

Workshop on
**ROLE OF PARTITIONING AND TRANSMUTATION IN THE
MITIGATION OF THE POTENTIAL ENVIRONMENTAL IMPACTS OF
NUCLEAR FUEL CYCLE**

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ICTP - Trieste, Italy

1774/8

R & D in Partitioning

Part I & II

T.G.Srinivasan
Indira Gandhi Centre for Atomic Research,
Kalpakkam, India

R & D in Partitioning

Part I

ACTINIDE IN SPENT FUEL

UOX 45 GWd/t (4 years cooled)																	
1 H															2 He		
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	Ln	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	An	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun								

LANTHANIDES	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
ACTINIDES	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

- ACTINIDES MAJEURS
- ACTIVATION PRODUCTS
- FISSION PRODUCTS
- FISSION AND ACTIVATION PRODUCTS
- ACTINIDES MINEURS

Courtesy : Bernard Boullis, CEA

Swedish CTH Process (Chalmers Tekniska Hogskola)

- ❖ Developed and hot tested utilizing HDEHP to treat commercial HLW
- ❖ PUREX aqueous raffinate adjusted to 6 M HNO_3 and NO_x treated
- ❖ 1 M HDEHP/kerosene is used in the first SX cycle to remove U, Np and Pu together with most of the Fe, Zr, Nb and Mo, The loaded organic phase is first washed with an HNO_3 -HF solution to remove Zr and Nb and then stripped with ammonium carbonate
- ❖ A mixture of ammonia and manitol are added to the organic phase before stripping to avoid precipitation of iron
- ❖ The strip solution is evaporated to recover the ammonium carbonate for recycle and then acidified to recover the U, Np and Pu
- ❖ Test runs demonstrated that 99.99% of U, 98.9 % of the Np and > 99.99 of the Pu can be recovered in the first extraction cycle
- ❖ The second extraction cycle uses 50% TBP in kerosene to reduce the acidity of the aqueous phase to prepare it for a second low-acid HDEHP cycle

Swedish CTH Process (Chalmers Tekniska Hogskola)

- ❑ In addition to extracting HNO_3 , TBP also extracts Pd, Ru and Tc leaving Am and Cm plus the light lanthanides in a 0.1 M HNO_3 aqueous raffinate
- ❑ Nitric acid is recovered by scrubbing with water and then evaporated and distilled to produce 9 M HNO_3 . The HNO_3 is then reused to prepare the feed for the first extraction cycle. The Tc, Ru and Pd can be recovered from the strip solution by anion exchange
- ❑ The third and final extraction cycle in the CTH process consists of the extraction of Am and Cm, together with the light lanthanides, from the raffinate of the second extraction cycle using a solution of 1 M HDEHP in kerosene
- ❑ At this stage the trivalent actinides can be selectively stripped from the light lanthanides using a diethylenetriamine pentaacetic acid (DTPA)-lactic acid mixture, or the actinides together with the lanthanides can be stripped using 6 M HNO_3
- ❑ If the trivalent actinides are partitioned from the lanthanides, a final HDEHP extraction cycle is required to remove the trivalent actinides from the DTPA-lactic acid solution

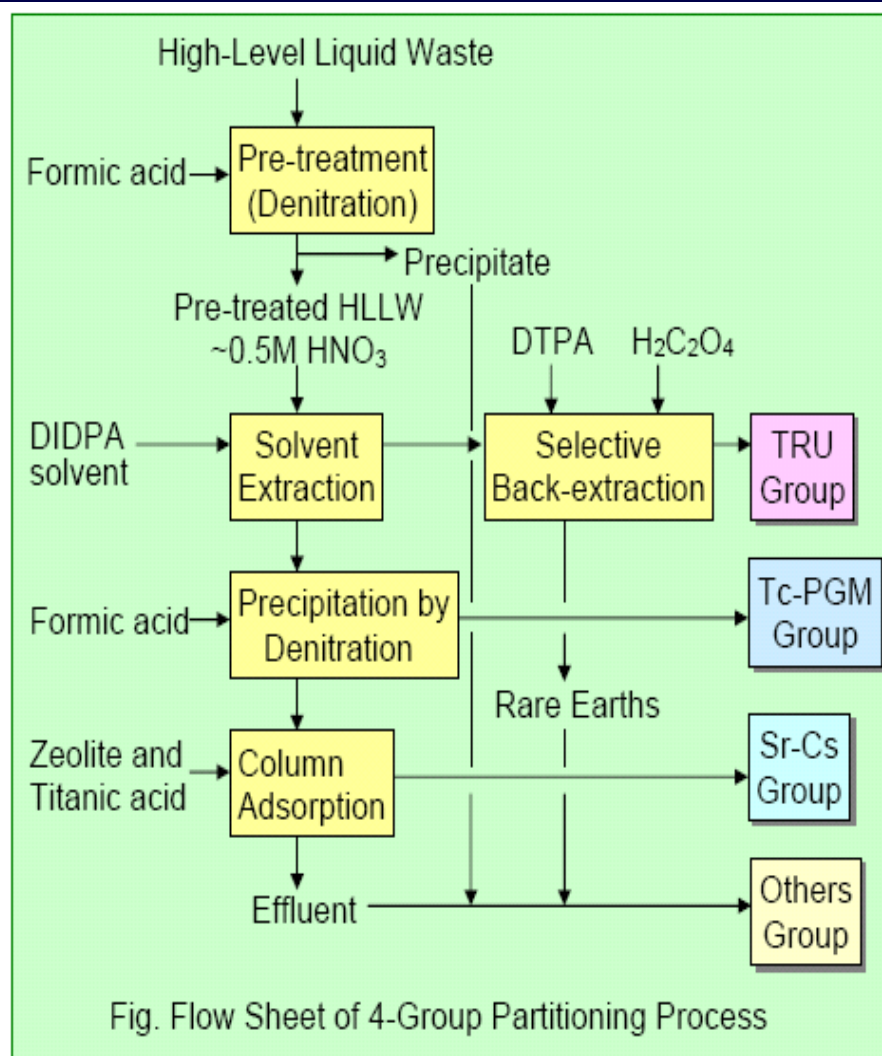
Swedish CTH Process (Chalmers Tekniska Hogskola)

- ❖ Successfully tested by processing 20 L of synthetic HLW feed using a number of 150 mL mixer-settlers
- ❖ Analytical results indicated behaviour as predicted
- ❖ Sr and Cs in the raffinate from the third extraction cycle can be sorbed on inorganic ion exchangers such as titanates and zeolites for disposal
- ❖ The major advantage of the CTH process
 - ❖ utilizes two commercially available, low cost extractants
- ❖ The major disadvantages
 - ❖ multi-extraction cycles (at least three)
 - ❖ two different extractants
 - ❖ strip solutions require further processing to recover the TRUs
- ❖ In addition, a significant acidity adjustment is required before trivalent actinides can be extracted
- ❖ A process this complex would be very costly and difficult to operate on a plant

Partitioning Activities in Japan JAERI

- ❖ JAERI developed four-group partitioning process for the treatment of the HLL wastes resulting the reprocessing by the PUREX process of UOX / MOX LWR spent fuels
- ❖ JAERI proposes to separate Np and Tc during the implementation of the PUREX process
- ❖ The HLLW partitioning process includes the following steps :
 - 1) Partitioning of the Minor Actinides (Np, Am and Cm)
 - 2) Extraction of Cs and Sr
 - 3) Extraction of Tc and PGMs
 - 4) The remaining mixture of wastes constitutes the 4th category of elements of the initial mixture treated

The Four Group Partitioning Process, Courtesy : Kimura, JAEA



✓ 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 > 10⁴

✓ 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.

