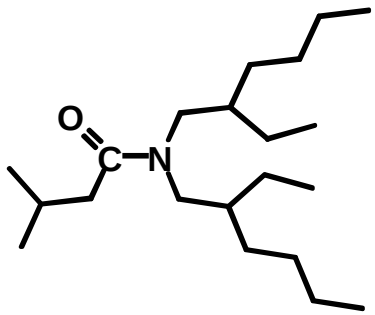
Selective separation of U (1/2)

Extraction of U(VI) by BAMA

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

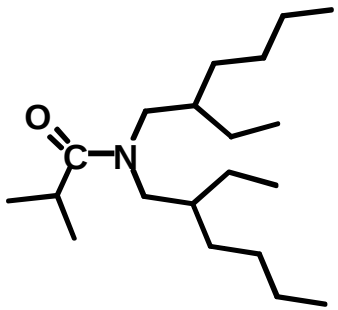


Branched Alkyl Monoamide(BAMA)



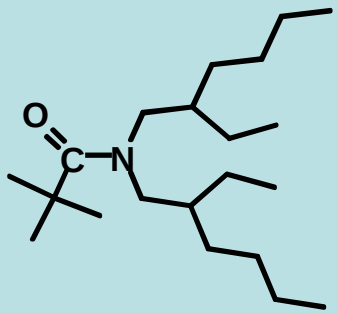
N,N-di-(2-ethyl)hexyl-3-methyl-butanamide (D2EHMBA)

SF:D_U/D_{Pu} = 3.6



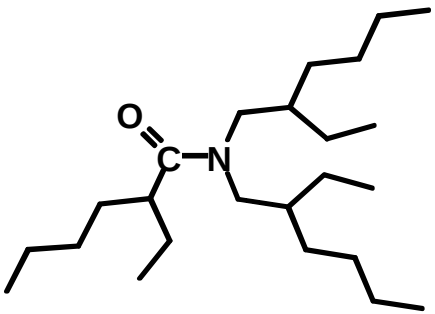
N,N-di-(2-ethyl)hexyl-2-methyl-propanamide (D2EHMPA)

79.4



N,N-di-(2-ethyl)hexyl-2,2-dimethylpropanamide (D2EHDMPA)

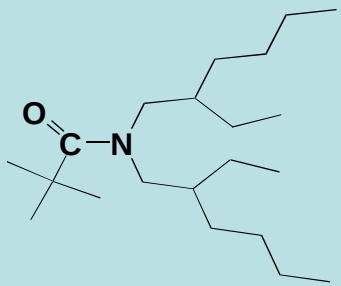
182



N,N-di-(2-ethyl)hexyl-(2-ethyl)hexanamide (D2EH2EHA)

71.3

Selective separation of U (2/2)

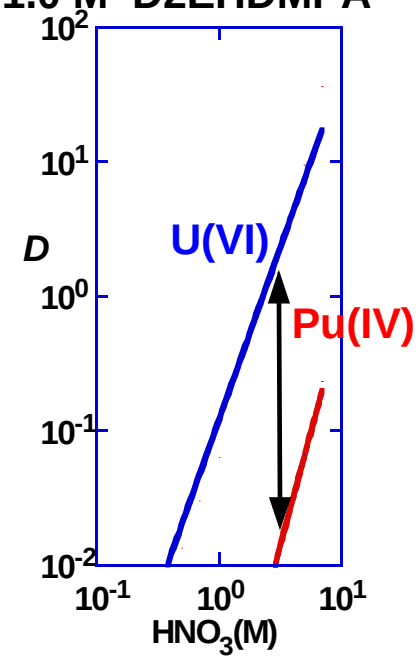


N,N-di(2-ethyl)hexyl-2,2-dimethyl-propanamide (D2EHDMPA)

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).

