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

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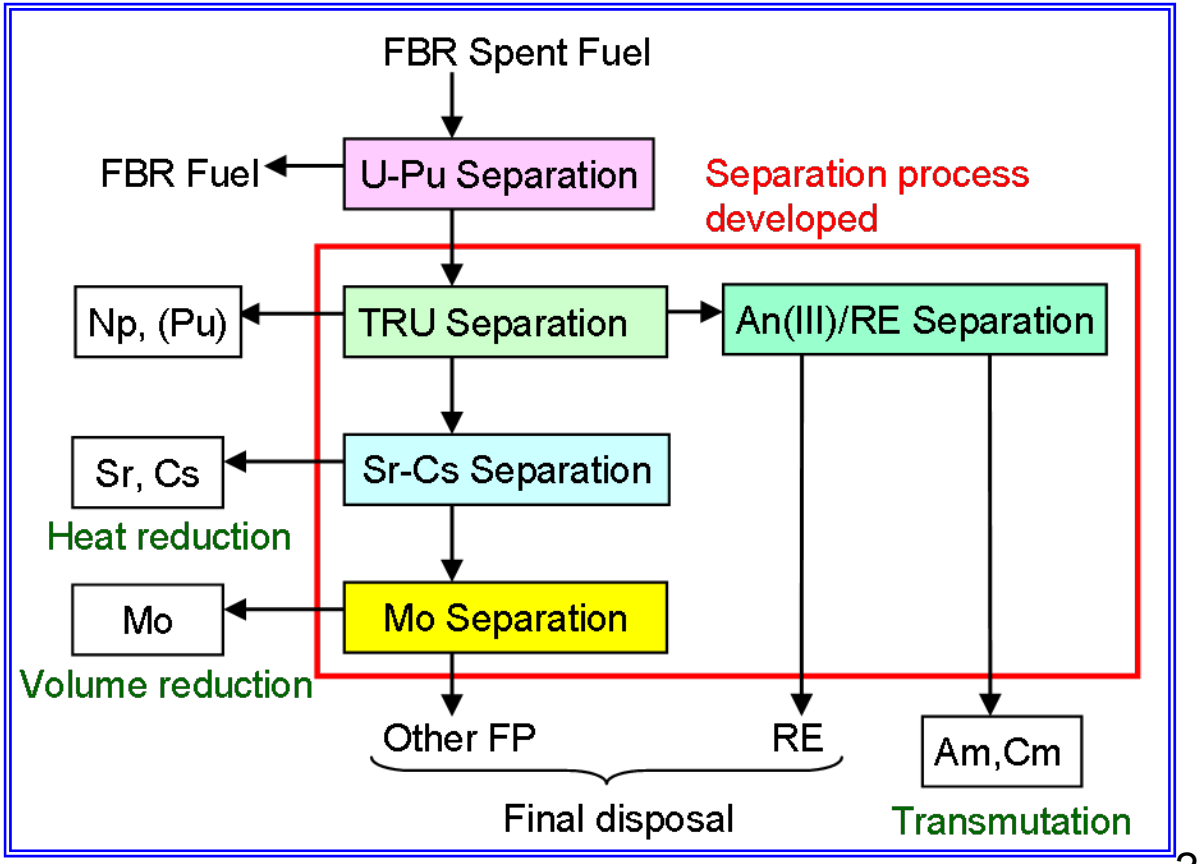
Concept of the process development

- 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)

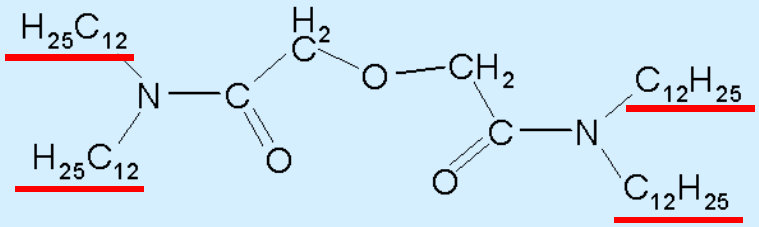
Purpose of the separation	• TRU separation for transmutation • FP separation for reduction of volume and heat in HLW

- 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

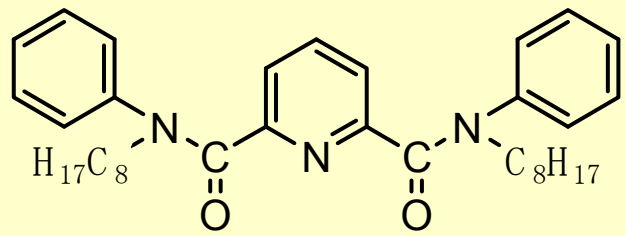


Extractants and adsorbents applied



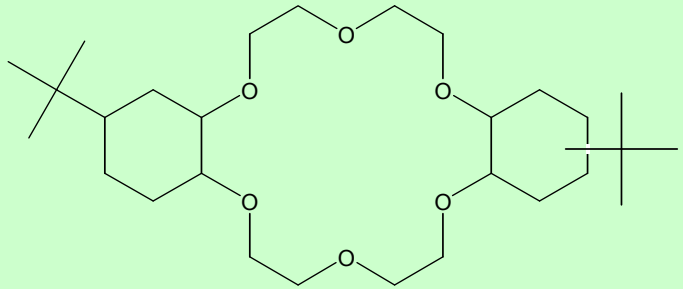
TDdDGA (Dodecyl-DGA) for TRU separation

N,N,N'N'-tetradodecyldiglycolamide



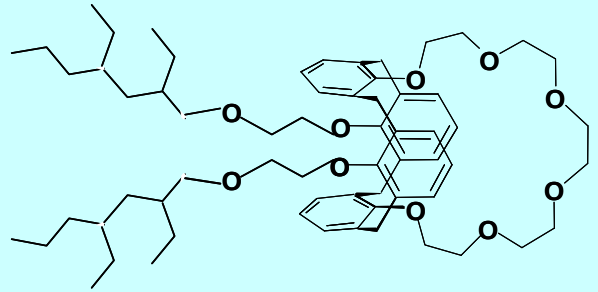
Oct.PDA for An(III)/RE separation

N,N'-dioctyl-*N,N'*-diphenyl-pyridine-2,6-dicarboxyamide



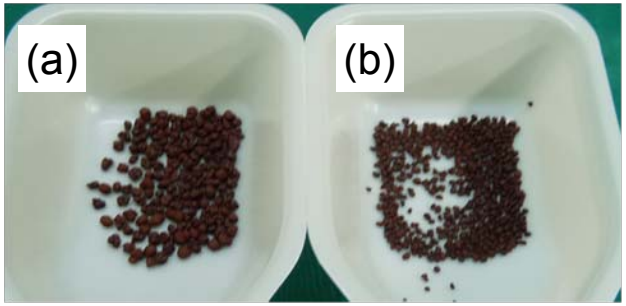
DtBuCH18C6 for Sr separation

di-t-butylcyclohexano-18-crown-6



Calix-crown R14 for Cs separation

1,3-[(2,4-diethyl-heptylethoxy)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 HNO_3 concentration
- Very low D of An(III) at low HNO_3 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).
  H_2O_2 was applied. H_2O_2 also reduces D of Zr.

Org. phase : 0.1M TDdDGA - *n*-dodecane
Aq. phase : 0.1M HEDTA - 0.5M H_2O_2 - HNO_3

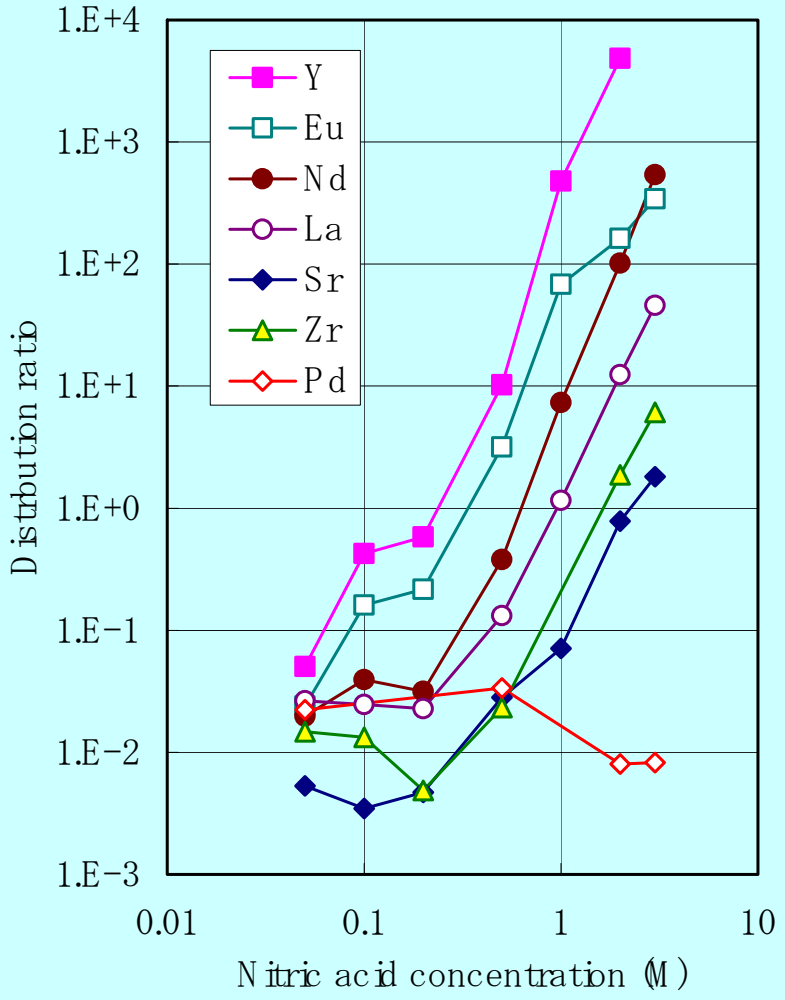


Fig. Dependence of distribution ratio on the HNO_3 concentration in the presence of HEDTA and H_2O_2

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.