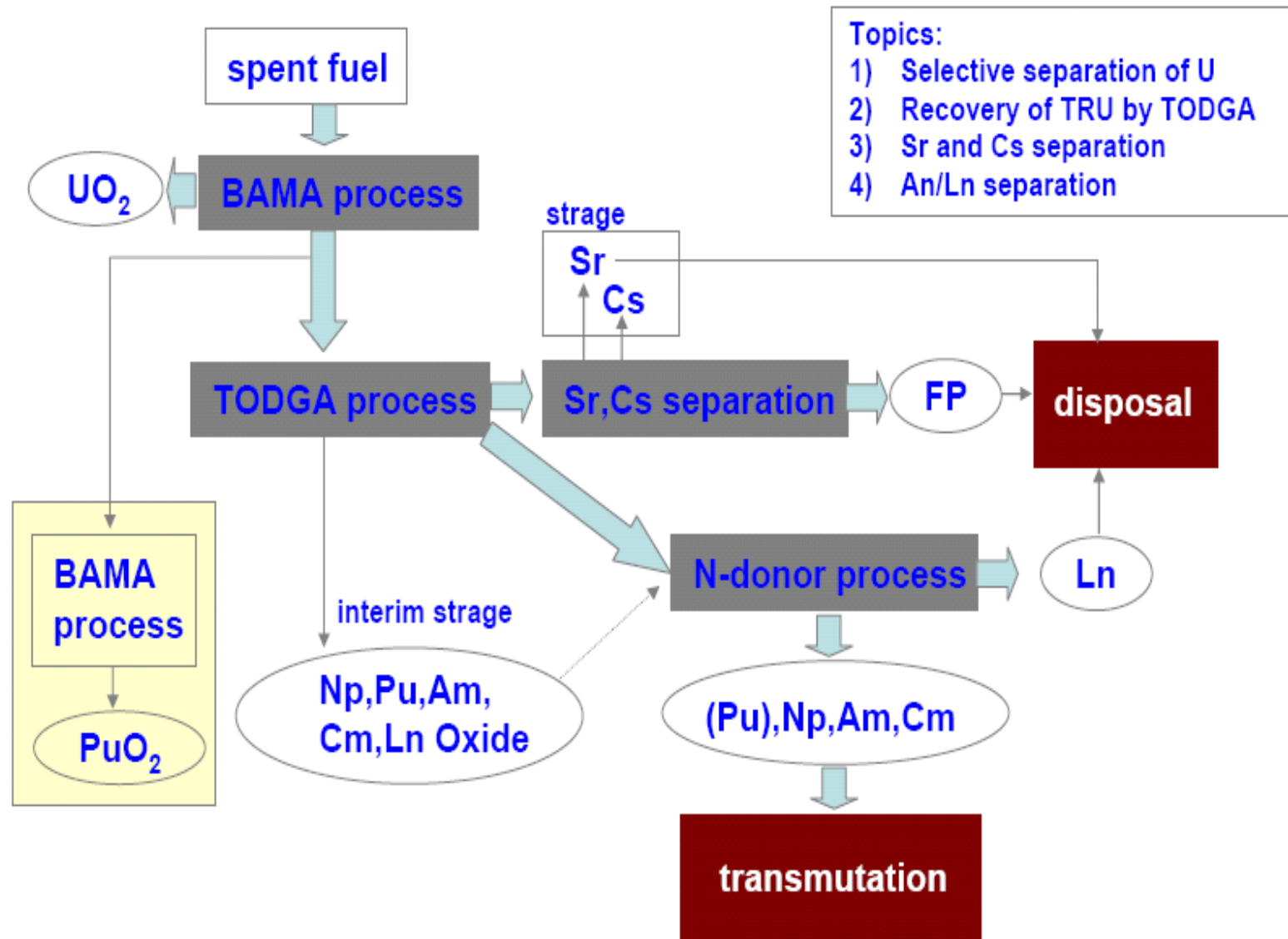
Partitioning Activities in Japan

JAERI

JAERI proposes to treat the spent fuel by ARTIST Process
(Amide-based Radio-resources Treatment with Interim Storage of Transuranica)

- ❑ Phosphorus-free agents consisting of C, H, O and N (CHON principle)
- ❑ BAMA & DOHA : Separation of U, Pu
- ❑ TOGDA : An, Ln recovery
- ❑ N-donor ligand : An/Ln separation

ARTIST Process Courtesy : Kimura, JAEA



JRC-ISPRA/HDEHP Process

- ❖ Joint Research Centre-Ispra Establishment, Italy, has developed and tested a process to treat commercial HLW
- ❖ The JRC-ISPRA process is somewhat similar to the CTH process
- ❖ The process begins by performing either an exhaustive TBP extraction or HDEHP extraction of a PUREX raffinate that has been concentrated 10-fold
- ❖ Residual U, Np and Pu are removed by the TBP or HDEHP
- ❖ The raffinate is denitrated to pH 2 using formic acid, clarified and extracted using 0.3 M HDEHP -0.2 M TBP in dodecane to remove Am, Cm and light lanthanides
- ❖ Partitioning of Am and Cm from light lanthanides is performed by a Reverse TALSPEAK process, or the actinides and lanthanides can be stripped together using 4 M HNO₃
- ❖ Batch extraction tests with actual HLW demonstrated >99% removal of Am and Cm after a single extraction from a feed solution with a pH of 2.76

JRC-ISPRA/HDEHP Process.....

- ❖ The Pu left in the precipitate formed during the denigration step after formic and nitric acid washings varied from 2 to 0.6%
- ❖ The JRC-ISPRA process suffers from the same problems as the CTH process
- ❖ A multicycle process of this type would be most difficult and very costly to operate on a plant-scale
- ❖ Formation of precipitates of varying alpha contamination is also a drawback

Japanese/DIDPA Process

- ❖ The third SX system using an acidic extractant has been developed by a team of chemists from the Japan Atomic Energy Research Institute
- ❖ JAERI has used diisodecyl phosphoric acid (DIDPA)
- ❖ The major difference between DIDPA and HDEHP is that the former can extract light trivalent actinides from higher acidities, for example, 0.5 M rather than < 0.1 M HNO_3 required by HDEHP
- ❖ As with the CTH process, the major motivation is to reduce the quantity of HLW for disposal
- ❖ The HLW is generated by reprocessing fuel from commercial nuclear power plants
- ❖ The process consists of four steps
- ❖ The first step is an SX cycle using TBP to remove the small amount of U and Pu left in the raffinate from PUREX

