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International Symposium on
"Present Status and Future Perspective
for Reducing Radioactive Wastes
～Aiming for Zero-Release～"

Current Status and Perspective of R&D
—Element Separation—

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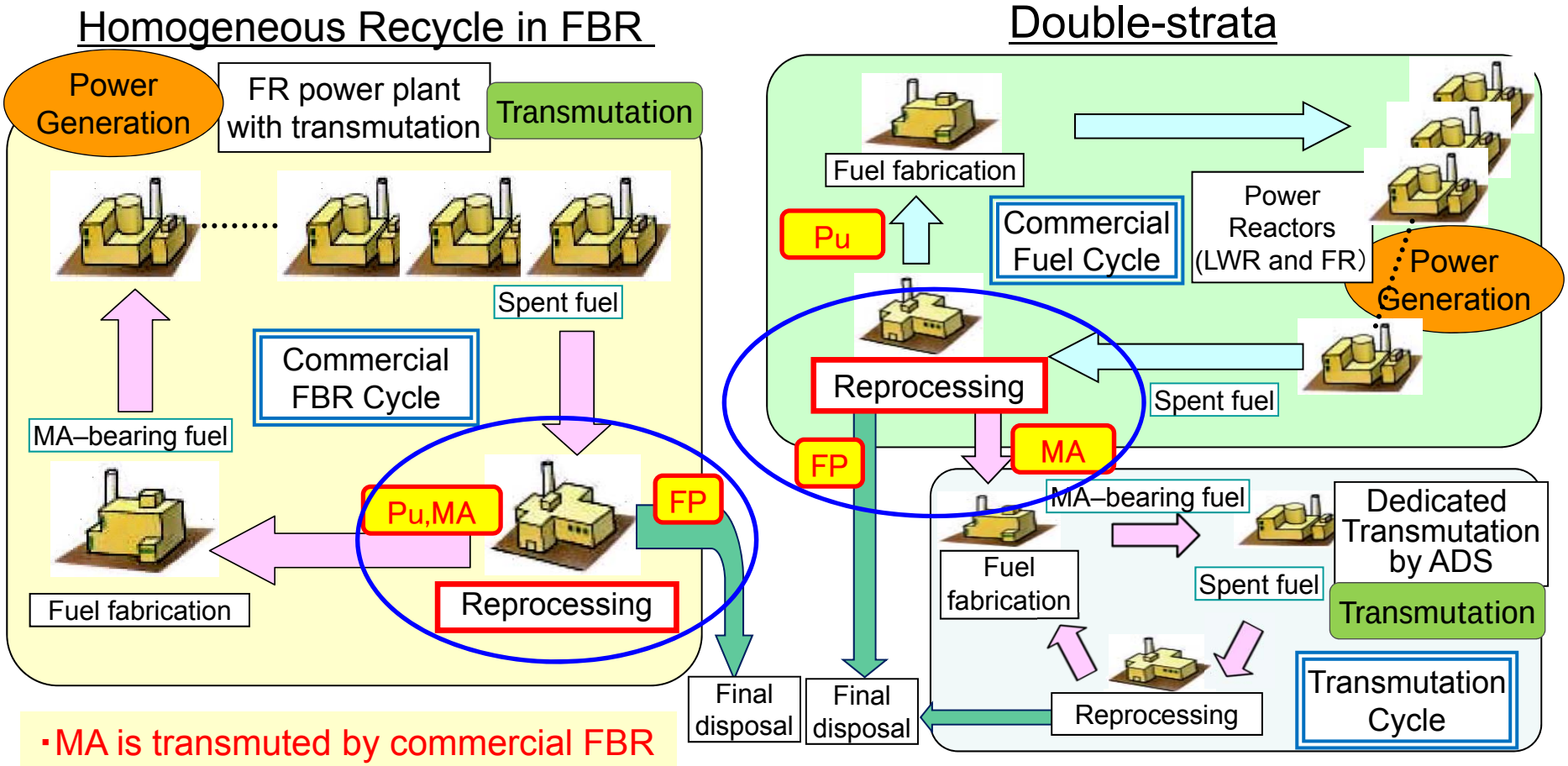
Two Types of Fuel Cycles for P and T Technology



・MA is transmuted by commercial FBR power plants in a closed cycle

Reprocessing in both system can accept the same separation technology.

・Transmutation cycle is attached to commercial cycle.
・ADS is used as dedicated transmutation system.
・MA can be confined into a small cycle and transmuted efficiently.

FP: Fission Product
MA: Minor Actinide (Np, Am, Cm)
ADS: Accelerator-Driven System

High-level Liquid Waste -Start solution for MA separation-

PWR spent fuel：Initial enrichment 4.5%、Burn-up 45GWd/t、cooled for 5 years
MA-recycle fast reactor spent fuel (FR-MA)：core fuel + axis blanket (69.4%：30.6%)
Core fuel：Initial composition Pu19.6%, MA0.92%、Burn-up 147.1GWd/t、cooled for 5 years
Blanket fuel：Depleted uranium (0.3%)、Burn-up 21GWd/t　（Average burn-up 108.5GWd/t）

※ based on data in JAEA Review 2008-037 “Handbook on Process and Chemistry of Nuclear Fuel Reprocessing”.

All figures were obtained per 1 ton of spent fuel.