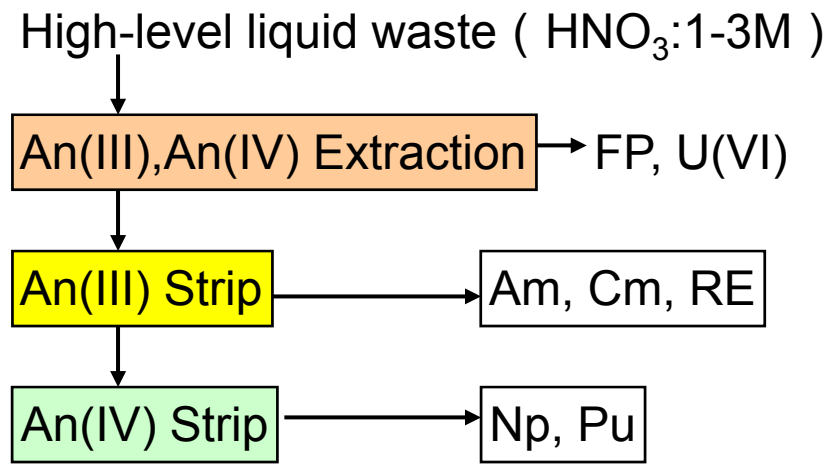
- It contains residual U, Pu and Np, and these three actinides should be controlled.

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 HNO_3.
- 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



1) Am test
2) High loading test

Continuous extraction test with Am (Am Test)

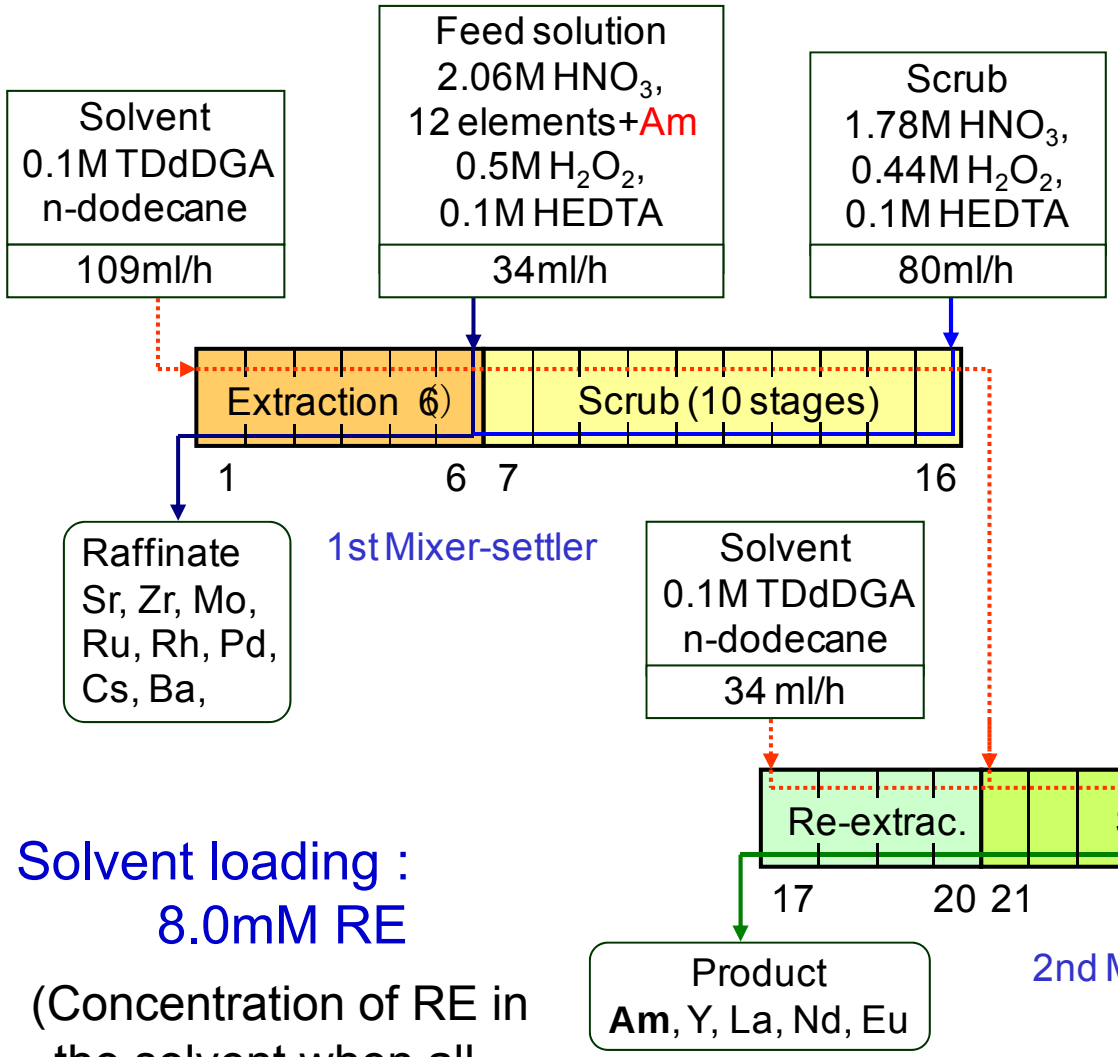


Table Composition of the feed solution

Element	Concentratio (mM)	Element	Concentratio (mM)
Sr	1.65	Pd	7.71
Y	0.93	Cs	10.22
Zr	9.59	Ba	3.92
Mo	6.58	La	7.80
Ru	9.85	Nd	13.84
Rh	2.94	Eu	3.05
HNO_3	2.0 M	Am-241	6×10^3 Bq/ml

Solvent loading :
8.0mM RE

(Concentration of RE in the solvent when all the RE are extracted without accumulation.)

No problem in the mixer-settler operation

Good phase separation, No third phase formation

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

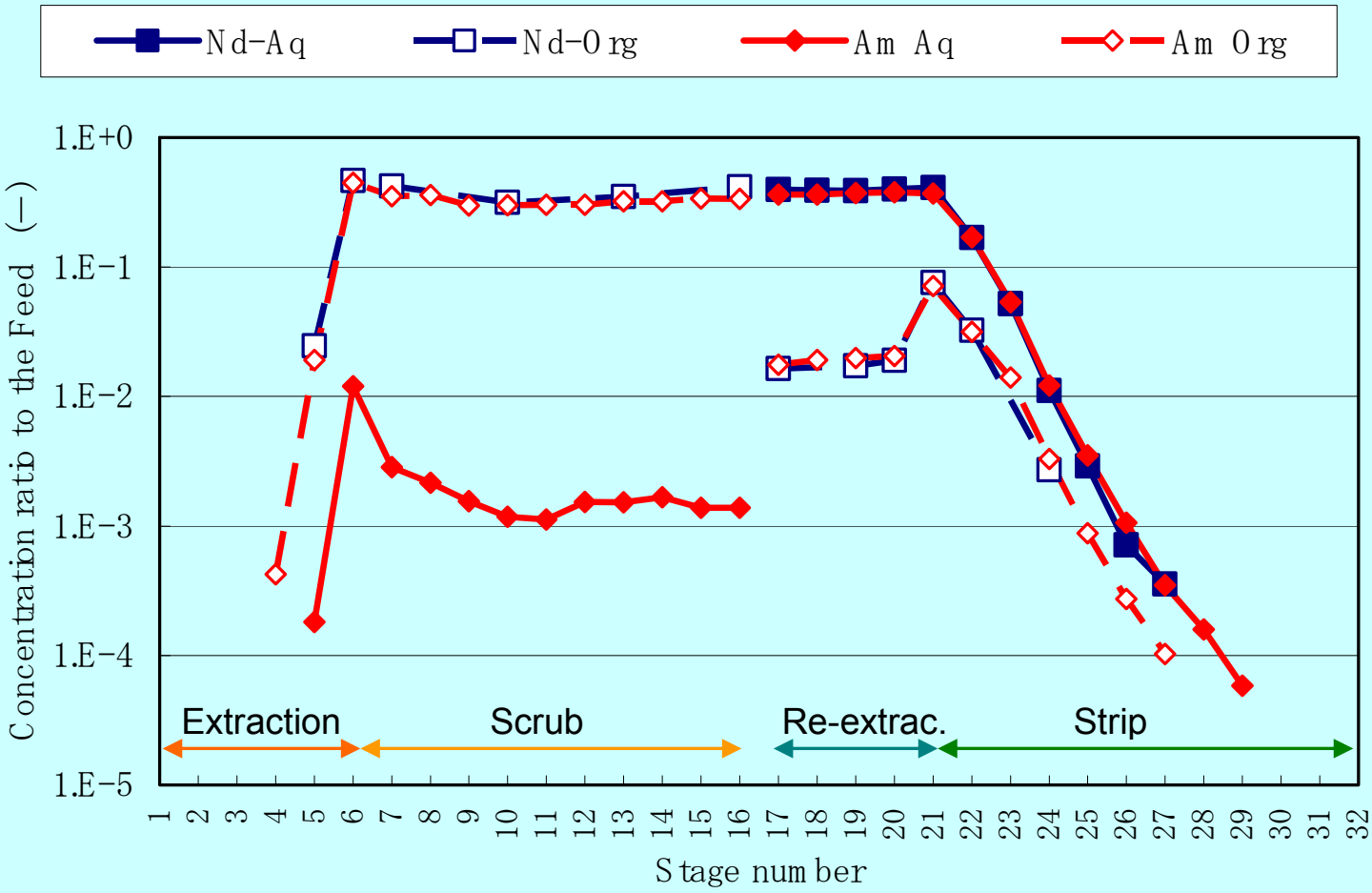


Fig. Concentration profiles of Am and Nd in the first and second mixer-settler, plotted with concentration ratio to the feed solution

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

No difference in concentration profiles of Am and Nd.
→ Nd is a almost perfect substitute for Am in this system.