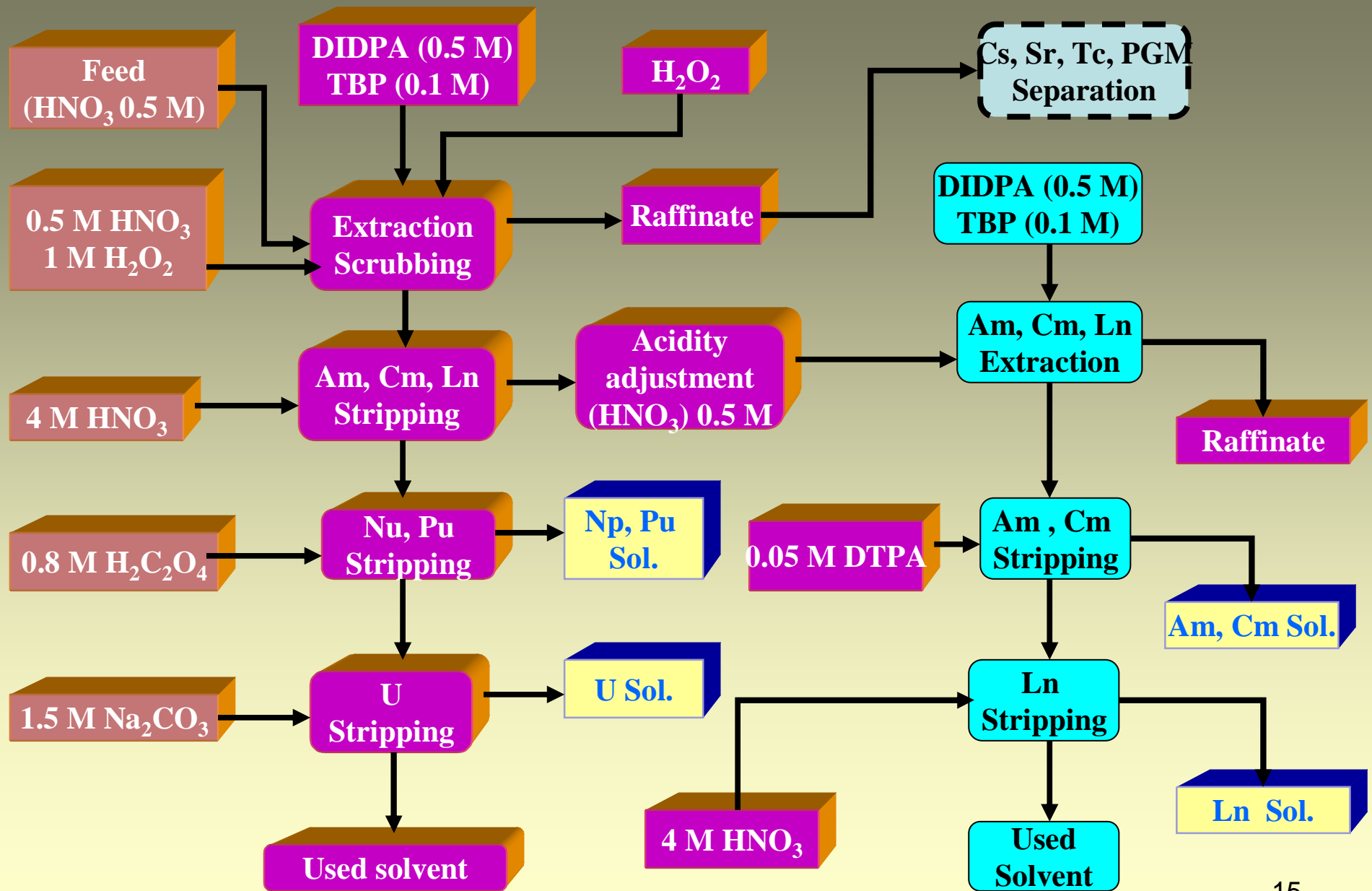
Japanese/DIDPA Process.....

- ❖ The second step involves a denitration of the raffinate from the first extraction with formic acid
- ❖ The second step has two objectives; first, to reduce the acidity to pH 0.5 to allow the efficient extraction of Am and Cm with 0.5 M DIDPA -0.1 M TBP-dodecane; and second, to precipitate zirconium and molybdenum (as $Zr(MoO_4)$) that interfere with the subsequent extraction of Am and Cm
- ❖ The third step involves the extraction of Am and Cm with 0.5 M DIDPA -0.1 M TBP-dodecane
- ❖ If the feed for the Am/Cm SX step is made 0.5 to 1M in H_2O_2 , at least 99.7% of the Np can also be removed
- ❖ The fourth and final step of the process involves the selective stripping of Am and Cm with 0.05 M DTPA -1 M lactic acid
- ❖ As with the CTH process, the raffinate from step 3 can be treated with inorganic ion exchange materials to remove Sr and Cs

Japanese/DIDPA Process.....

- ❖ The flow sheet has been tested in a 16-stage bank of mixer settlers using actual commercial HLW
- ❖ Greater than 99.99% of the Am and Cm were extracted with DIDPA
- ❖ Overall results showed that the process behaved as predicted
- ❖ The same advantages and disadvantages listed for the CTH and JRC-ISPRA processes apply equally to the Japanese process
- ❖ In addition, an eight-fold dilution of the HLW may be required to prevent formation of a gelatinous precipitate in the DIDPA process solvent and the percentage of TRU precipitated during the formic acid denigration step can be significant if the pH increases to 1.0
- ❖ Both of the last two points are major drawbacks to implementing such a process on a plant-scale

DIDPA Process



SETFICS (JNC, Japan)

Solvent Extraction for Trivalent f-elements Intra-group Separation in CMPO-complexant System

- ❖ The SETFICS process constitutes a modification of the TRUEX process based on $O\Phi DiBCMPO$
- ❖ The separation of TRUs is done by successive stripping from the loaded solvent, including also the use of DTPA for An(III)/Ln(III) separation
- ❖ This process has not been tested yet with genuine HAWs
- ❖ The possible drawbacks of this process are:
 - ❖ the limited stripping efficiency
 - ❖ the management of salts and DTPA containing effluents