Higher ratio of residual U in PWR. Higher ratio of MA and Pu in FR-MA

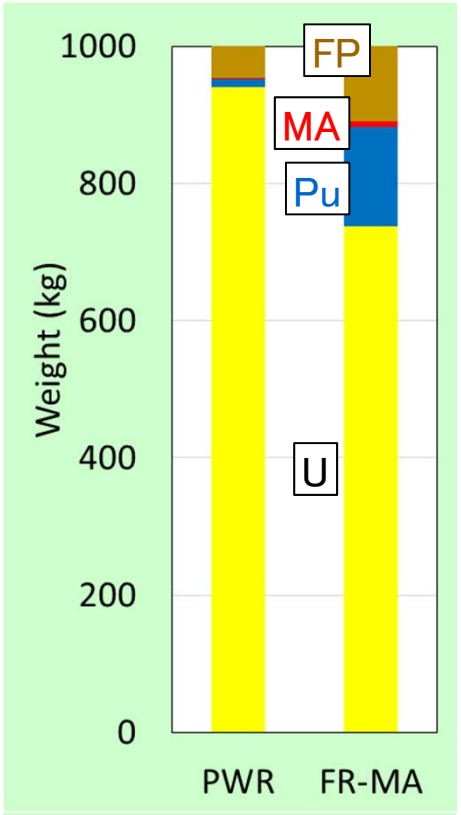


Fig. Example of spent fuel composition

Reprocessing
(U, Pu recovery)

U, Pu 99.5%
Np 95%
Kr, Xe 100%
Br, I 99%
removal

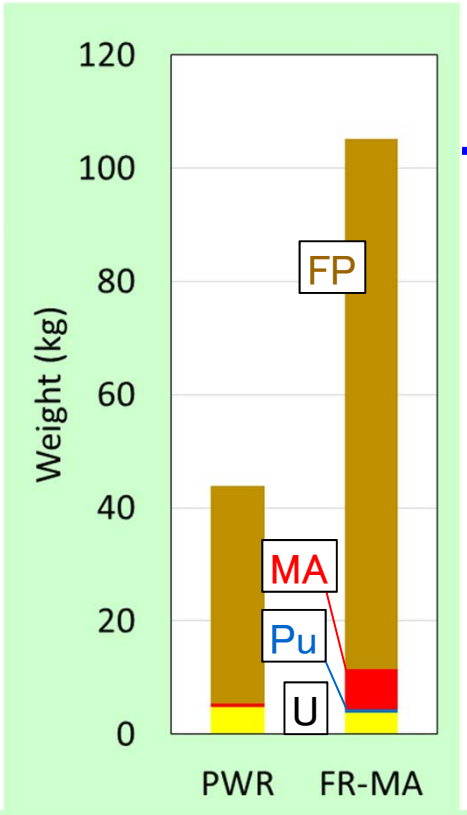
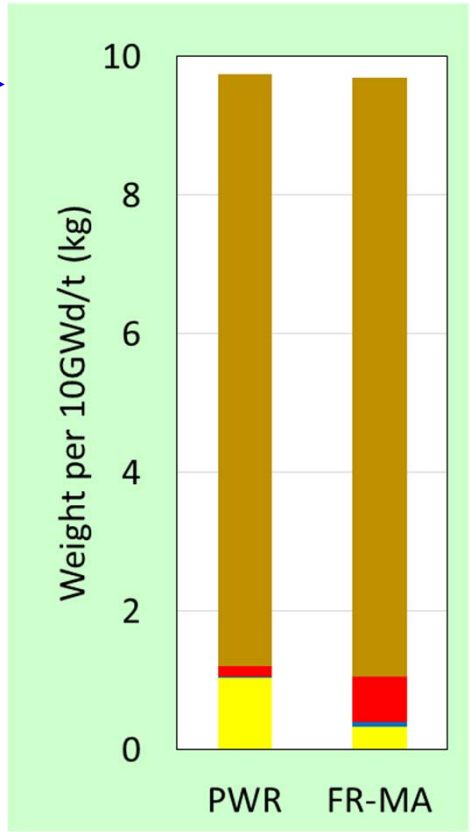


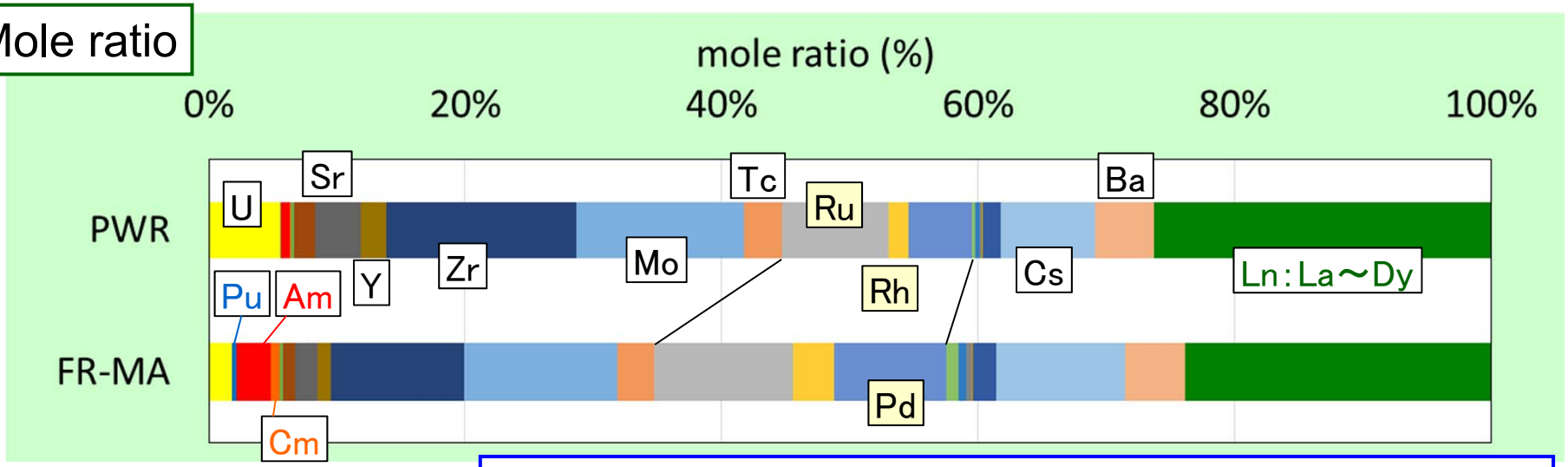
Fig. Example of element composition after reprocessing