Results of Am Test (2) - Sr, Zr, Pd behavior -

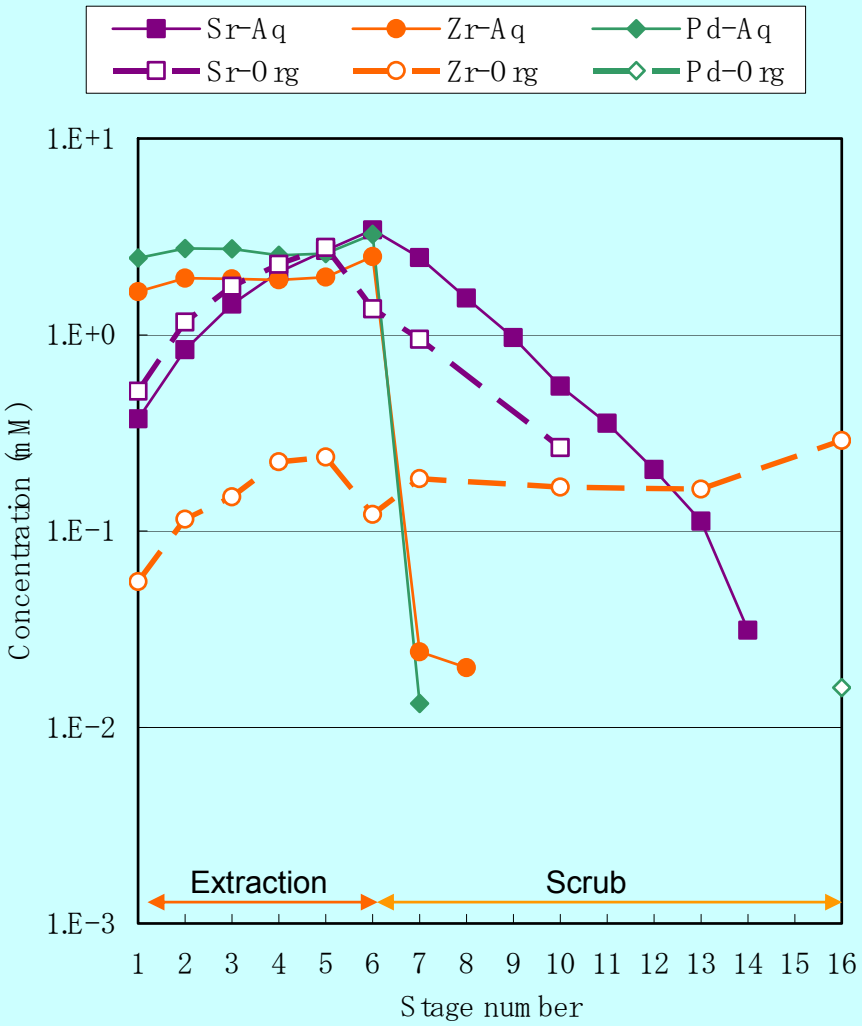


Fig. Concentration profiles of Sr, Zr, Pd in the first mixer-settler

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

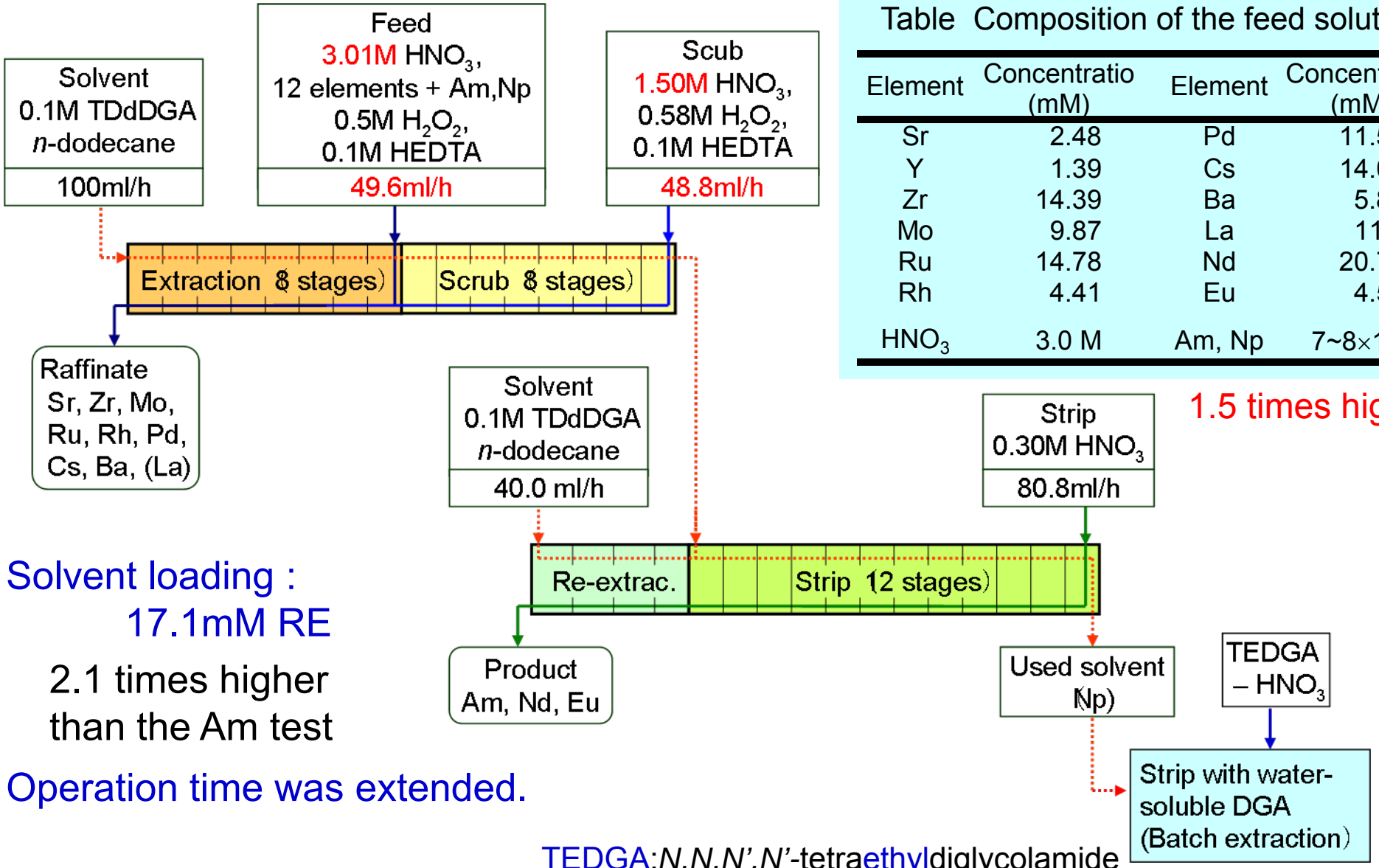


Table Composition of the feed solution

Element	Concentratio (mM)	Element	Concentratio (mM)
Sr	2.48	Pd	11.56
Y	1.39	Cs	14.07
Zr	14.39	Ba	5.87
Mo	9.87	La	11.7
Ru	14.78	Nd	20.75
Rh	4.41	Eu	4.57
HNO_3	3.0 M	Am, Np	$7\sim8\times10^3$

1.5 times higher

Solvent loading :
17.1mM RE

2.1 times higher than the Am test

Operation time was extended.

TEDGA:*N,N,N',N'*-tetraethyldiglycolamide

Results of High loading Test - Am, Np -

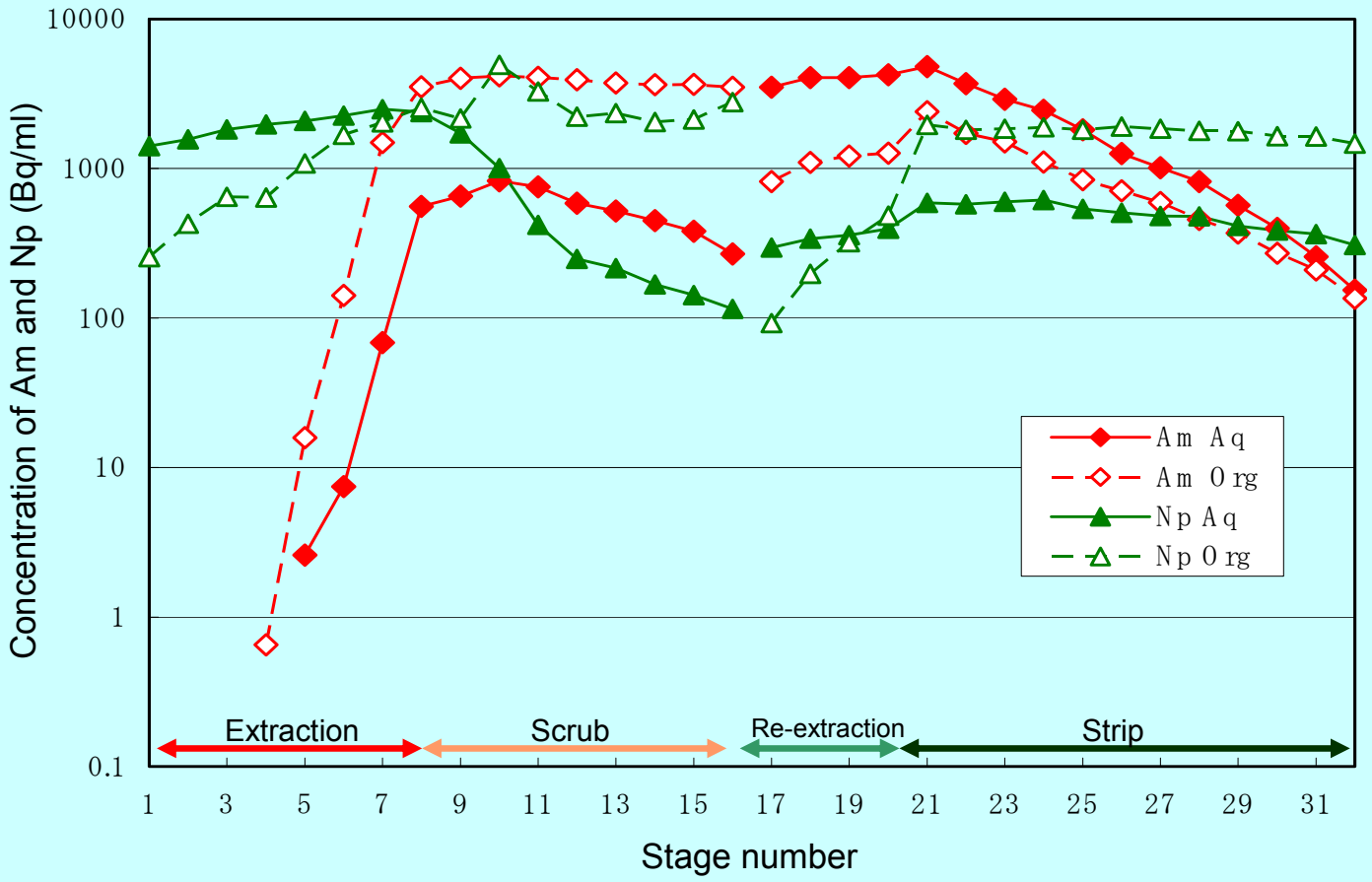


Fig. Concentration profiles of Am and Np in the first and second mixer-settler in the High loading test

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.