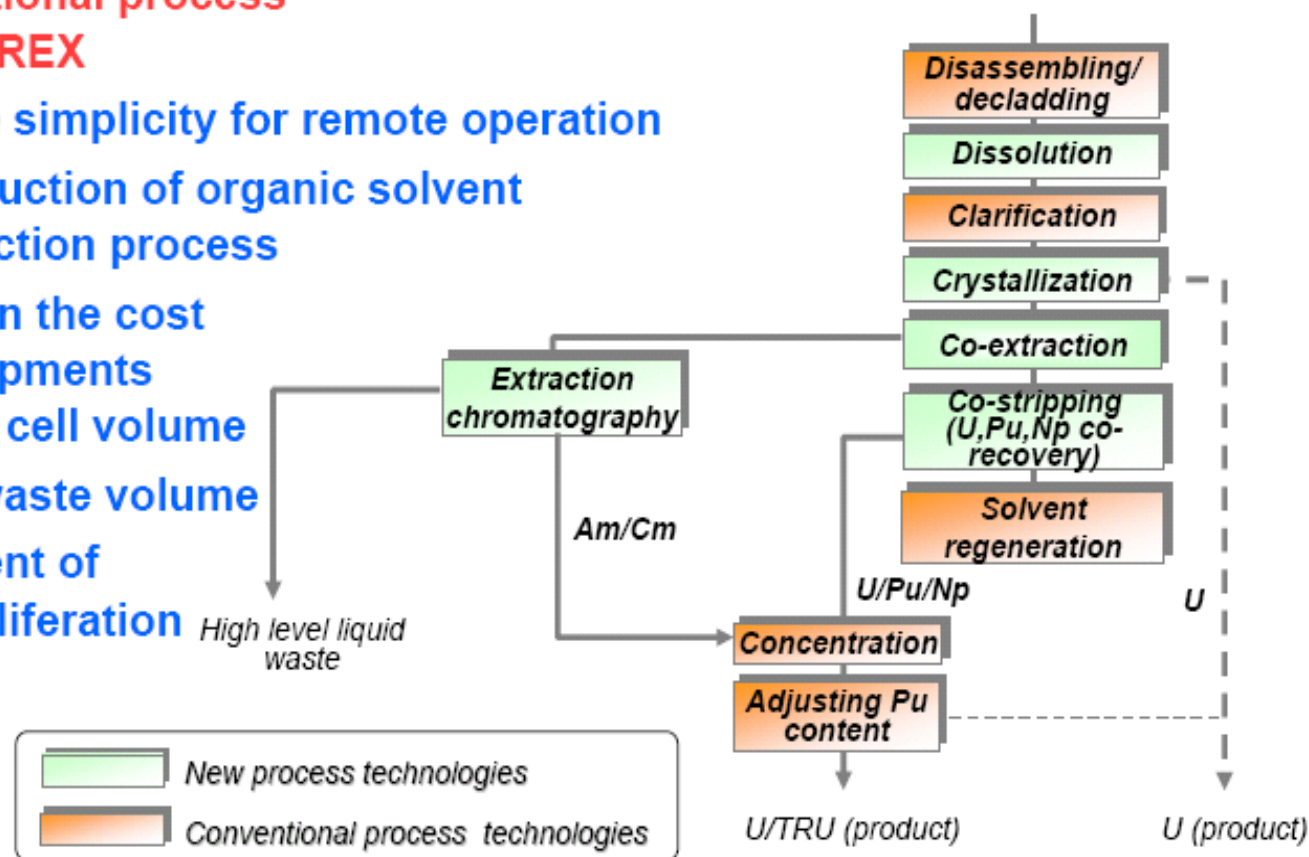
NEXT

New Extraction System for TRU Recovery

NEXT Process, Courtesy : Kimura, JAEA

NEXT (New Extraction System for TRU Recovery) process is expected to have some advantages over the conventional process based on the PUREX

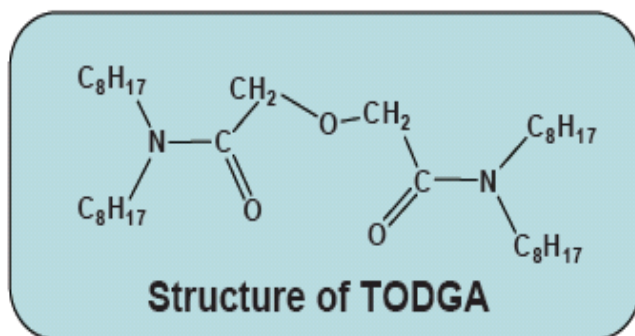
- The relative simplicity for remote operation
- Volume reduction of organic solvent in the extraction process
- Reduction in the cost for the equipments and the hot cell volume
- Reducing waste volume
- Enhancement of nuclear proliferation resistance



Schematic Flow of the NEXT Process

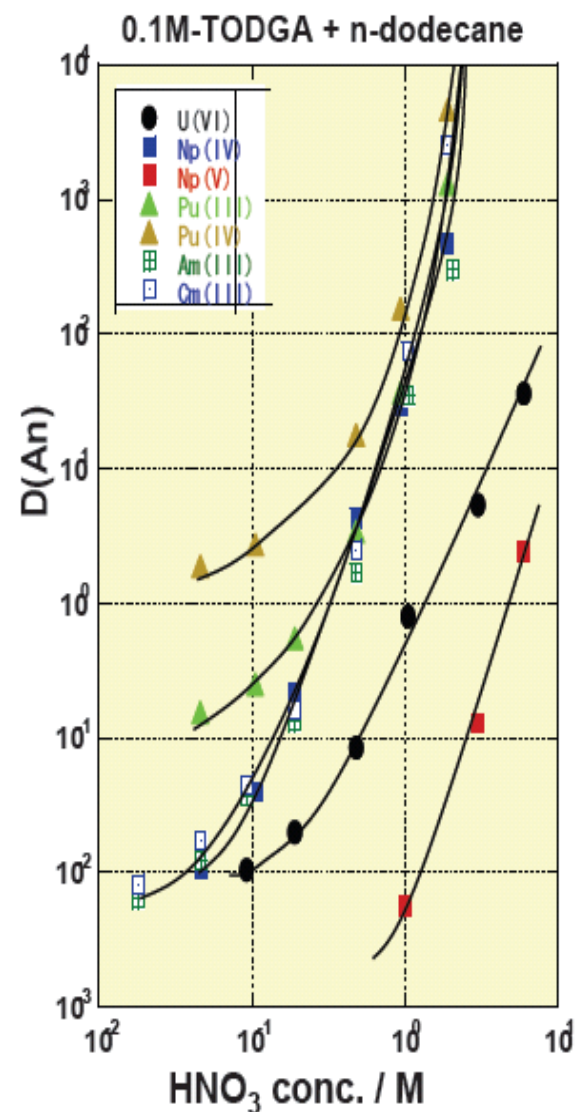
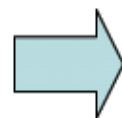
TODGA extraction characteristics, Courtesy : Kimura, JAEA

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

$$D(\text{An}) > 1000$$



French studies on partitioning

1992-1995: 3rd Frame Work Programme (FWP)

- High-Level Liquid Waste Partitioning by Means of Completely Incinerable Extractants

• 1996-1999: 4th FWP

- New Partitioning Techniques (NEWPART) for Minor Actinides

• 2000-2003: 5th FWP

- PARTNEW

- CALIXPART

- PYROREP

• 2004-06

• EUROPART

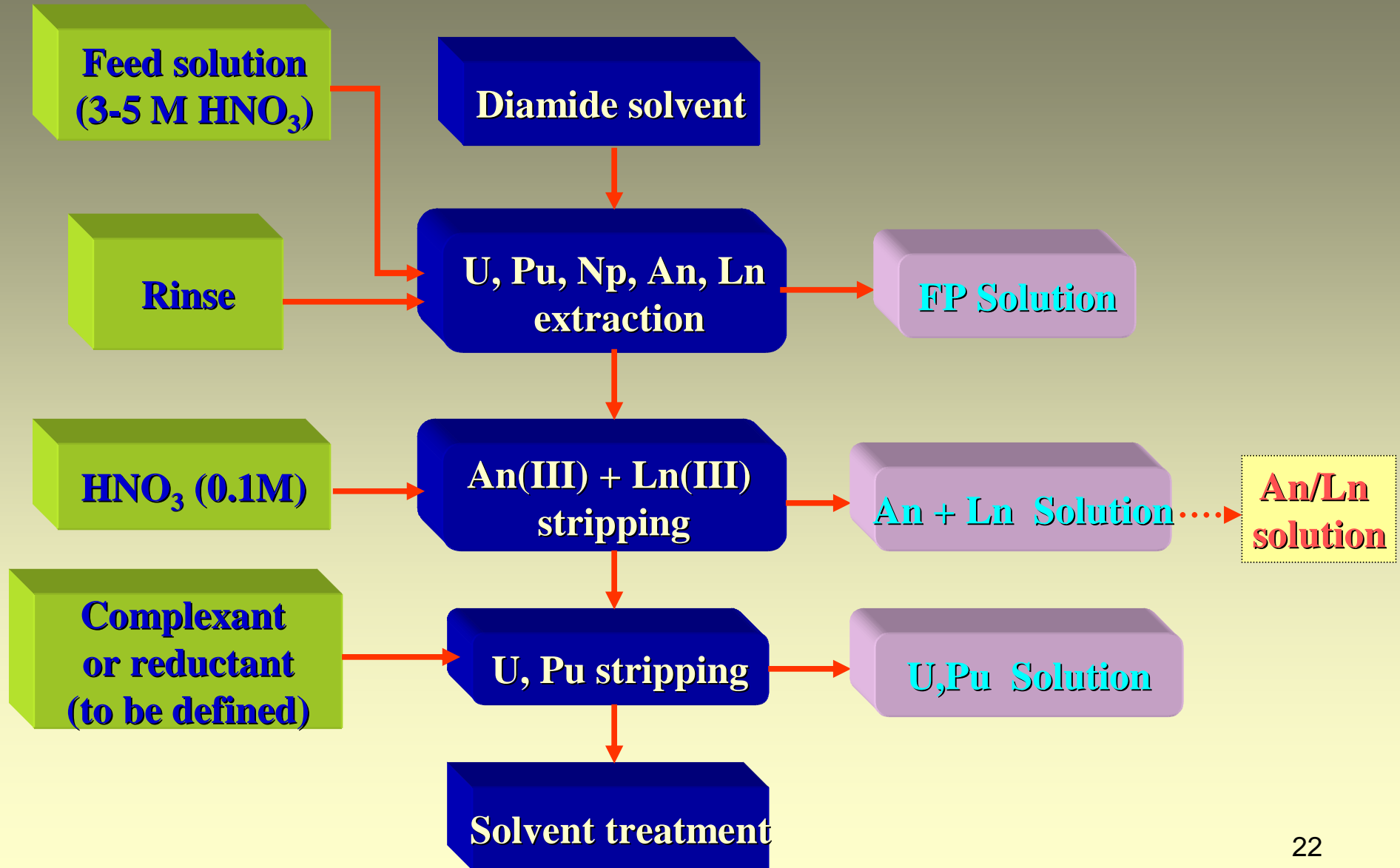
PALADIN (CEA, France)