Normalized by 10GWd/t



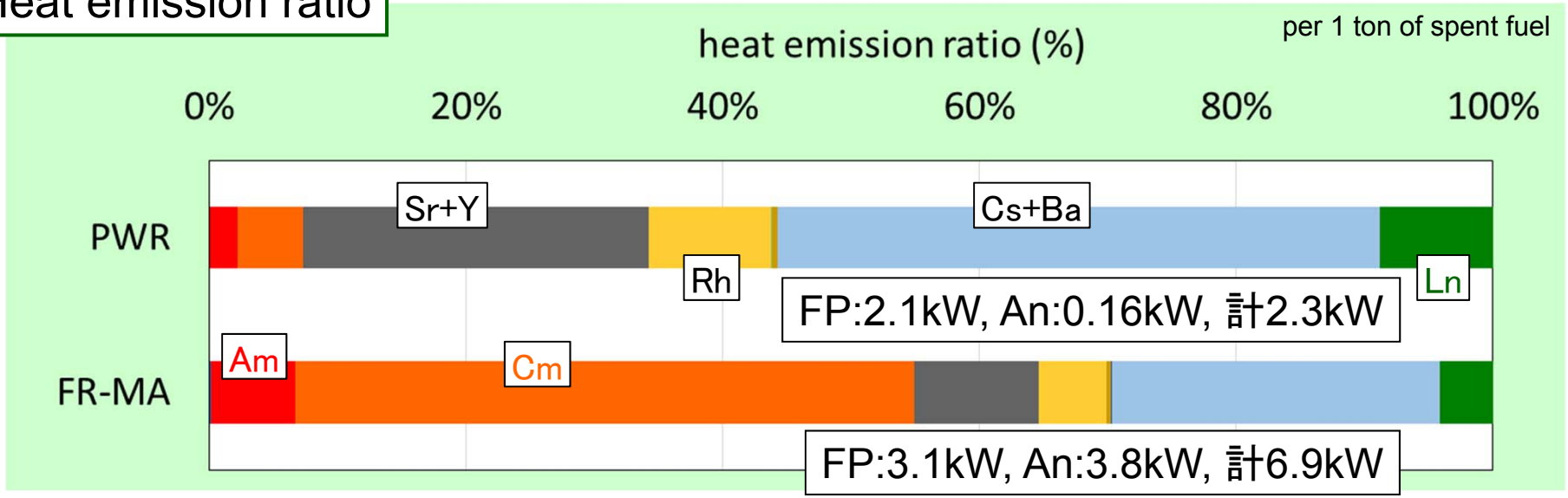
High-level Liquid Waste -Start solution for MA separation-

Mole ratio



Higher ratio of Am-Cm and PGM (Ru, Rh, Pd) in FR-MA

Heat emission ratio



Very high ratio of heat emission by Cm in FR-MA

※ based on data in JAEA Review 2008-037 “Handbook on Process and Chemistry of Nuclear Fuel Reprocessing”

Element to be separated

1) Minor Actinides (MA) = Np, Am, Cm

- Long-lived nulides to be transmuted
- Np can be separated together with U and Pu, and therefore main MA to be separated from HLLW are Am and Cm.
- Am and Cm are stable in trivalent state (An(III)), and rare earths (RE) shows similar behavior.
  Mole ratio of An(III) to RE is 0.025 in PWR and 0.136 in FR-MA
- In many cases, An(III) are separated by two steps.

2) Heat emitters = Sr, Cs

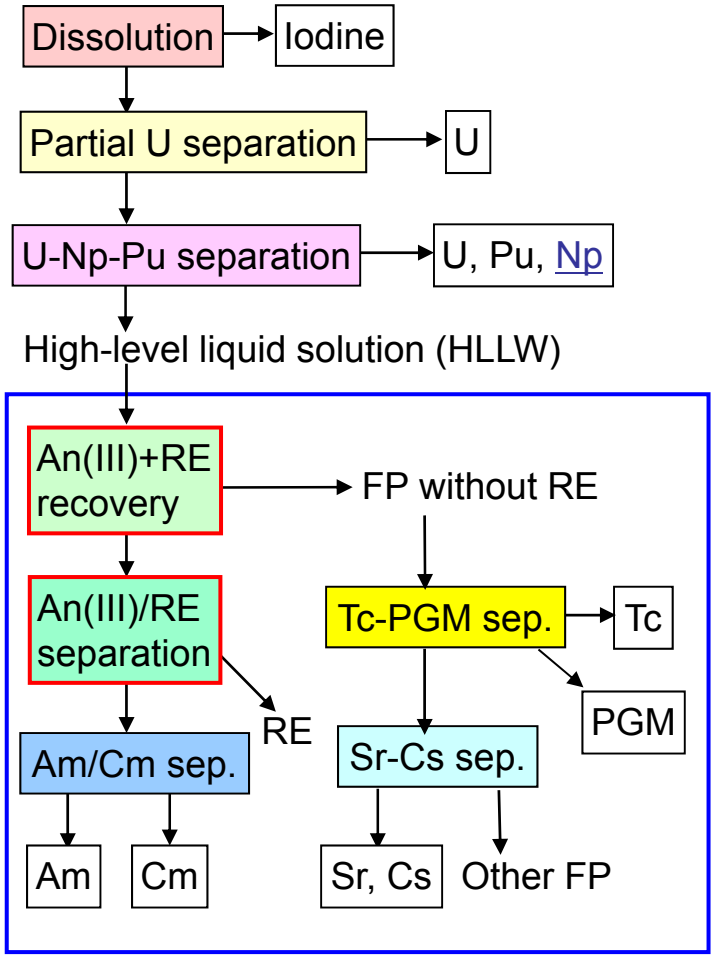
- Most of the heat by FP are emitted by Sr and Cs.
- Highly loaded waste form would be possible after Sr and Cs removal.