1.0 M D2EHDMPA

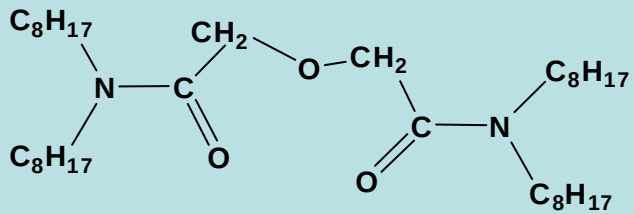


1.5 M D2EHDMPA (3.0 M HNO_3)

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) · · · · · · $D_{FP} \leqq 0.1$
4. 0.5 M U(VI)-Tc(VII) · · D_{Tc} = 0.4

Total recovery of TRU (1/2)

JAEA developed a novel extractant, N,N,N',N'-tetraoctyldiglycolamide (TODGA) for the recovery of actinide ions.

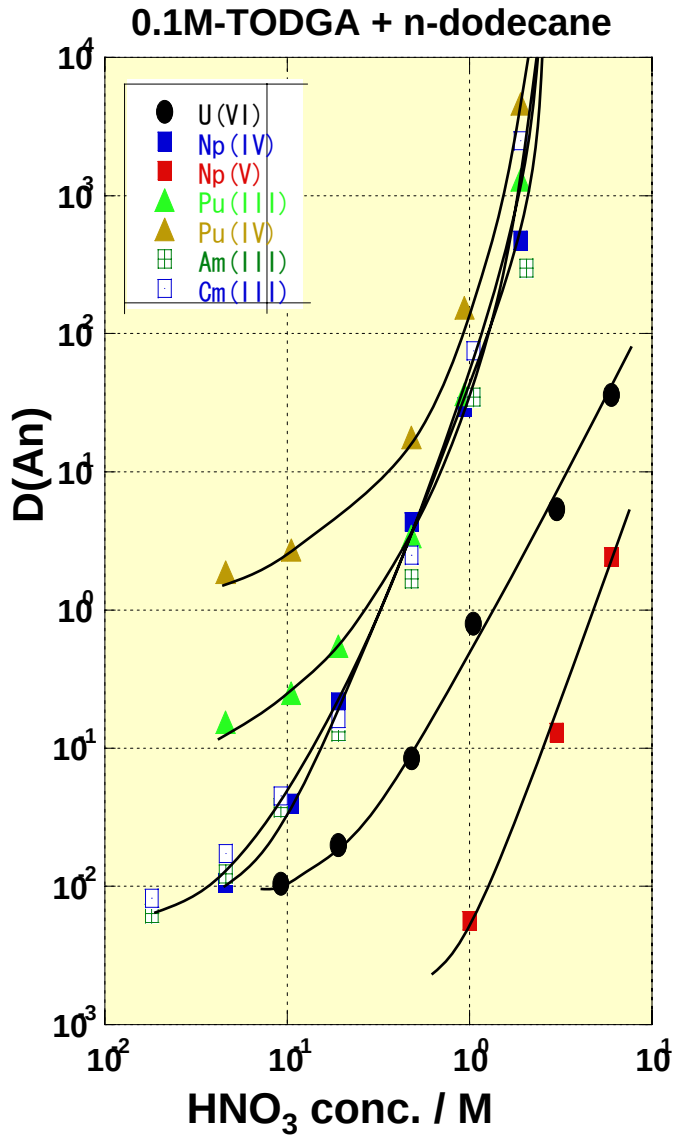


Structure of TODGA

- High solubility in n-dodecane

- Strong extractability for An(III) and An(IV) from higher HNO_3 solution

D(An) > 1000

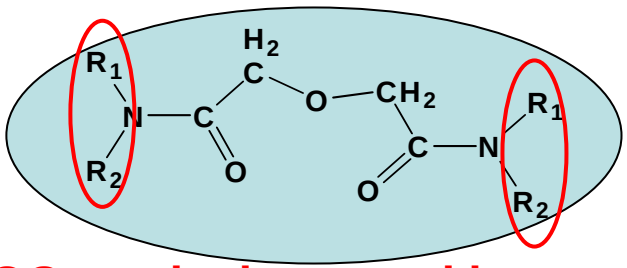


Total recovery of TRU (2/2)

Recent progress

-The limit of metal concentration (LOC)