- ❖ This process is based on the use of a mixture of extractants: a malonamide (DIAMEX process extractant)+ HDEHP, the extractant of the TALSPEAK process
- ❖ In the metal nitrate extraction step, carried out at 3-5 M HNO_3 , trivalent An and Ln are extracted with the malonamide
- ❖ An(III)/Ln(III) separation is done by contacting the loaded solvent with a pH adjusted aqueous solution containing DTPA where HDEHP plays the role
- ❖ This process was recently successfully tested in the ATALANTE facility (CEA/Marcoule, France)
- ❖ The possible drawbacks of this process are :
 - ❖ necessity to use 2 extractants
 - ❖ need of pH adjustment
 - ❖ co-extraction of numerous ions
 - ❖ solvent clean-up not yet defined

France (CEA)

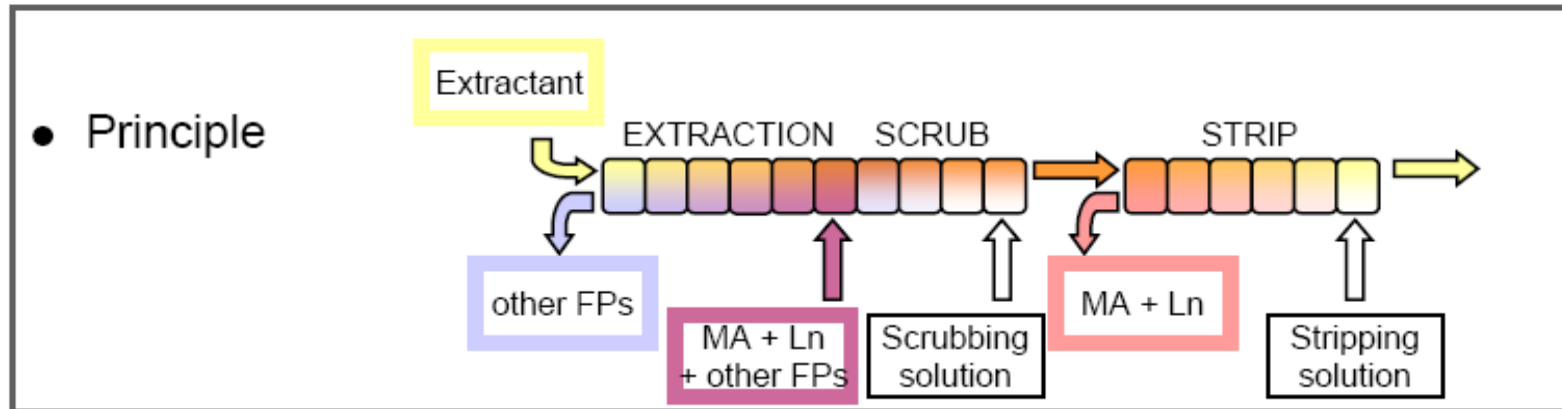
- ❖ The strategy developed by the CEA for partitioning the nuclear wastes of LWR closed cycle concerns 6 LLRNs to separate from the wastes:
3 MAs (Np, Am and Cm) and 3 FPs (I, Tc and Cs)
- ❖ This strategy is based on the development of successive liquid-liquid extraction processes:
 - (i) The improved PUREX process for U, Pu, Np, I and Tc separations
 - (ii) The DIAMEX process for trivalent Am+Cm extraction
(FP lanthanides (III), Ln, are co-extracted)
 - (iii) The SANEX process for Am+Cm/Ln(III) separation
 - (iv) The SESAME process for Am/Cm separation
 - (v) The CALIXCROWN process for Cs separation
- ❖ Some countries (USA, Japan, Czech Republic and Russian Federation), have also developed integrated separation of MAs and FPs
- ❖ For example, the use of a solvent containing a mixture of cobalt dicarbollide+dioxide of diphosphine allows the combined extraction of Cs + Sr + (Am + Cm) + Ln

DIAMEX Process

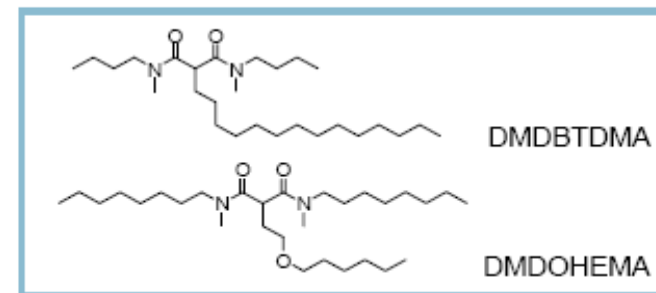


DIAMEX PROCESS : HOT RUNS

- Principle



- 6 hot runs (CEA, ITU) from 1998 to 2003
 - ◆ On synthesized and genuine feeds
 - ◆ Using various type of contactors
- Main results
 - ◆ Validation of the performances of both reference malonamides
 - ◆ Recovery of minor actinides and lanthanides higher than 99.9 %