3) Platinum group metals (PGM) = Ru, Rh, Pd

- Valuable elements
- They shows bad effect in vitrification

4) Long-lived fission products = Tc

- Tc can be separated with PGM in many cases.
- to be transmuted, and also a valuable element

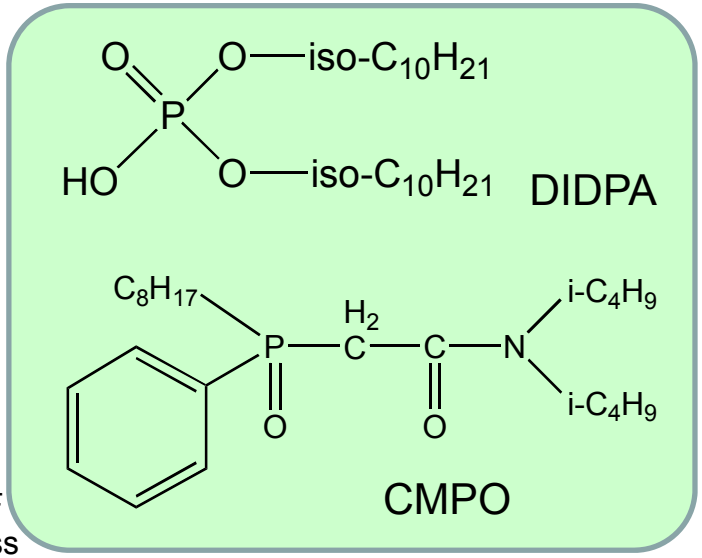


Example of separation process flow

MA Separation（An(III) Separation）

Separation Process for MA with an extractant, DIDPA or CMPO was tested with real HLLW and the separation performance was confirmed in JAEA.

Experimental apparatus in NUCEF for tests of DIDPA extraction process with real HLLW from LWR SF



Experimental apparatus in CPF for tests with real HLLW from FR SF

Both processes have, however, drawbacks to be overcome.

DIDPA extraction : Nitric acid concentration of HLLW should be reduced, which results in formation of precipitation. Waste generation by P atom.

CMPO extraction : Huge volume of solution. Waste generation by P atom.

New research and development

① Application of some new extractants

② Application of extraction chromatography

Solvent extraction and Extraction chromatography

1）Solvent extraction : separation method using difference in distribution equilibrium between aqueous phase such as nitric acid solution and organic phase containing extractant(s) by each element

Advantage : Easy continuous operation giving high recovery with high purity. Much experience in nuclear industry.

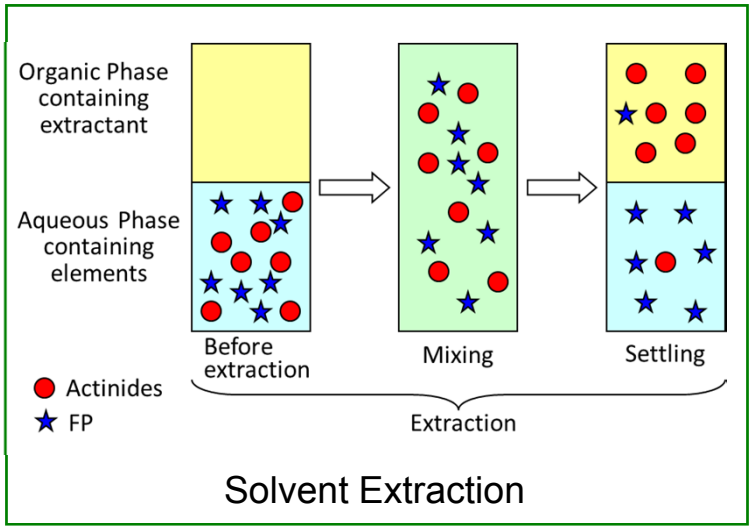
Problem : Treatment of spent solvent. Scale of extractors. The third phase formation.

2）Extraction chromatography : extraction between solution and adsorbent which is impregnated with extractant(s).