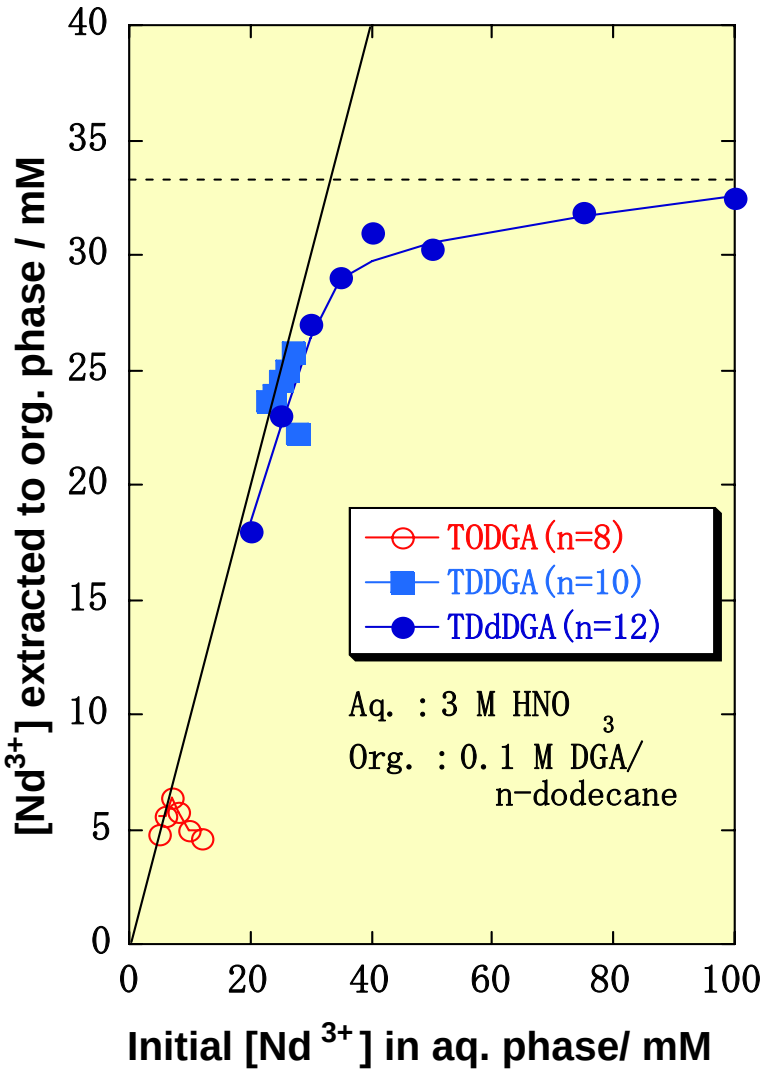
12 mM for Nd(III), 13 mM for Pu(IV)
in 0.2 M TODGA/3 M HNO_3



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)

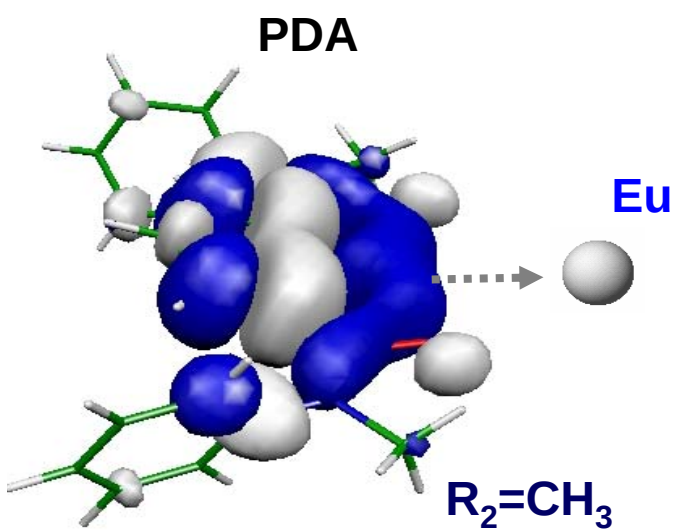


Separation of MA/rare earths (1/2)