Comparison of concentration profiles

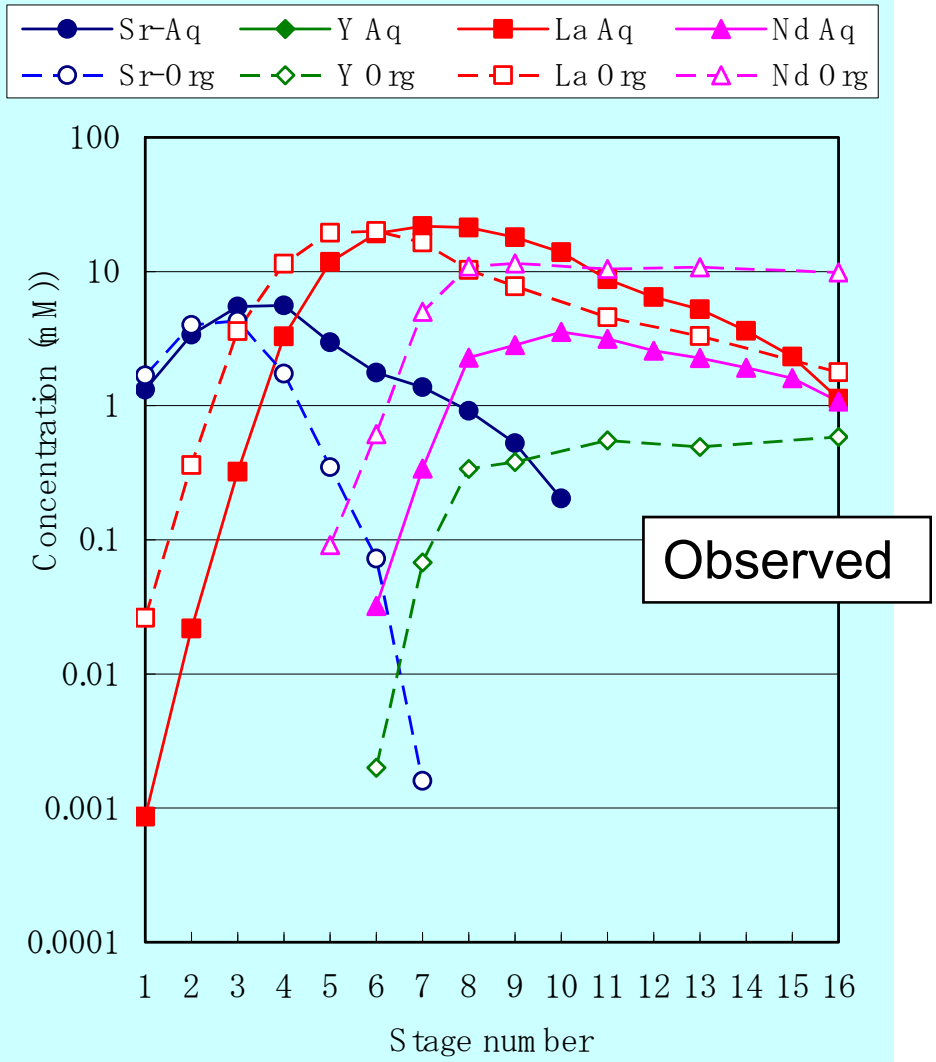


Fig. Concentration profiles of Sr and RE in the High loading test.

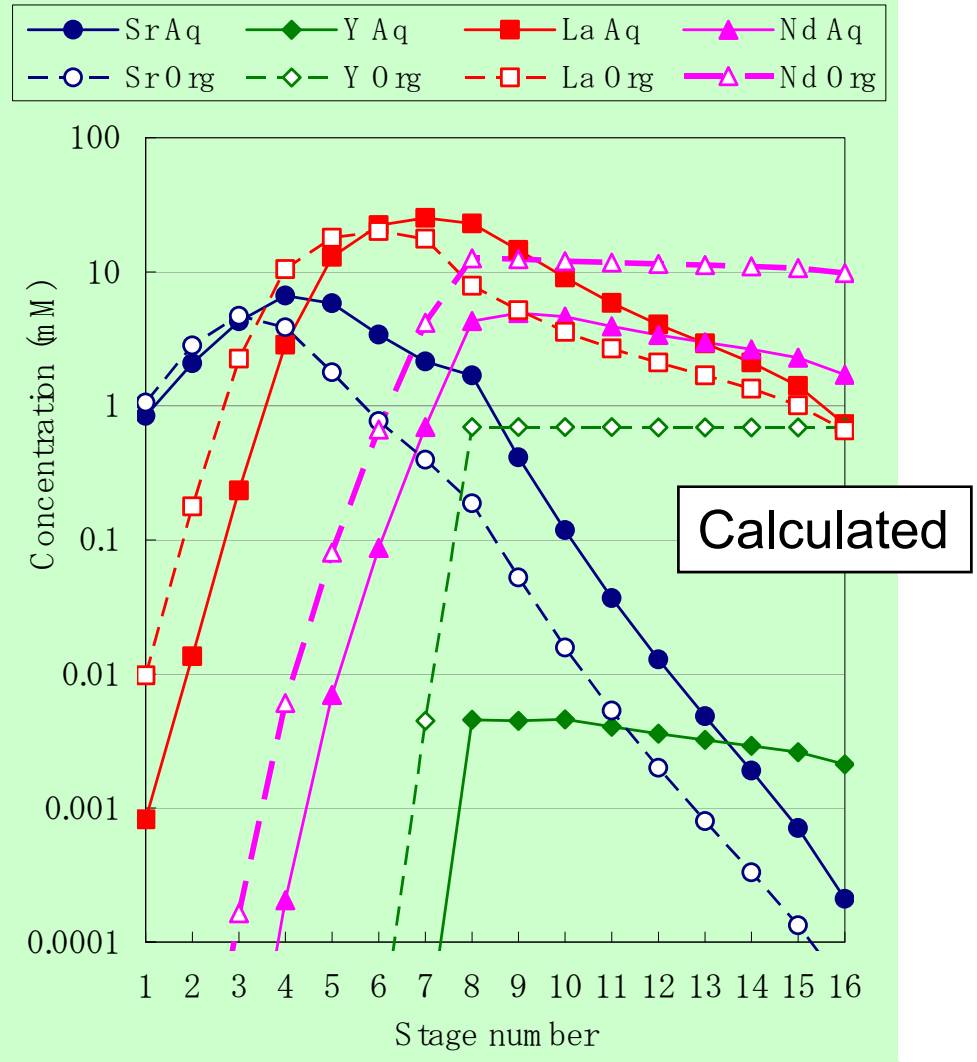


Fig. Concentration profiles of Sr and RE at a transient state calculated by simulation code, PARC-MA.

Results of TRU extraction step development

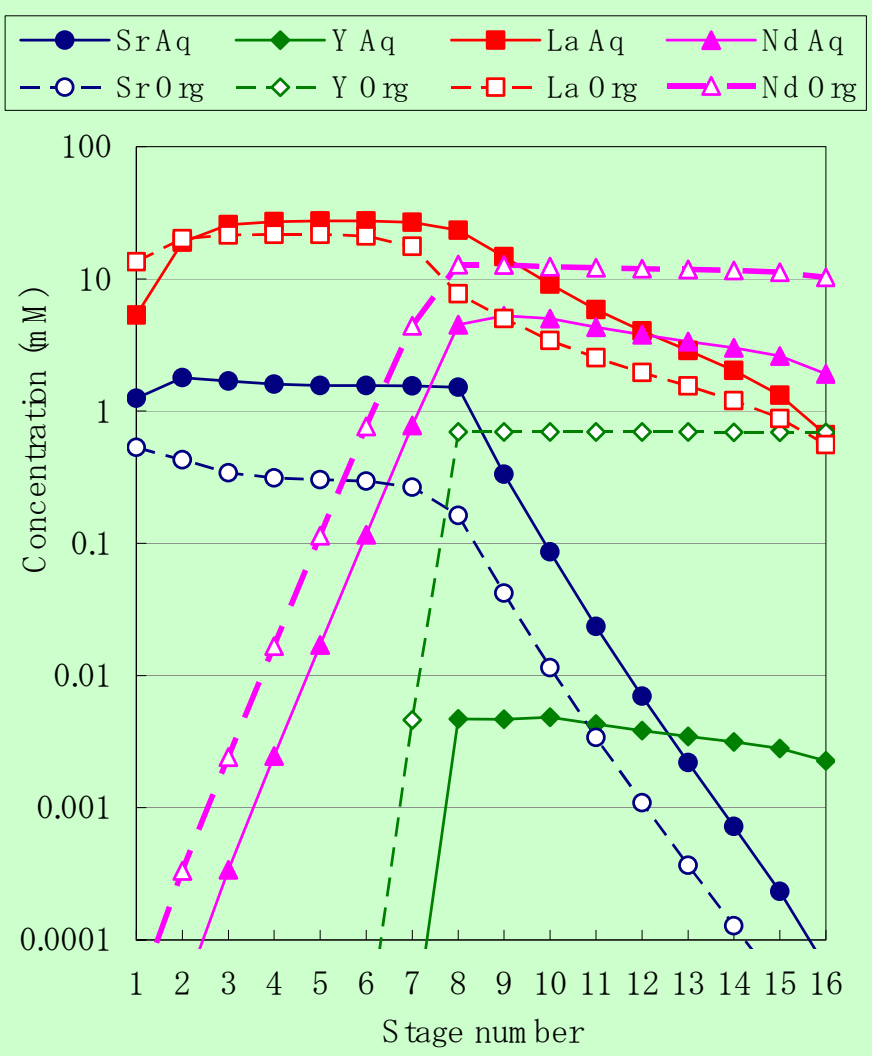


Fig. Concentration profiles of Sr and RE calculated by simulation code, PARC-MA at a steady state .

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.