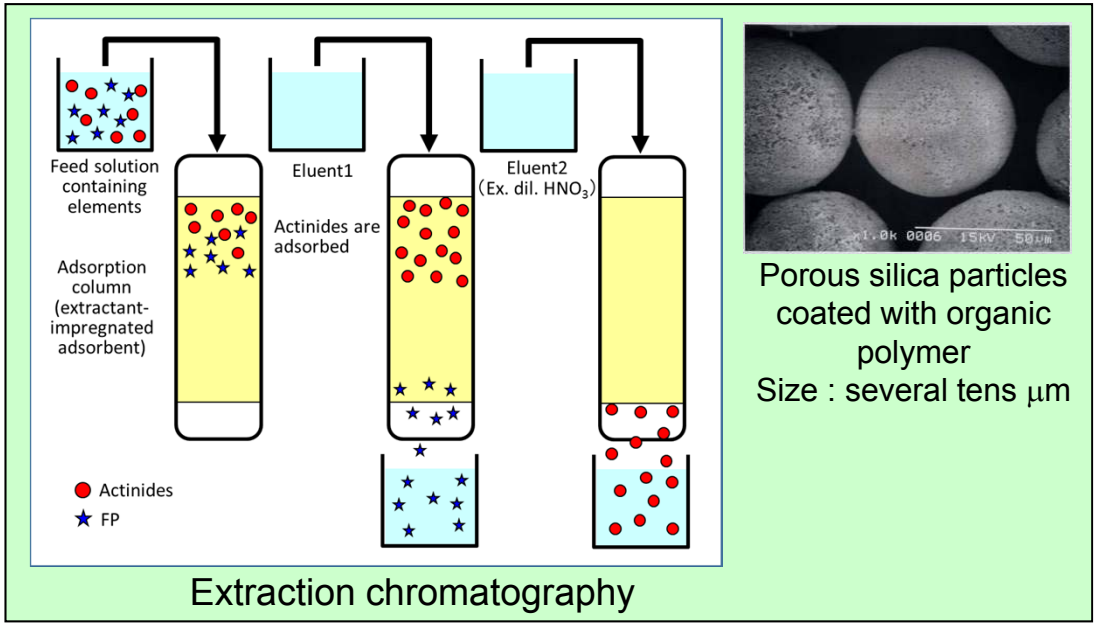
Advantage : No diluent. High separation factor. Compact apparatus.

Problem : Less experience in nuclear industry. Difficulty in remote operation.

※ Problem of adsorbent swelling was solved by using porous silica particles.



Solvent Extraction



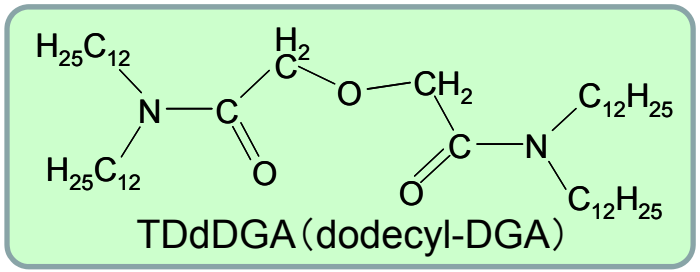
Extraction chromatography

Porous silica particles coated with organic polymer
Size : several tens μm

Development of new extractants for An(III)+RE recovery

Requirements for An(III)+RE extractants

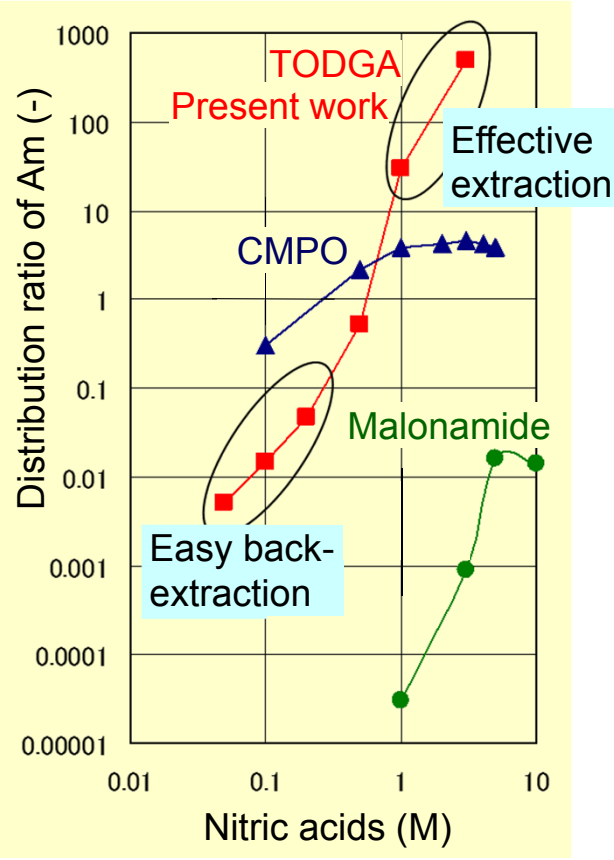
- Extraction from the solution of high nitric acid concentration to avoid precipitation
- Effective extraction and back-extraction
- Compound without P to avoid secondary waste



TDdDGA（dodecyl-DGA）

Tridentate DGA extractants are developed.

- An(III) can be extracted from 1~3M nitric acid solution and back-extracted with 0.1M nitric acid
- Amide compound without P (CHON principle)
- Soluble in n-dodecane
- TDdDGA has high extraction capacity without formation of the third
- Acceptable durability against radiation



Status of TDdDGA extraction process development

- Continuous extraction tests using simulated HLLW with Am tracer gave the Am recovery of more than 99.99%.
- Process simulation code was developed.
- Optimization of process condition is underway.
- Tests with real HLLW will be carried out as a next step.

DGA extractant is also applied to extraction chromatography.