N-type donor extractant for An(III)/RE(III) separation

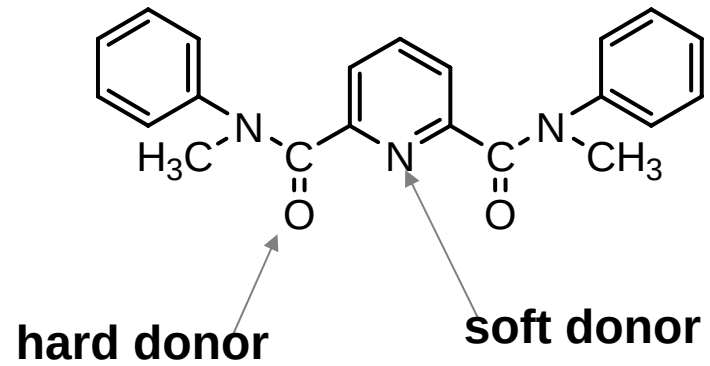
Separation in acidic solution and chemical stability were problem.

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



Electronic structure of PDA molecule (calculated by Gaussian98)

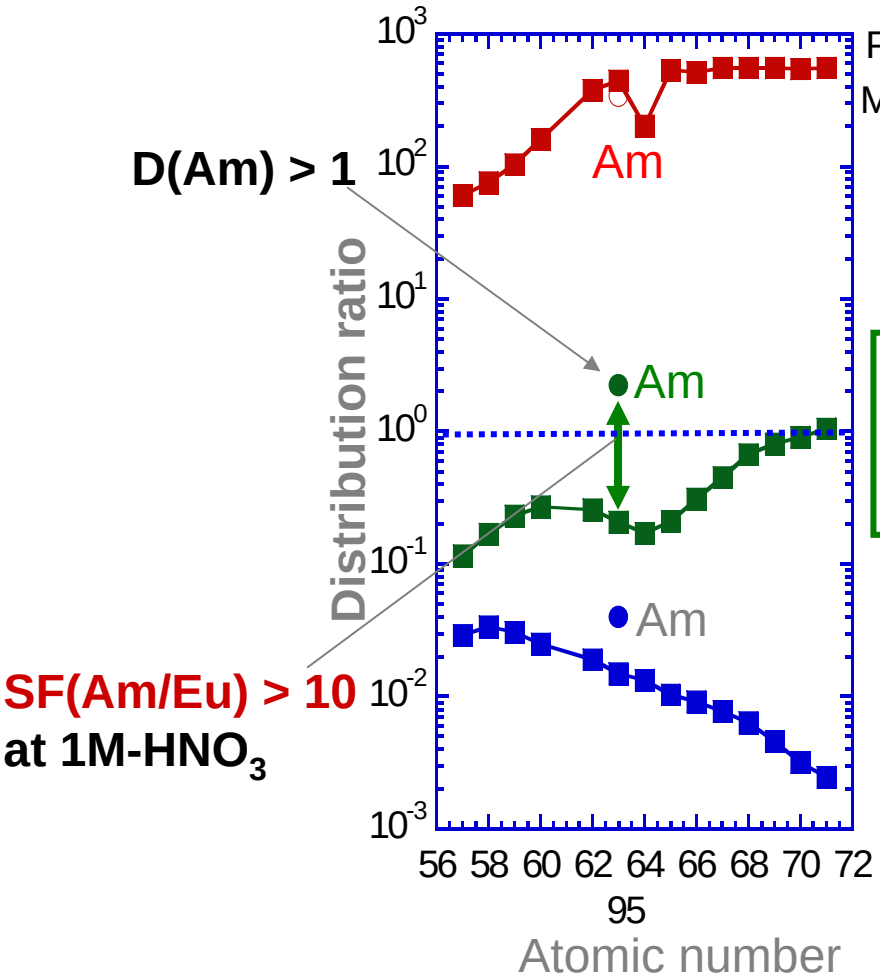
NO-donor type extractant
Pyridine amide

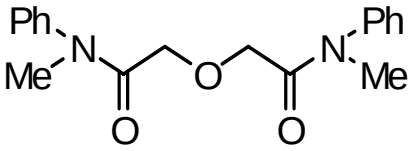


Molecular design is required to improve the SF(Am/Lns)