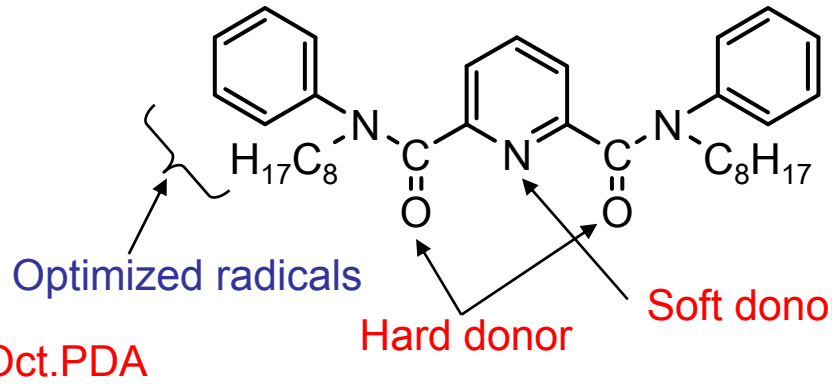
Element behavior in the TRU extraction step

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

An(III)/RE separation : PDA extractant

Hetero-donor type extractant,
pyridine-dicarboxyamide



Oct.PDA
: N,N'-dioctyl-N,N'-diphenyl-pyridine-2,6-dicarboxyamide

- Very stable in HNO_3 media
- Separation factor is not so high, particularly in extraction with *n*-dodecane solution

➡ Applied to extraction chromatography

Distribution coefficient at 5M HNO_3
Am:22.8, Nd:4.8, Eu:7.8, Gd:8.4 (cm^3/g)

Separation factor Am/Nd:4.8, Am/Gd:2.7

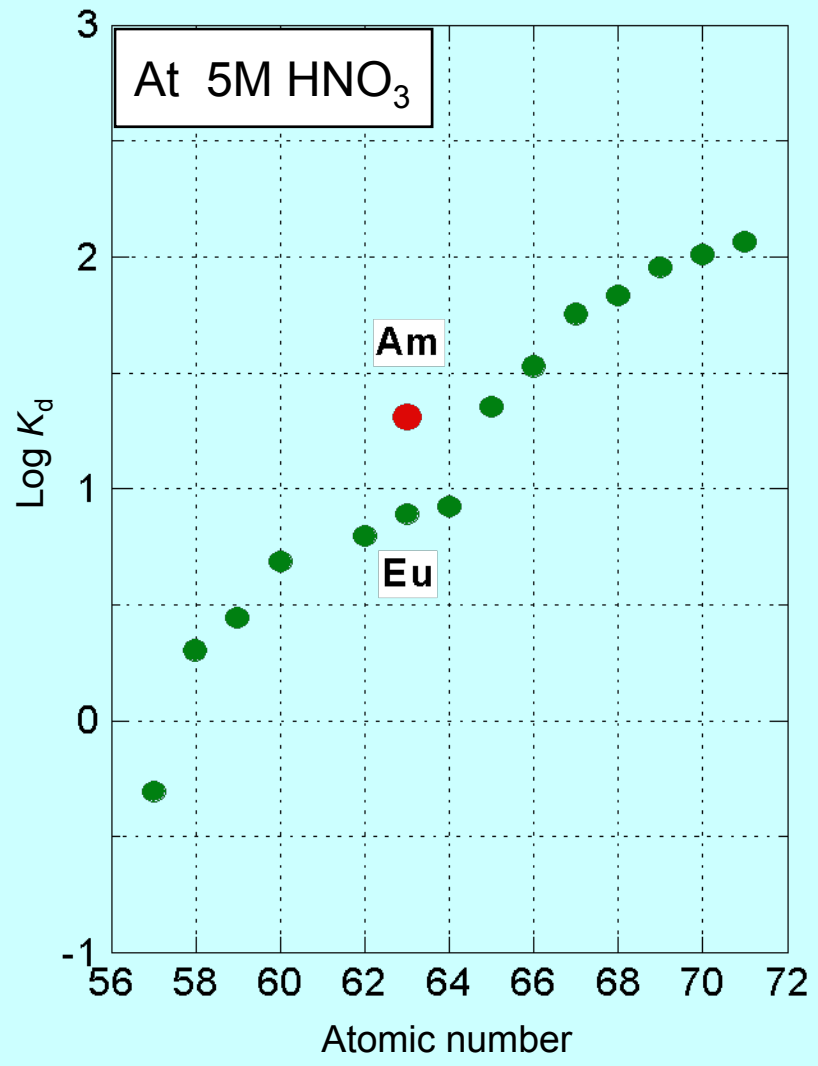


Fig. Distribution coefficient (K_d) obtained by batch adsorption experiments

Results of Am/Eu separation

Oct-PDA was successfully impregnated into Amberlite XAD-4 resin.

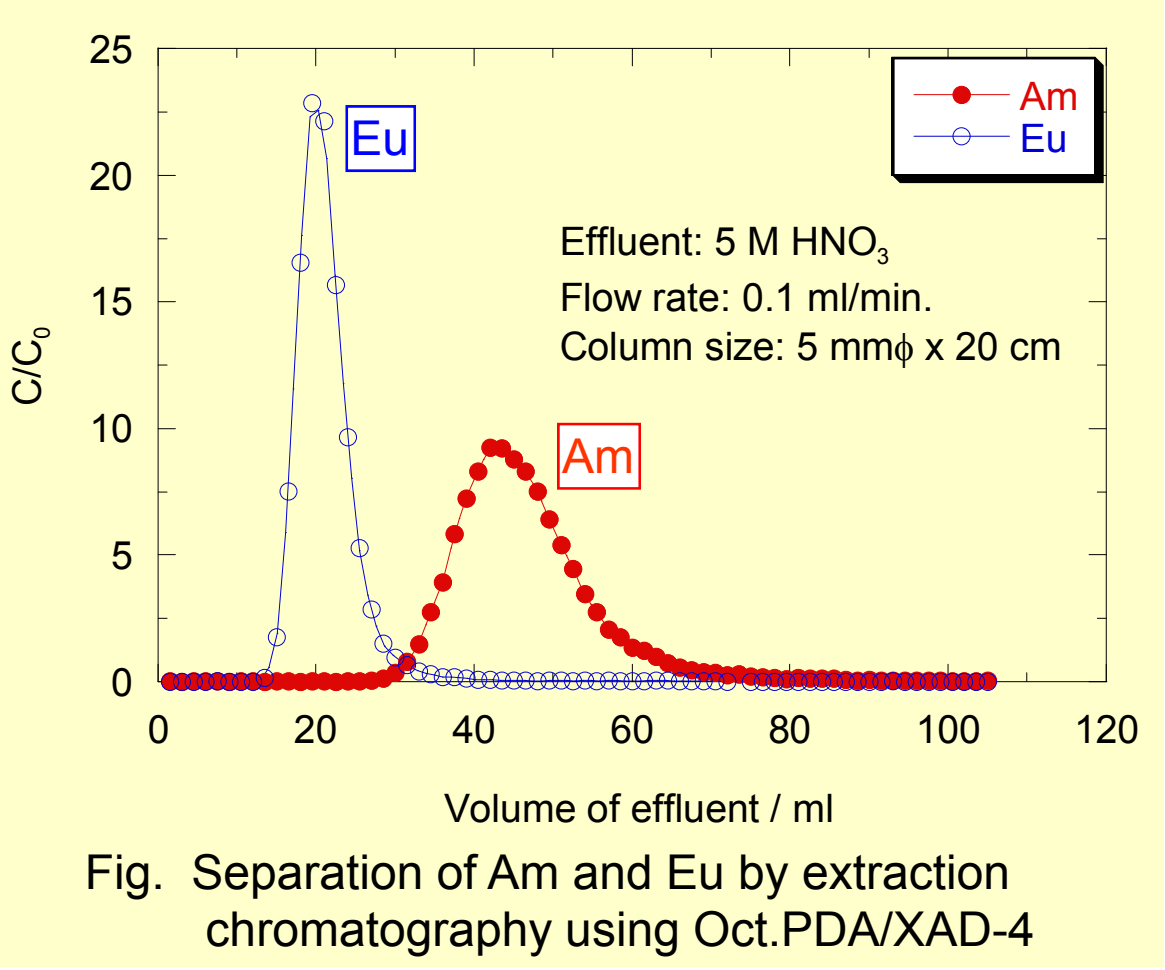
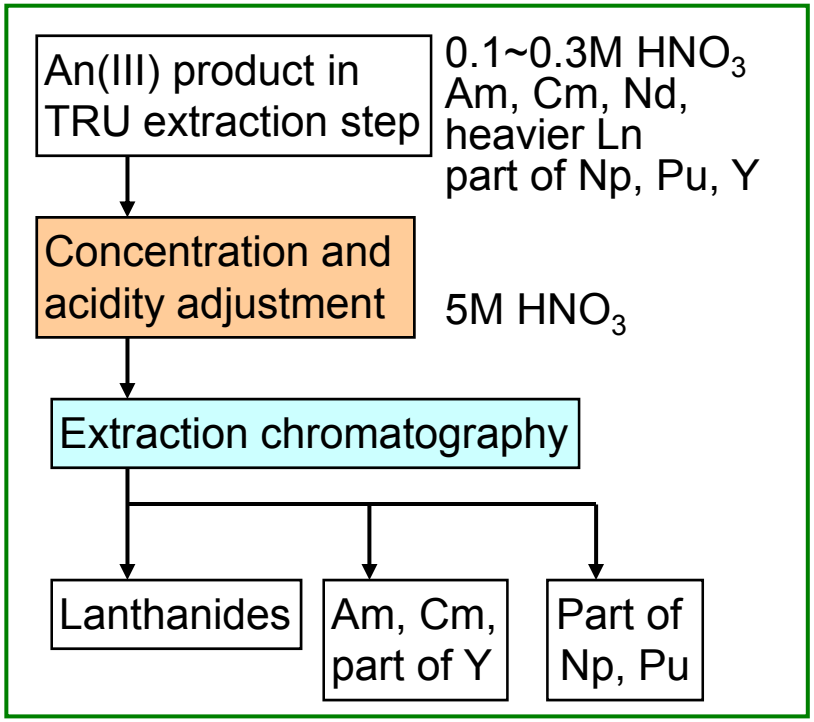


Fig. Separation of Am and Eu by extraction chromatography using Oct.PDA/XAD-4

Sufficient separation of Am(III) from Eu(III) in 5 M HNO_3 was achieved by Oct-PDA/XAD-4 column.