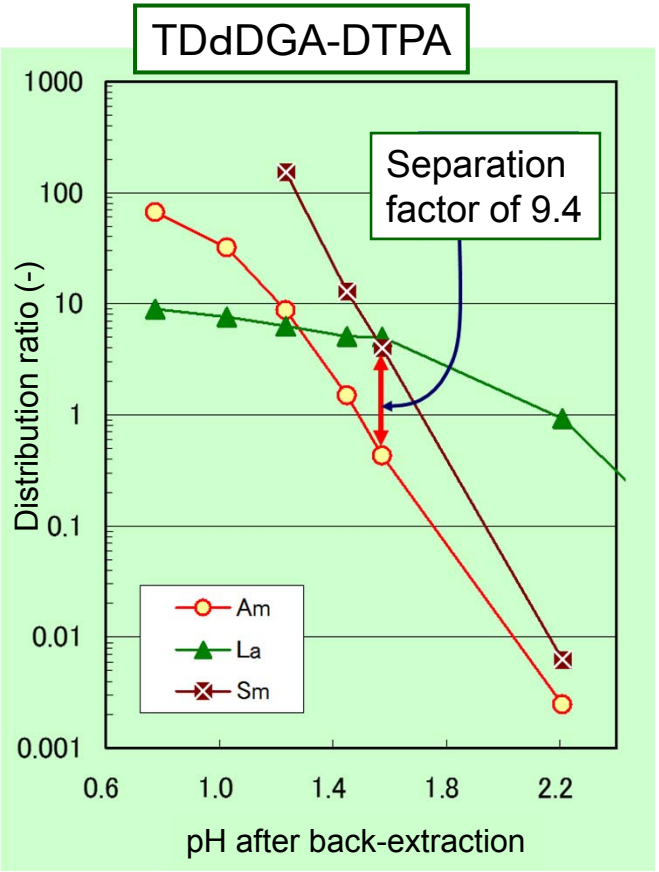
An(III)／RE separation by solvent extraction

In both DIDPA extraction and CMPO extraction, a complexing agent, DTPA, is used for An(III)／RE separation, which makes more stable complex with An(III).

Problem ・Treatment of organic phase and aqueous solution including complexing agent

・ Control of pH ・ secondary waste

Separation by the combination of TDdDGA and DTPA is also examined and separation factor of 9.4 between Am and RE was confirmed (figure)



・ Study on soft-donor extractants

※soft-donor : nitrogen(N), sulfur(S)

↔ hard-donor : oxygen(O)

Soft-donor extractant gives higher distribution ratio with An(III) than with RE.

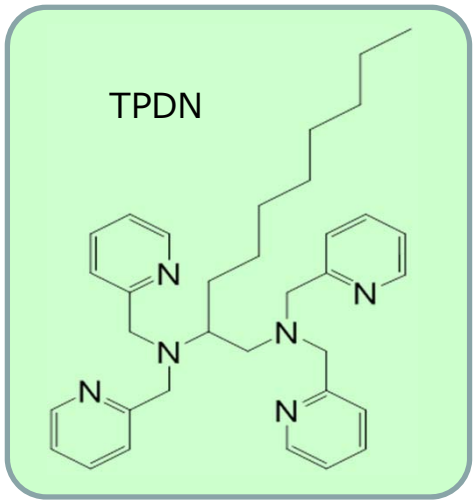
→ Selective extraction of An(III)

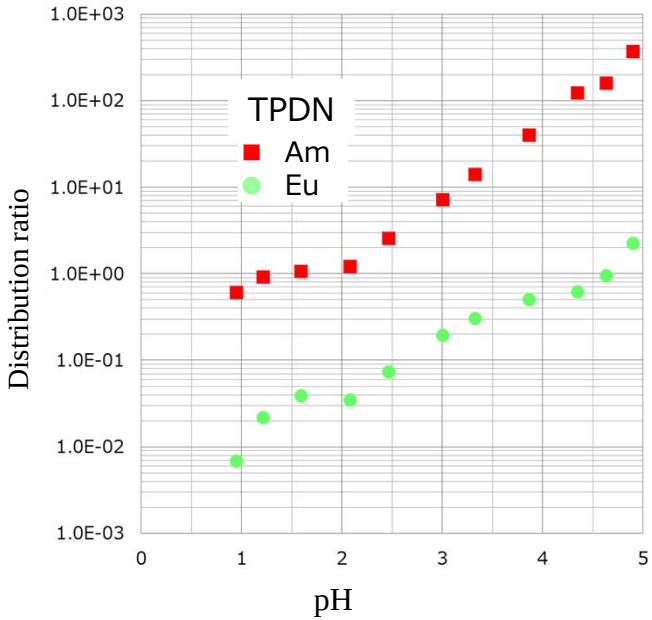
・ Hybrid extractants which have both soft and hard donor in the molecule are also studied.

Still in the stage of extractant selection and basic data acquisition

An(III)／RE separation by solvent extraction

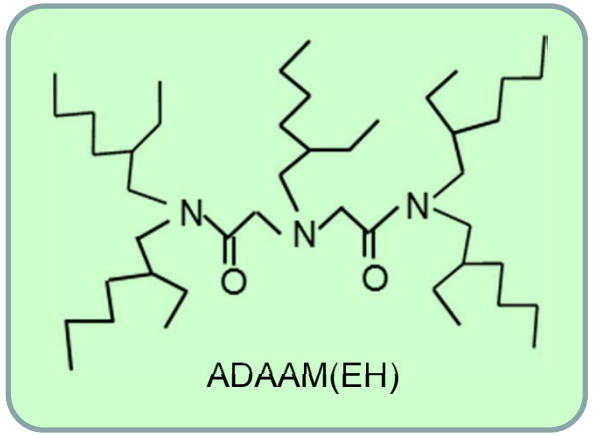
Multi-dentate N donor extractant, TPDN, provide Am/Eu separation （center figure)





Organic phase : [TPDN] = 10 mM in nitrobenzene
Aqueous phase : pH = 1.0 ～ 4.8

Hybrid type extractants, ADAAM(EH) is being examined and separation factor of more than 20 was obtained between Am and Eu



Application of TPDN to extraction chromatography is also examined.