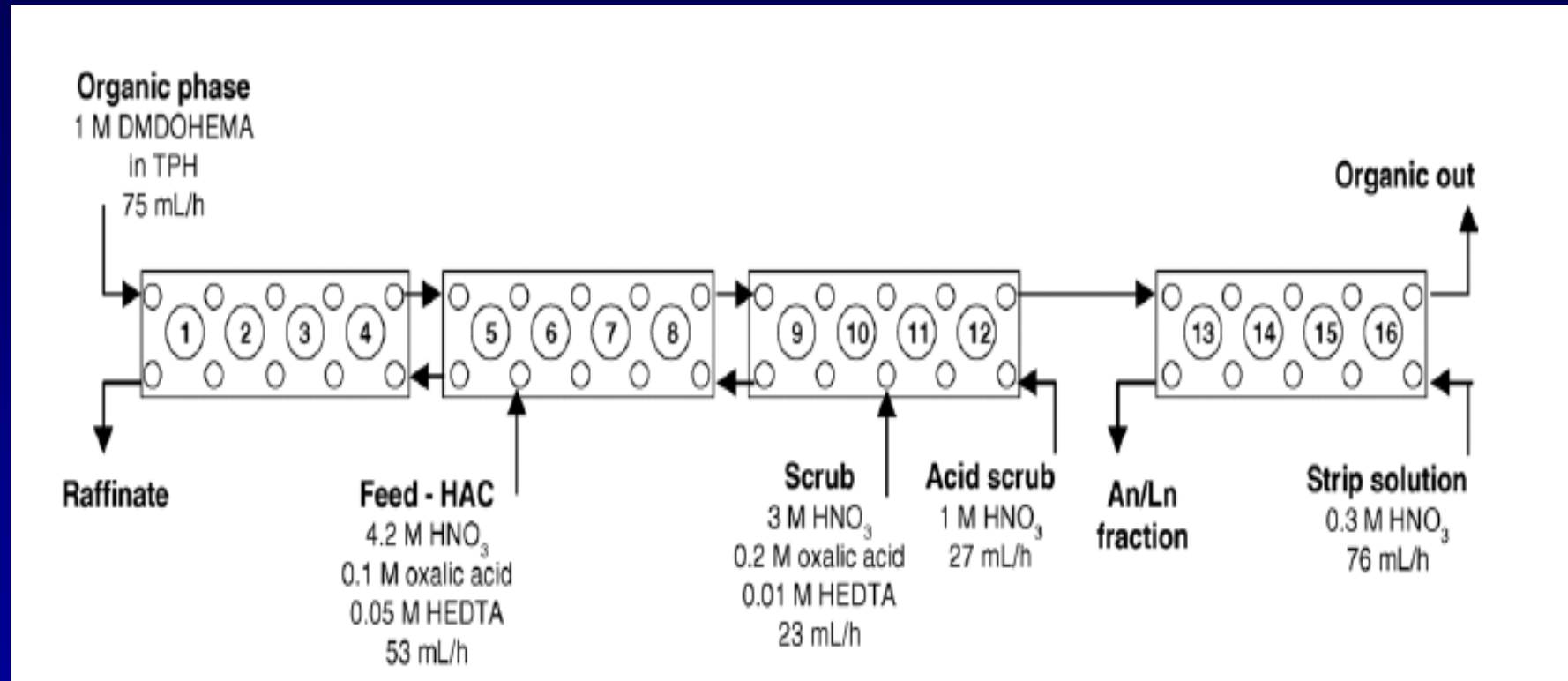
Courtesy : Bernard Boullis, CEA

DIAMEX Hot Runs in France

	<i>ITU</i> 1998	<i>ENEA/FZJ</i> 1998	<i>ATALANTE</i> 1999	<i>ATALANTE</i> 2000	<i>ITU</i> 2002	<i>ITU</i> 2003
Duration	4 h	11 h	45 h	38 h		3.5 h
Contactator	C - C	M - S	M - S	C - C	C - C	C - C
Extractant	DMDBTDMA	DMDBTDMA	DMDOHEMA	DMDOHEMA	DMDOHEMA	DMDOHEMA
Feed	UOX2	UOX2	MOX	MOX	UOX2	MOX
Product	An(III) >99.7% Ru ~ 9 % Pd ~ 85 % Y ~ 18 %	Am 98.9 % Eu 98.2 % Ru 1 %	An(III) ~ 99.9 % Zr, Mo < d.l. Ru ~ 10 % Pd ~ 60 %	An(III) ~ 99.9 % Zr < d.l. Mo < d.l. Ru < d.l. Pd < d.l. Y ~ 60 %	Am ~ 99.96 % Cm > 99.7 % Ln(III) ~ 99.5 % Ru ~ 3 % Pd < d.l. Y ~ 15 % Tc ~ 62 %	Am > 99.7 % Cm > 99.9 % Y, Ln(III) ~ 99 % Zr < d.l. Mo ~ 0.6 % Ru ~ 6 % Pd < 1 %

Courtesy : Bernard Boullis, CEA

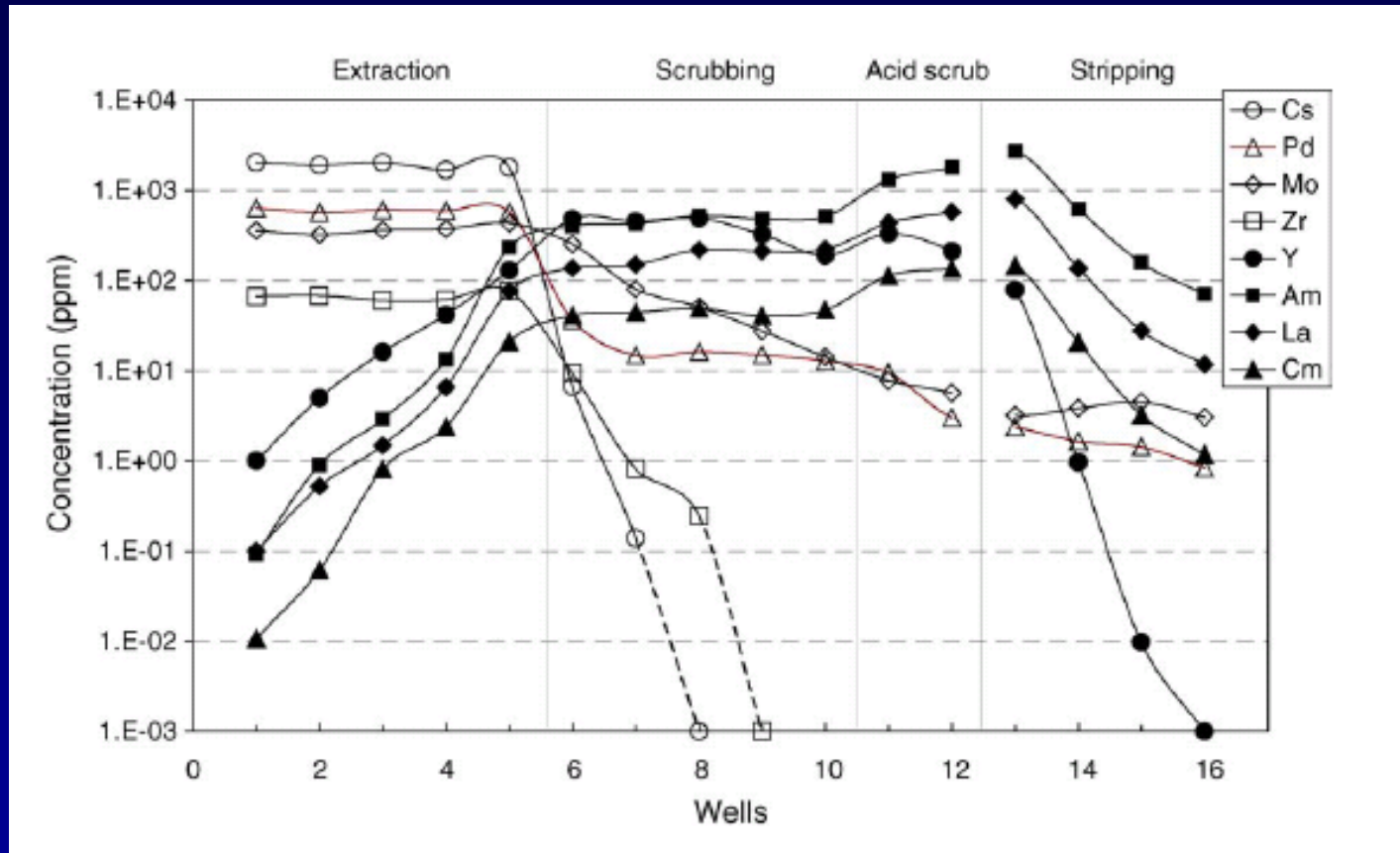
Flowsheet for DIAMEX-HAC run with DMDOHEMA a new reference extractant