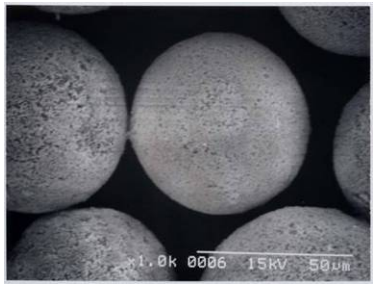
Np(IV) and Pu(IV) can be eluted with $H_2C_2O_4$.



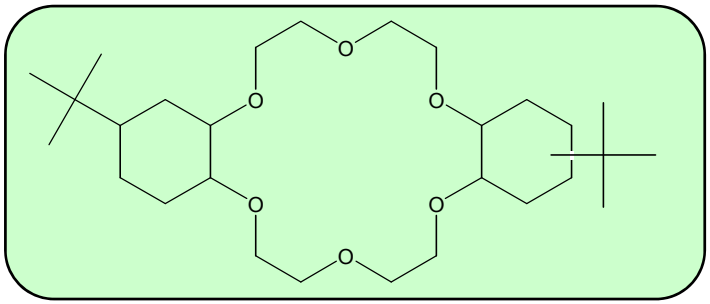
Concept of Sr-Cs separation process development

- 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

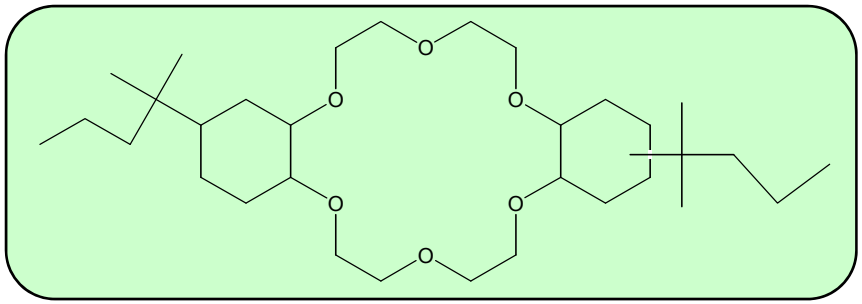
Porous silica particles coated with copolymer of formylstyrene and divinylbenzene (SiO_2-P) was used to support the extractant.



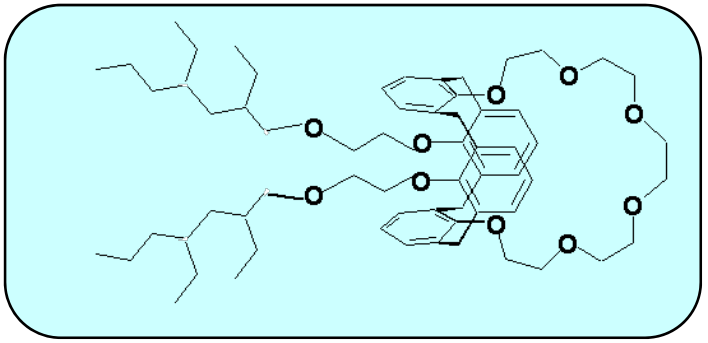
SiO_2-P



DtBuCH18C6 for Sr separation



DtHexCH18C6 for Sr separation → Selection of extractant



Calix-crown R14 for Cs separation

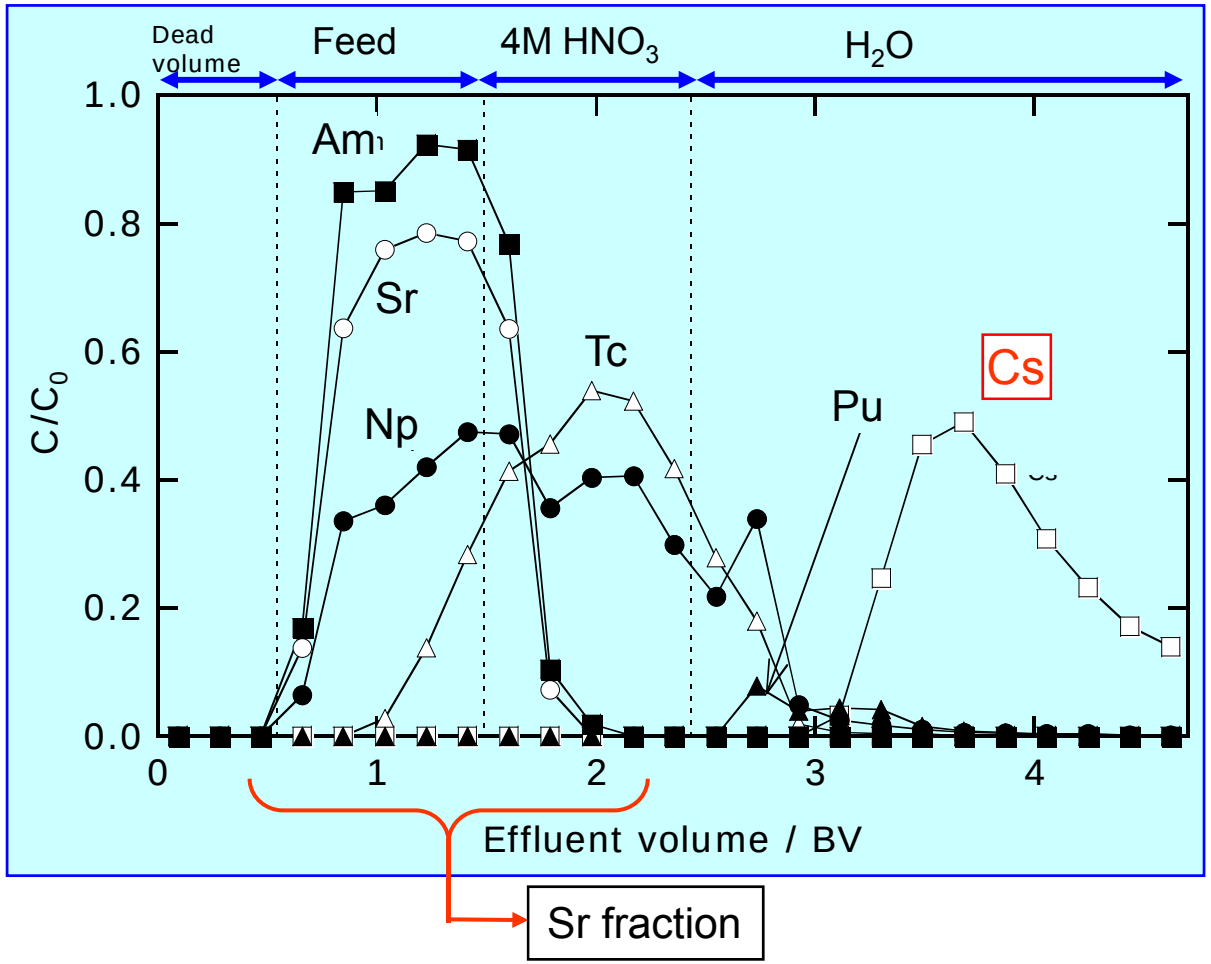
Modifier is required to adsorb Sr and Cs.

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

→
- Selection of modifier
- Optimum molar ratio of the modifier to the extractat

Column adsorption test for Cs separation

Cs separation with Cs adsorbent column



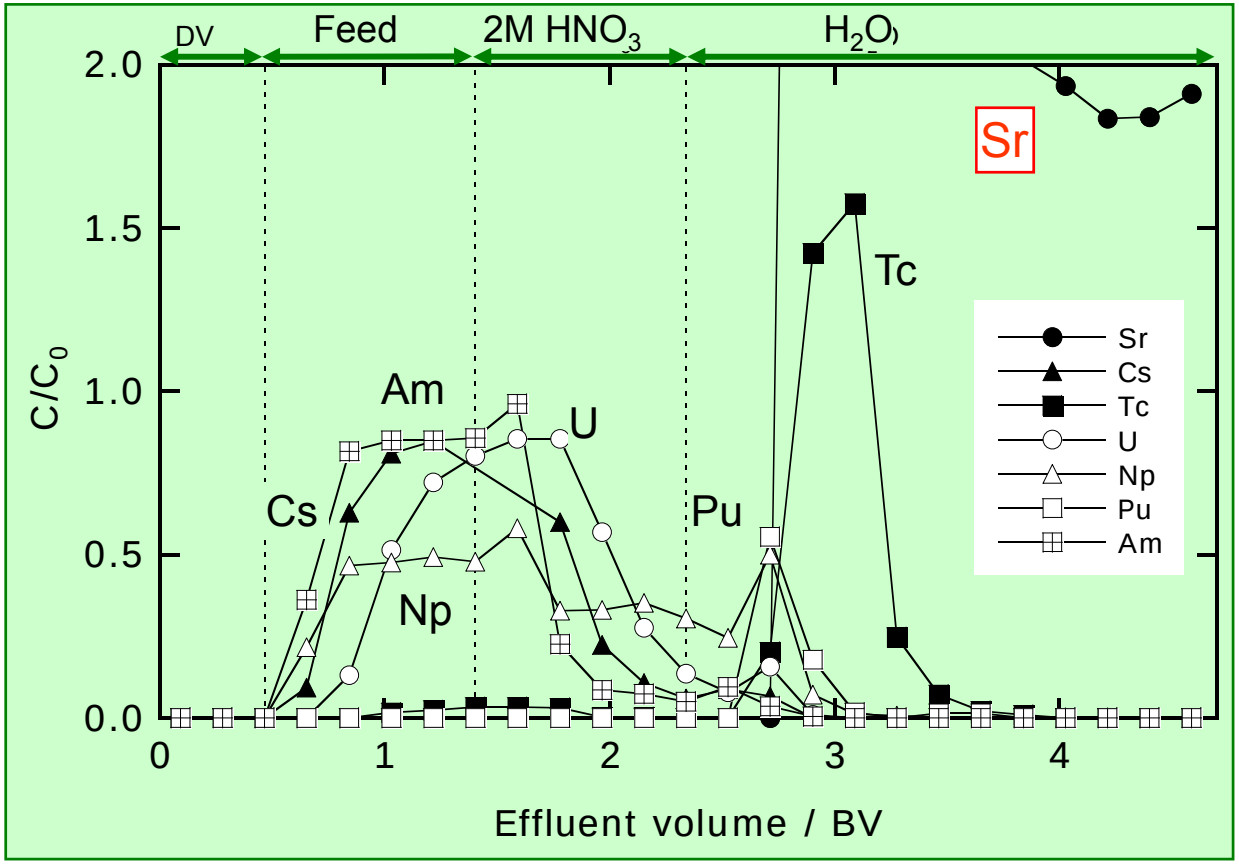
Extractant : Calix-crown R14
Modifier : 1-Hexadecanol
Modifier/Extractant = 4.17
Column : 10mmϕ×240mmH
Flow rate : 1cm^3/min
Feed : 4M HNO_3