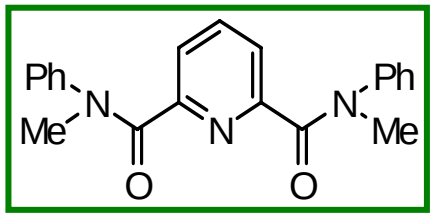
Separation of MA/rare earths (2/2)

Am/Ln separation from 1M-HNO_3

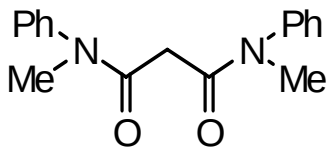




DGA

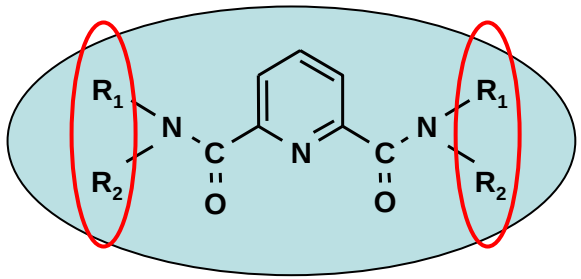


PDA



MA

- **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=Ph, R_2=CH_3

⇩

R_1=Ph, R_2=C_nH_{2n+1}
(n=4, 8, …)

Organic phase:
0.1M PDA + Chloroform

Separation of Sr-Cs (1/2)

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 HNO_3
  - 3300 ml g^{-1} (equilibrium, 4 days)
  - 2320 ml g^{-1} (24 h)
- No decrease of exchange capacity after leaching by 3M HNO_3 at 90 ºC for 2 days

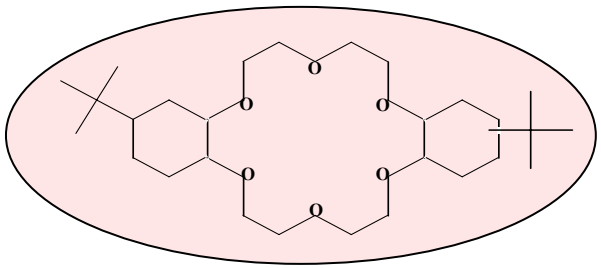
Na-Ti-Ta-O

- Nature
  - Ti:Ta = 0.26
  - Crystalline, pyrochlore
- Kd of Cs from 3 M HNO_3
  - 650 ml g^{-1} (equilibrium, 2 weeks)
  - 100 ml g^{-1} (24 h)
- No decrease of exchange capacity after leaching by 3M HNO_3 at 90 ºC for 2 days

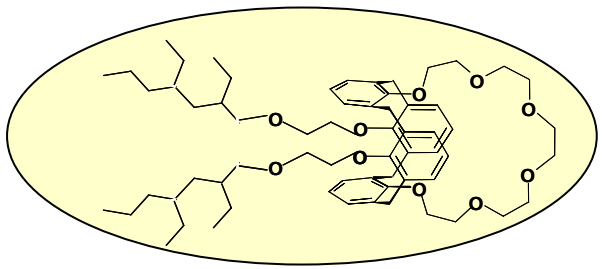
Separation of Sr-Cs (2/2)

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

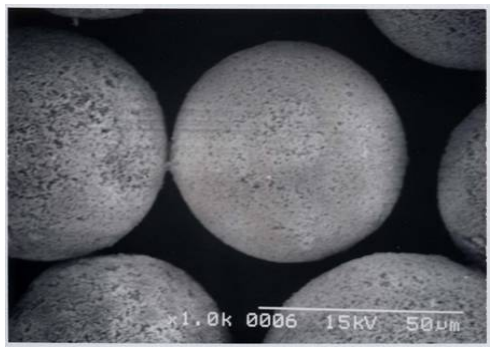


(1) di-t-butylcyclohexano-18-crown-6 (DtBuCH18C6)



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

- Porous-silica-based (composite with macro reticular type polymer) material (SiO_2-P) as a <u>non-conventional support</u>



SiO_2-P support

- 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).

Conclusion

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)