From :

Daniel Serrano-Purroy et al., *Separation and Purification Technology* 45 (2005) 157-162

Concentration Profiles in DIAMEX-HAC run



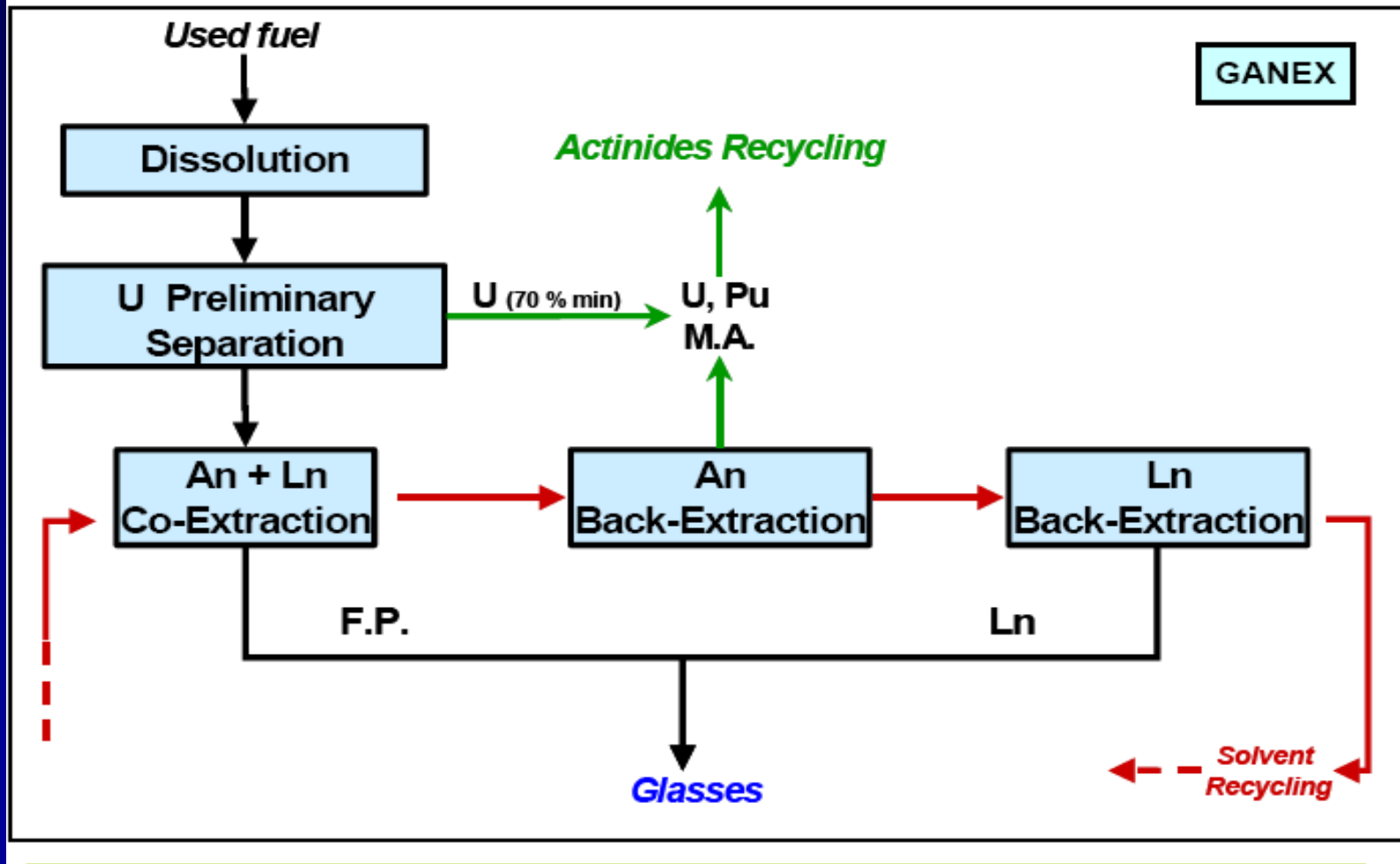
From :

Daniel Serrano-Purroy et al., *Separation and Purification Technology* 45 (2005) 157-162

Conclusions

- ❑ A concentration-denitration of genuine HAR has been carried out leading to a CF of 10 without significant lanthanide and actinide precipitation.
- ❑ Sr, Zr, Mo, Sn and Ba are the major components of the precipitate, which was formed mainly in the concentration step
- ❑ A16-stage extraction process using a centrifugal extractor battery has shown to efficiently separate the minor actinides, Am(III) and Cm(III)
- ❑ The process represents an excellent compromise between good extraction and even better back-extraction properties.
- ❑ Thus, recoveries above 99.9% for Am & Cm were achieved
- ❑ Oxalic acid and HEDTA were shown to be very efficient in preventing coextraction of Mo, Zr and Pd

Grouped Actinides Extraction : the GANEX Process



ANL HDHoEP (Bis-(hexoxyethyl) phosphoric acid) Process

- ❖ HDHoEP requires no adjustment of acidity up to a nitric acid concentration of 2.4 M
- ❖ The flow sheet developed and cold-tested on a PUREX aqueous raffinate generated by processing a light water reactor fuel with a burn up of 3300 MWd/Te
- ❖ A HLW simulant was prepared containing thirty components. The process solvent consisted of 0.5 M HDHoEP/diethylbenzene
- ❖ After a 1M HNO₃ scrub (O/A= 4), Am and Cm were stripped with 6 M HNO₃ (O/A= 2) and Np and Pu together with Zr, Nb, Mo and Fe were stripped with a mixture of 0.35 M oxalic acid and 0.35 M tetramethylammonium hydrogen oxalate (O/A = 2)
- ❖ The process solvent was washed with 8 M H₃PO₄ to remove any U and degradation products
- ❖ The entire process was operated at 50°C

ANL HDHoEP (Bis-(hexoxyethyl) phosphoric acid) Process.....

- ❖ A three extraction stage batch countercurrent test run removed 93% of the Am and Cm, 97% of the Np and 99.7% of the Pu
- ❖ Using eight extraction stages, the calculated amount of Am, Np and Pu extracted from the feed would be 99.8, 99.8 and 99.99%, respectively
- ❖ The process is much simpler than those based on HDEHP and DIDPA because it has only one extraction cycle and requires no acidity adjustment of the feed, provided that the HNO_3 concentration in the feed is not above 2.4 M

Drawbacks

- ❖ Diethylbenzene is used as diluent, not favorable due to low flashpoint
- ❖ The Am and Cm are recovered in 6 M HNO_3 , which would require extensive evaporation and recovery of concentrated nitric acid
- ❖ Np and Pu fractions would require further processing to remove macroquantities of Fe, Zr and Mo
- ❖ 8 M H_3PO_4 solvent wash will be contaminated with U and Y fission products