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

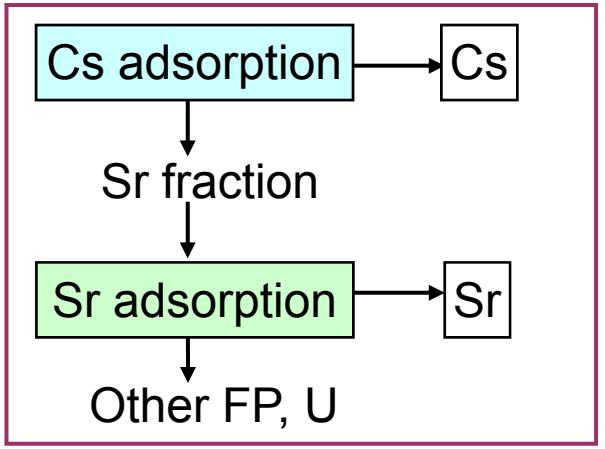
Sr separation with Sr adsorbent column



Extractant : DtBuCH18C6
Modifier : 1-Hexadecanol
Modifier/Extractant=1.25
Column : 10mmϕ×280mmH
Flow rate : 1cm^3/min
Feed : 2M HNO_3

Sr was eluted finally with water.

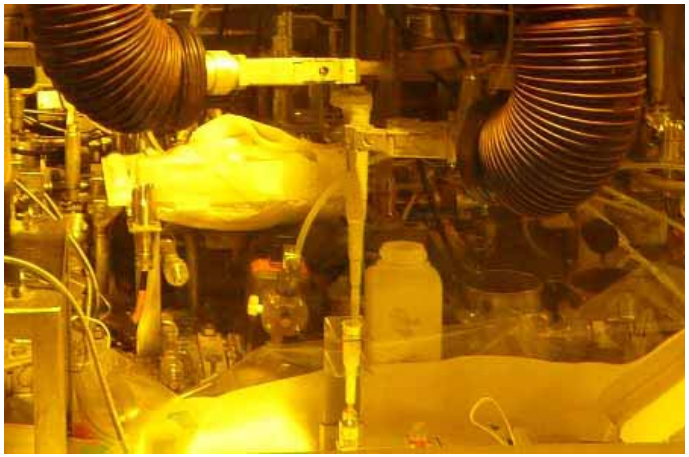
Cs should be separated before Sr separation.

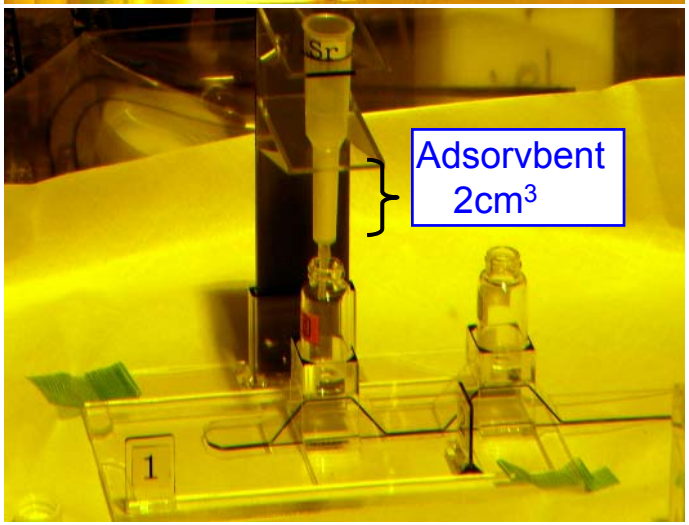


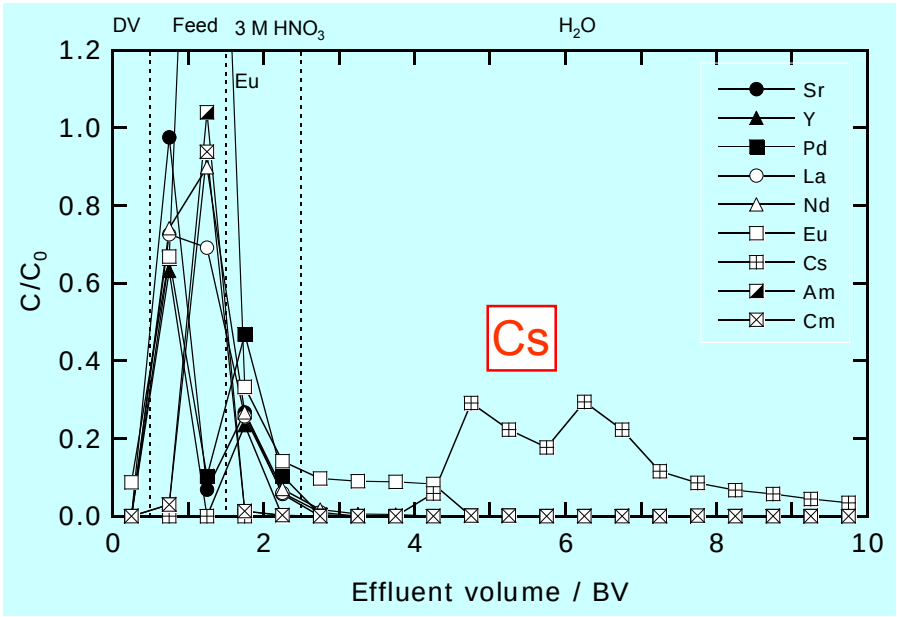
The adsorbent for Sr was less stable compared with the adsorbent for Cs because of the elution of the extractant.

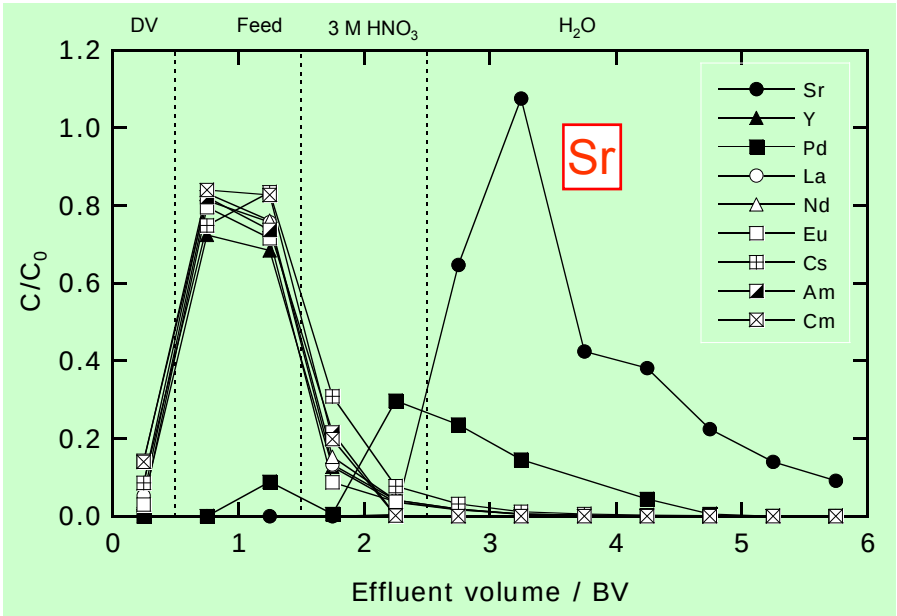
Cs-Sr separation test with a genuine HLLW

Feed: HLLW ($2cm^3$) Scrub: 3M HNO_3($2cm^3$)
Eluent: H_2O









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

↓

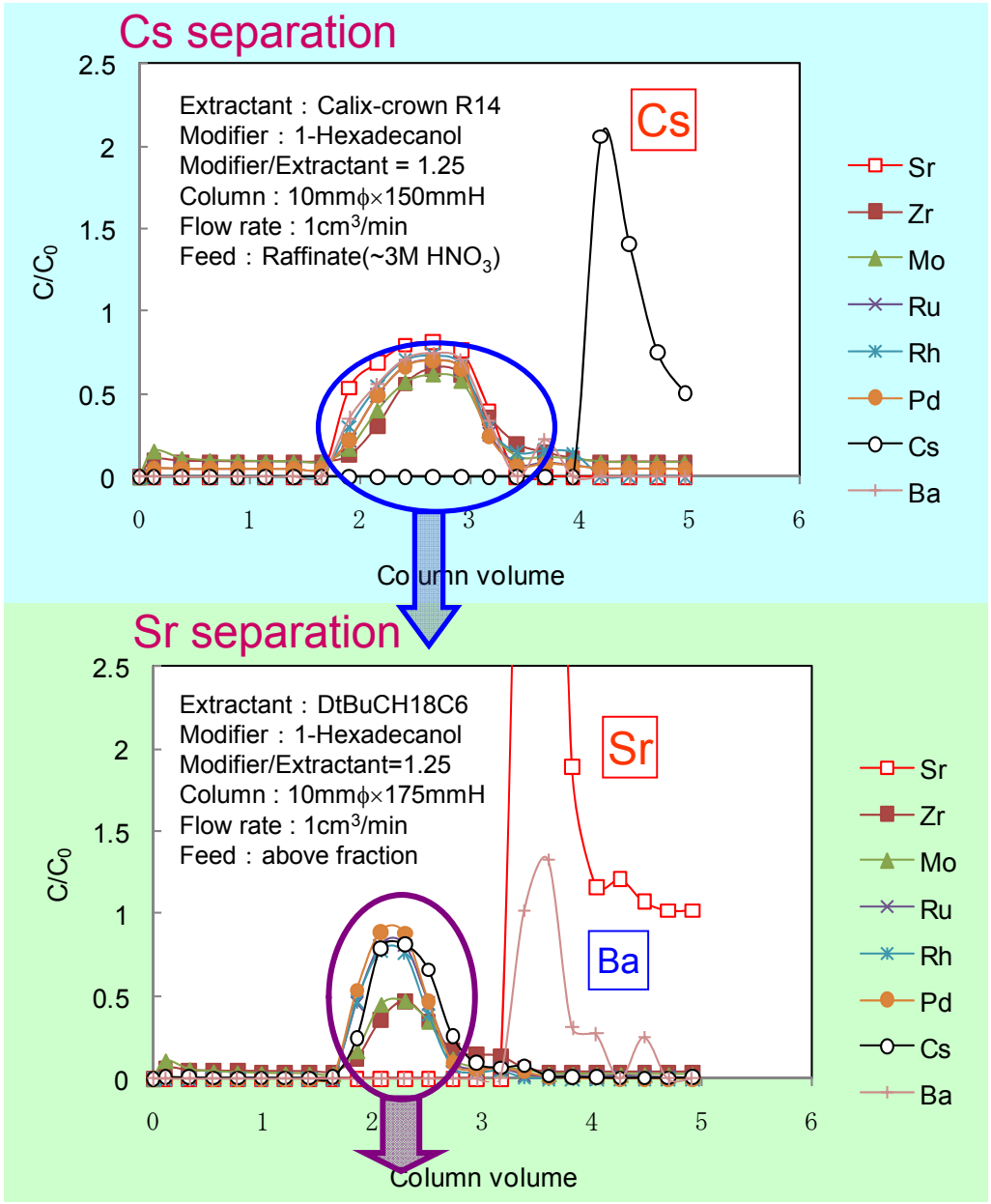
Eluent (Sr,Ba free)