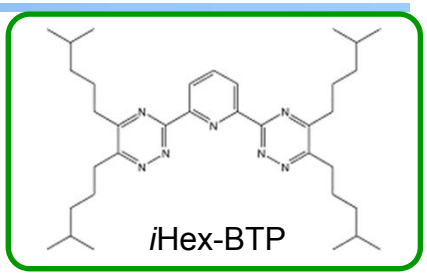
Status of separation process development and the near future

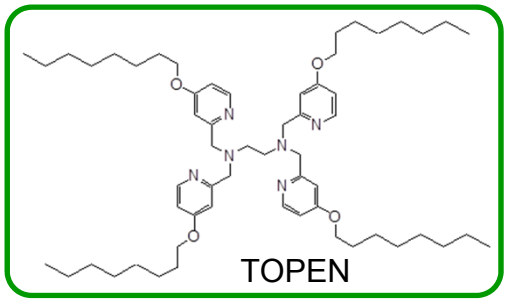
- Continue to obtain extraction data (extraction rate, extraction capacity, stability, etc.)
- Process integration with An(III)+RE recovery.
- After optimization of process condition and continuous extraction test with simulated HLLW, tests with real HLLW will be performed.

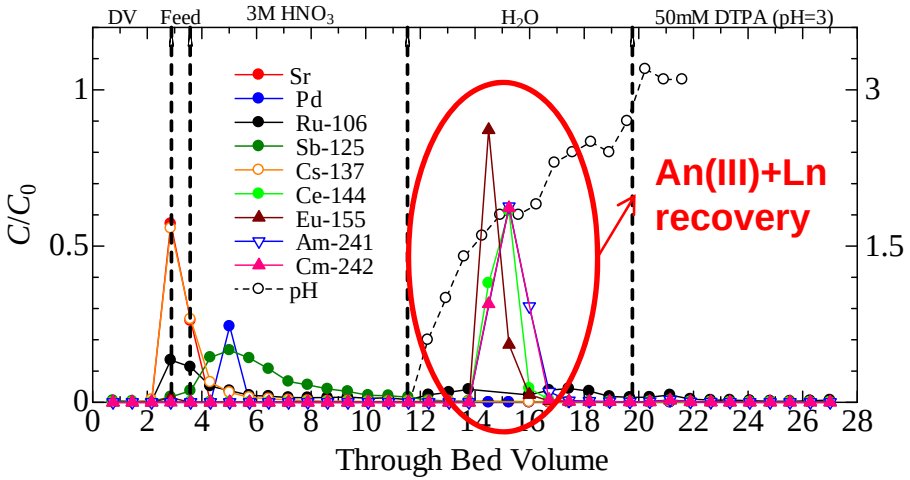
An(III) Separation by Extraction Chromatography

Adsorption/Elution assessment

- MA can be adsorbed by adsorbents with CMPO and TODGA from HLLW, and eluted with some FPs (Ln)
- MA can be adsorbed by adsorbents with R-BTP (*i*Hex-BTP) from HLLW, and eluted selectively
- MA can be adsorbed by adsorbents with HDEHP and TOPEN from diluted HNO_3 solution, and eluted selectively

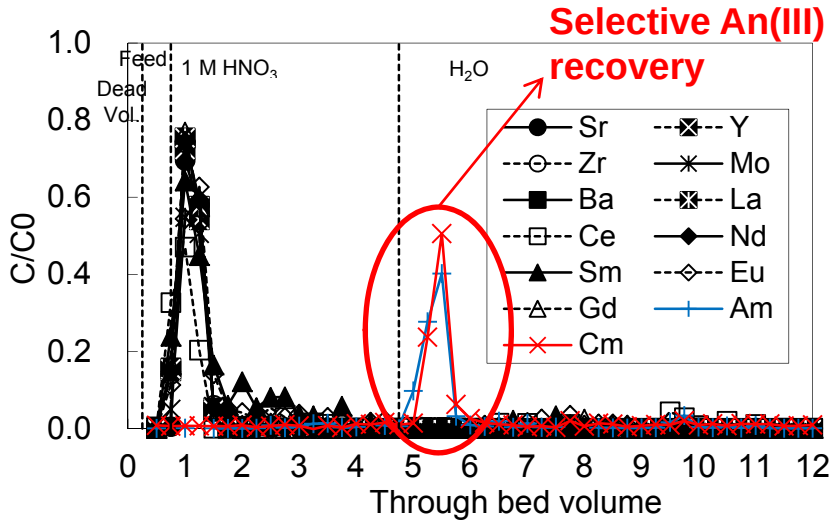






Chromatographic separation of real HLLW by the column with CMPO/SiO_2-P adsorbents (JOYO spent fuel test at CPF)