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

Adsorbent for Mo separation

Various metal oxide adsorbents were examined for Mo separation;

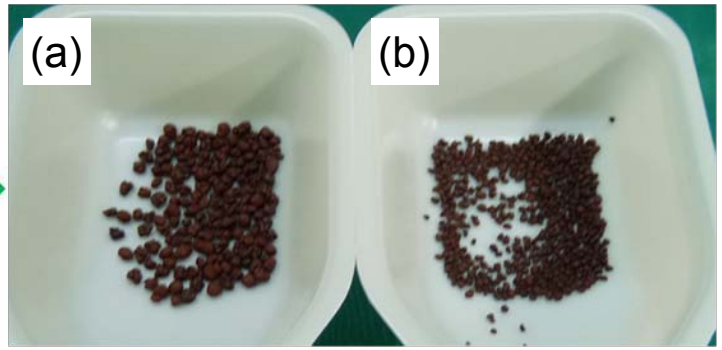
Fe-Pd oxide, Fe oxide, Mn oxide, Al oxide, Co oxide, amorphous Zr oxide

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.

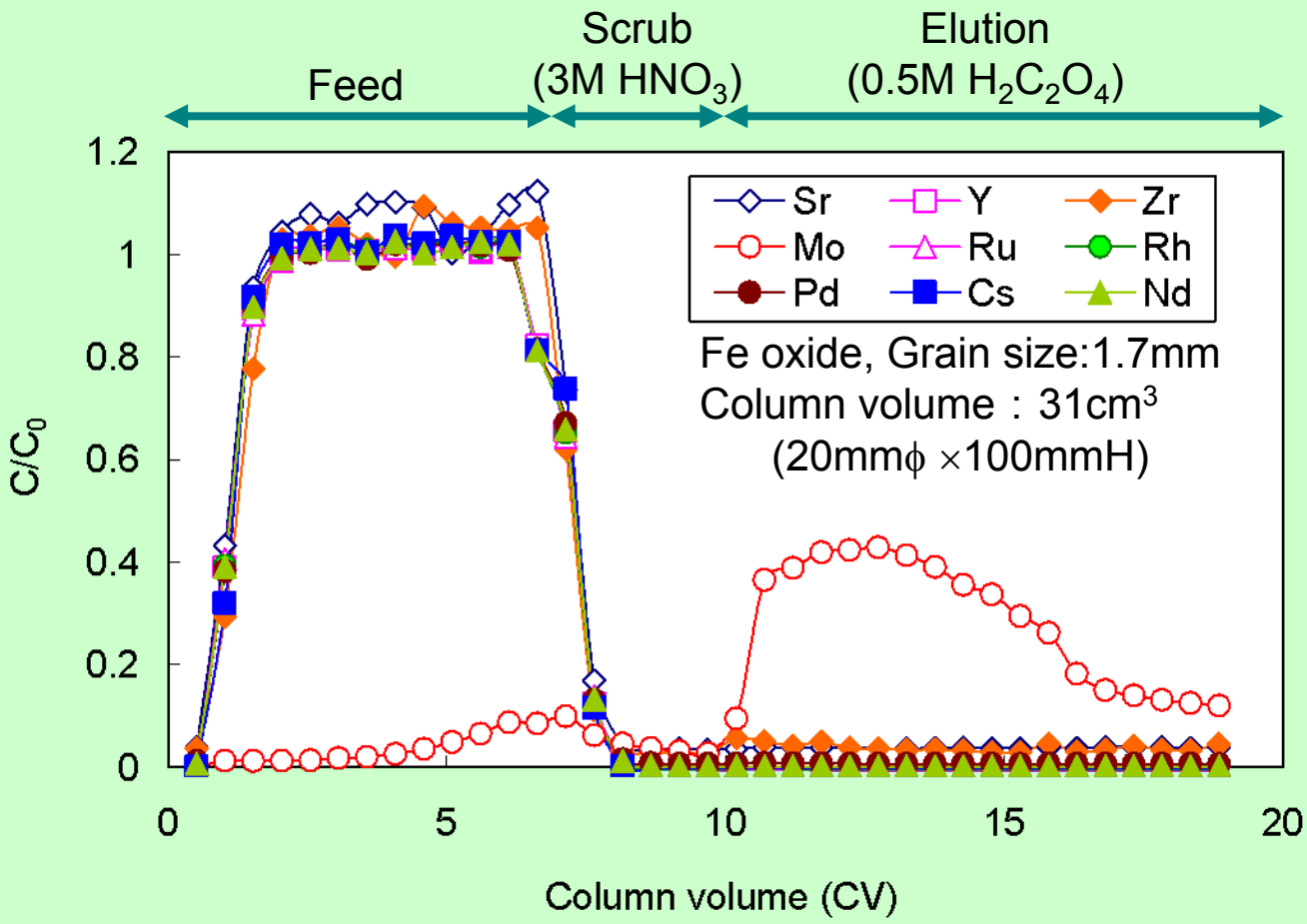
Before granulation
(Powder of Fe oxide)



Granulated Fe oxide adsorbent
Grain size: (a) 1.7mm, (b) 0.6mm

Column of the Fe adsorbent used in Mo separation tests

Column adsorption test for Mo separation



Almost no adsorption of FP except Mo.

Mo can be eluted with oxalic acid.

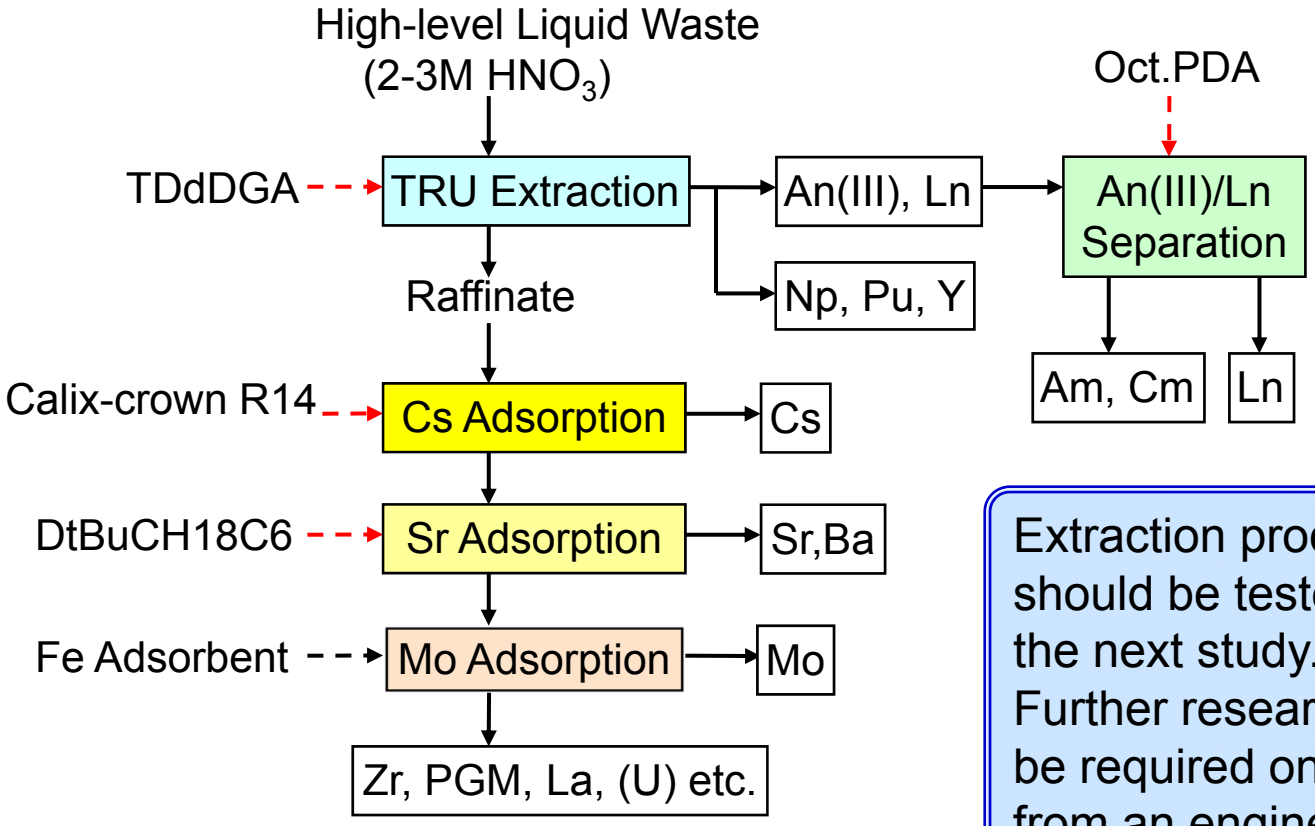
Mo can be separated from other fission products.

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

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Mr. M. Sato, Mr. H. Hagiya (JAEA)

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

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Thank you very much
for your attention