S. Watanabe, et al., *Proc. of GLOBAL2011* (2011)

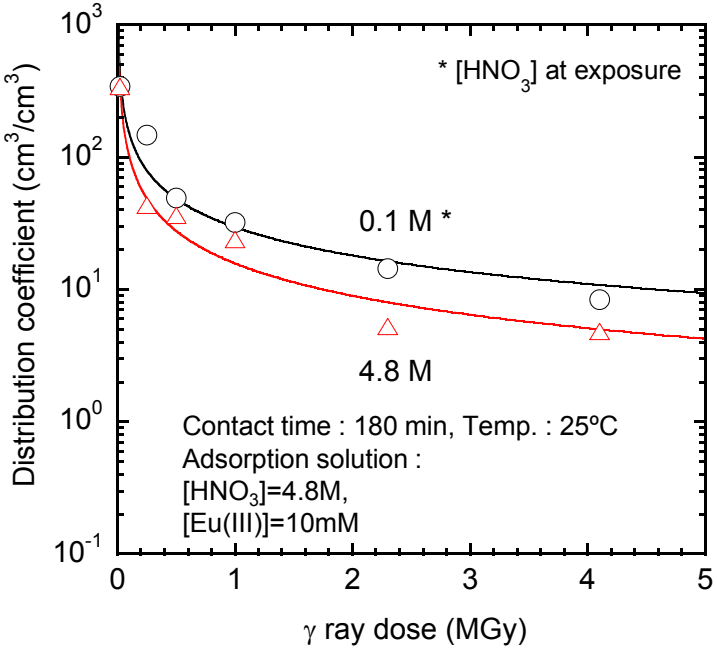


Chromatographic separation of real HLLW by the column with *i*Hex-BTP/SiO_2-P adsorbents (FUGEN spent fuel test at TRP)

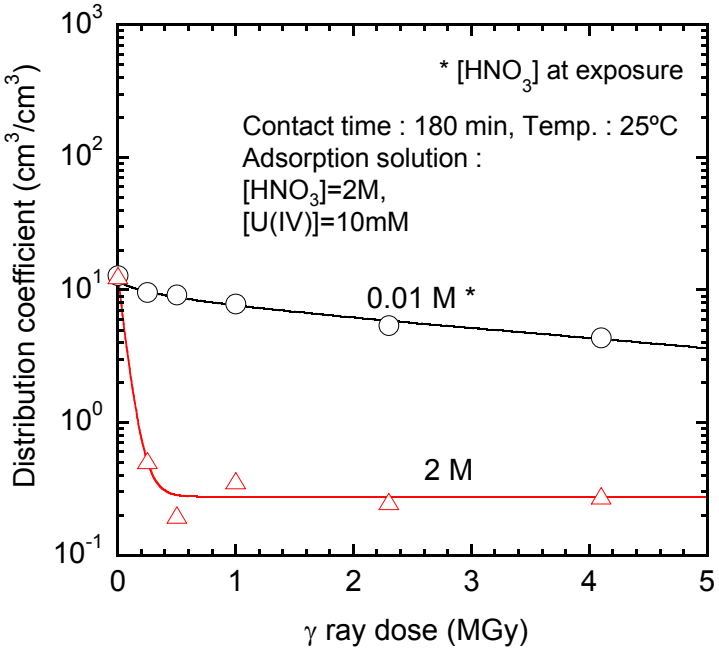
Y. Sano, et al., *IOP Conf. Ser.: Mater. Sci. Eng. 9 012064* (2010)

Durability of Adsorbents against Gamma Irradiation

- Durability assessment
  - Adsorbents with CMPO and TODGA have a similar durability
  - Adsorbent with R-BTP is unstable in high HNO_3 condition
  - Adsorbents with R-BTP, HDEHP and TOPEN have a similar durability in diluted HNO_3 condition



Distribution coefficient of Eu from 4.8M HNO_3 by TODGA/SiO_2-P adsorbents



Distribution coefficient of U from 2M HNO_3 by *i*Hex-BTP/SiO_2-P adsorbents

Y. Koma, et al., *Proc. of GLOBAL2009* (2009)

Separation of Fission Products

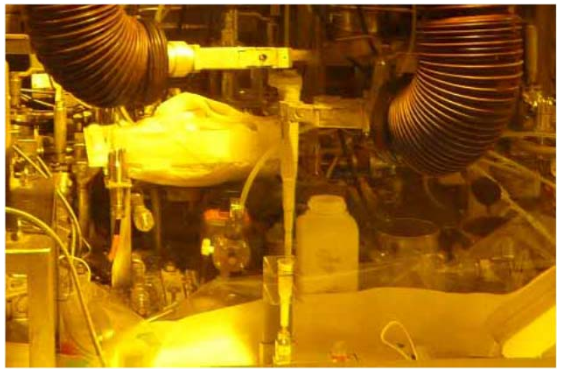
◎ Separation of Sr-Cs

(1) Adsorption with inorganic ion exchangers

- Titanic acid for Sr and Zeolite (mordenite) for Cs. The adsorbents can be converted to a stable form by calcination.
- Experiments with real HLLW showed a good performance for Sr-Cs recovery.
- Drawback : Reduction of acid concentration is required.

(2) Extraction chromatography

- Crown-ether for Sr and Calix-crown for Cs.
- Very small scale test with real HLLW was performed.
- Drawback : High cost for extractants.



Very small scale test with real HLLW for Sr-Cs separation by extraction chromatography

Performance of each separation process was confirmed. Integration of total process is important.

◎ Separation of Tc-PGM(Ru, Rh, Pd)

- Adsorption method with active carbon was developed.
- Precipitation method by denitration was tested with real HLLW, and the recovery of Tc-PGM was confirmed.
- Extraction with oxime for Pd separation and volatilization with electrochemical oxidation for Ru separation were investigated.

◎ Other elements

- Zr and Mo are separated by precipitation in DIDPA extraction.
- Separation process for Zr-Mo by extraction with HDEHP was developed.

Summary

- In An(III) separation and FP separation, several methods have been already confirmed to give good performance.
- Methods to give better separation performance should be investigated.
- High-level liquid solution from spent fuel of LWR and the solution after U-Pu recovery from spent fuel of fast reactor, as a starting solution of An(III) separation, can be treated in a similar manner considering the difference in actinide content.
- Integration of separation processes for An(III) and FP is important.
- Together with the real HLLW tests, cold mock-up tests in an industrial scale should be performed, and then it become possible to proceed to active tests in the industrial scale.