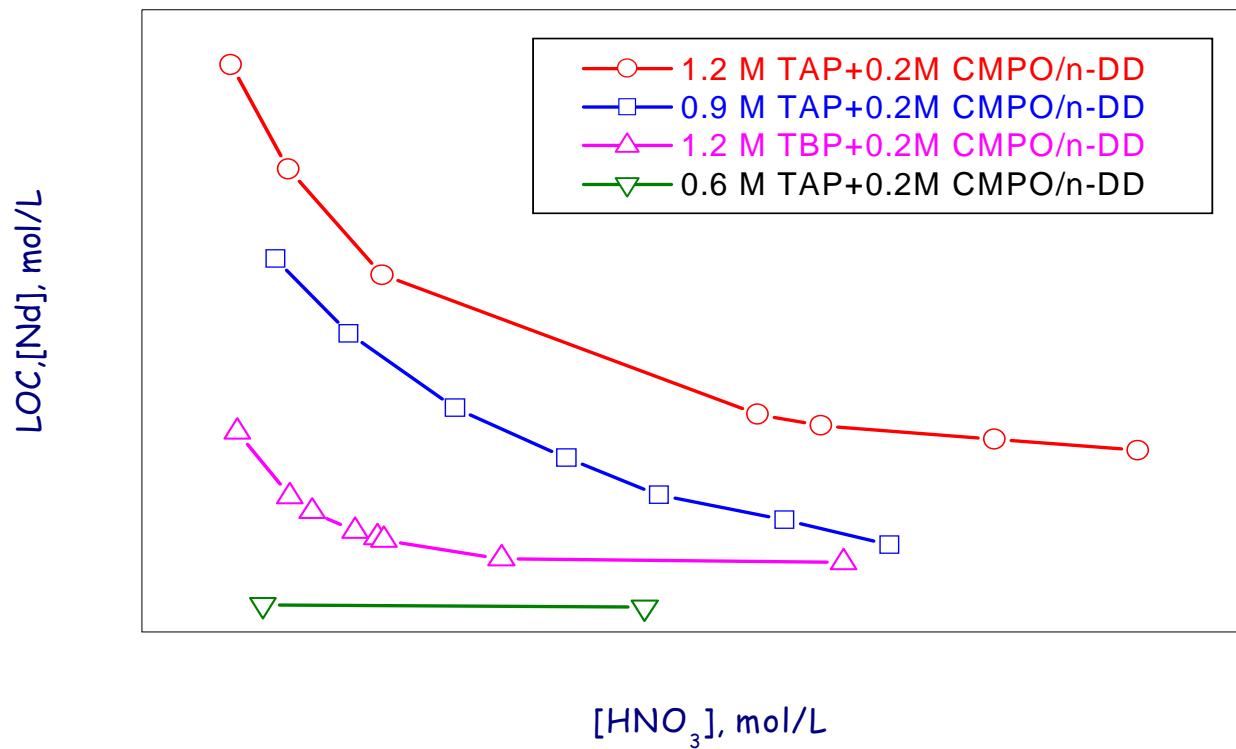
Studies in India on TRUEX

- ❖ Tested with HLW generated from PUREX processing of thermal reactor fuels
- ❖ Two process solvent formulations were used:
 - ❖ 0.2 M CMPO -1.2 M TBP-dodecane and
 - ❖ 0.2 MCMPO - 1.4 M TBP-dodecane
- ❖ Feed solutions were approximately 2 M in HNO_3
- ❖ In the first, TRUEX processing was carried out directly on the HLW
- ❖ In the second test run PUREX processing preceded TRUEX processing
- ❖ In both sets of experiments TRUEX effectively removed the alpha activity in the feed (residual activity less than 0.06% of the total)
- ❖ Stripping in succession with 0.04 M HNO_3 , 0.05 M HNO_3 - 0.05 M HF and 0.25 M Na_2CO_3 resulted in the usual actinide partitioning
- ❖ The stripped and washed process solvent did not contain any detectable activity above background

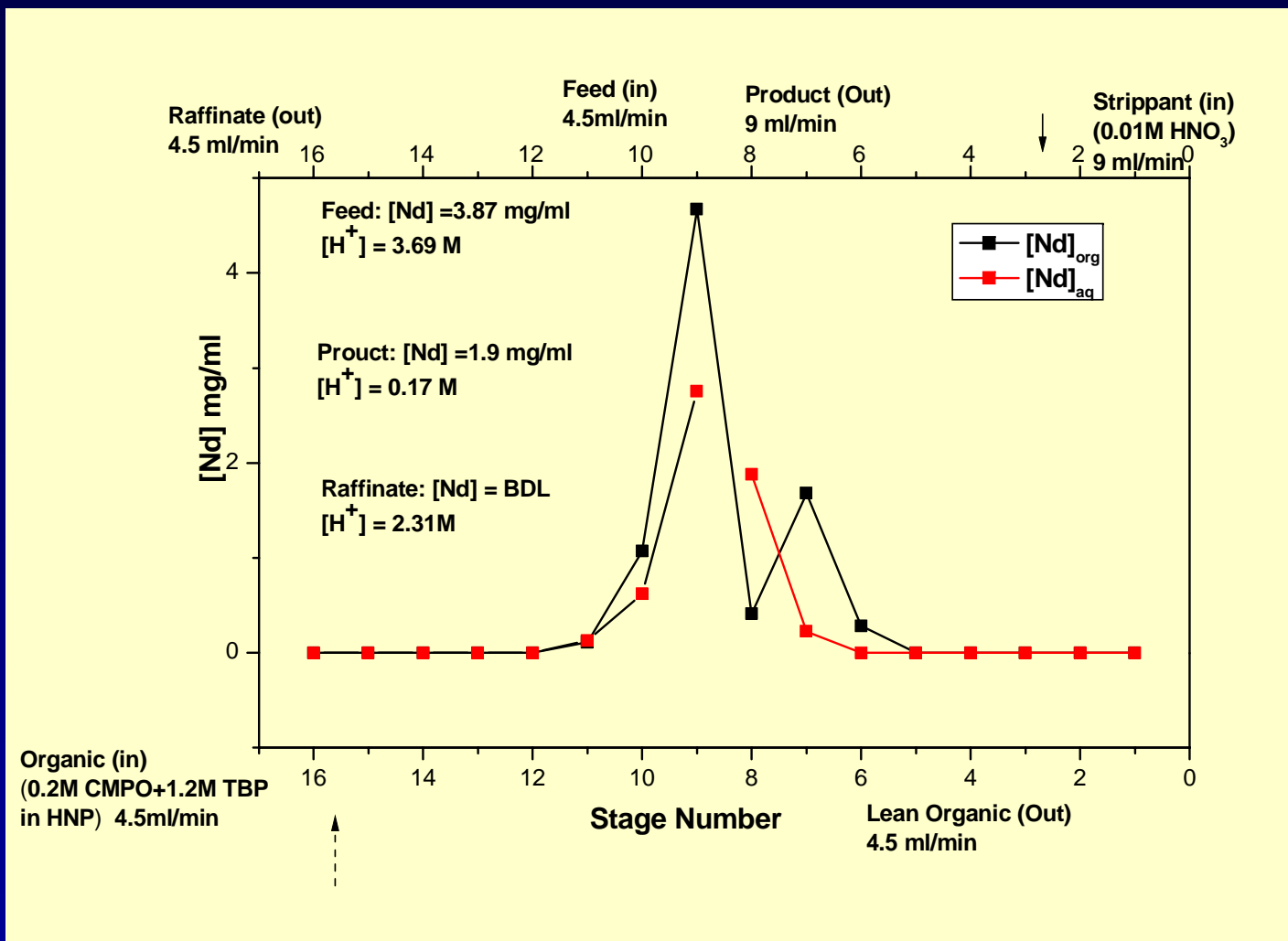


Studies on Partitioning

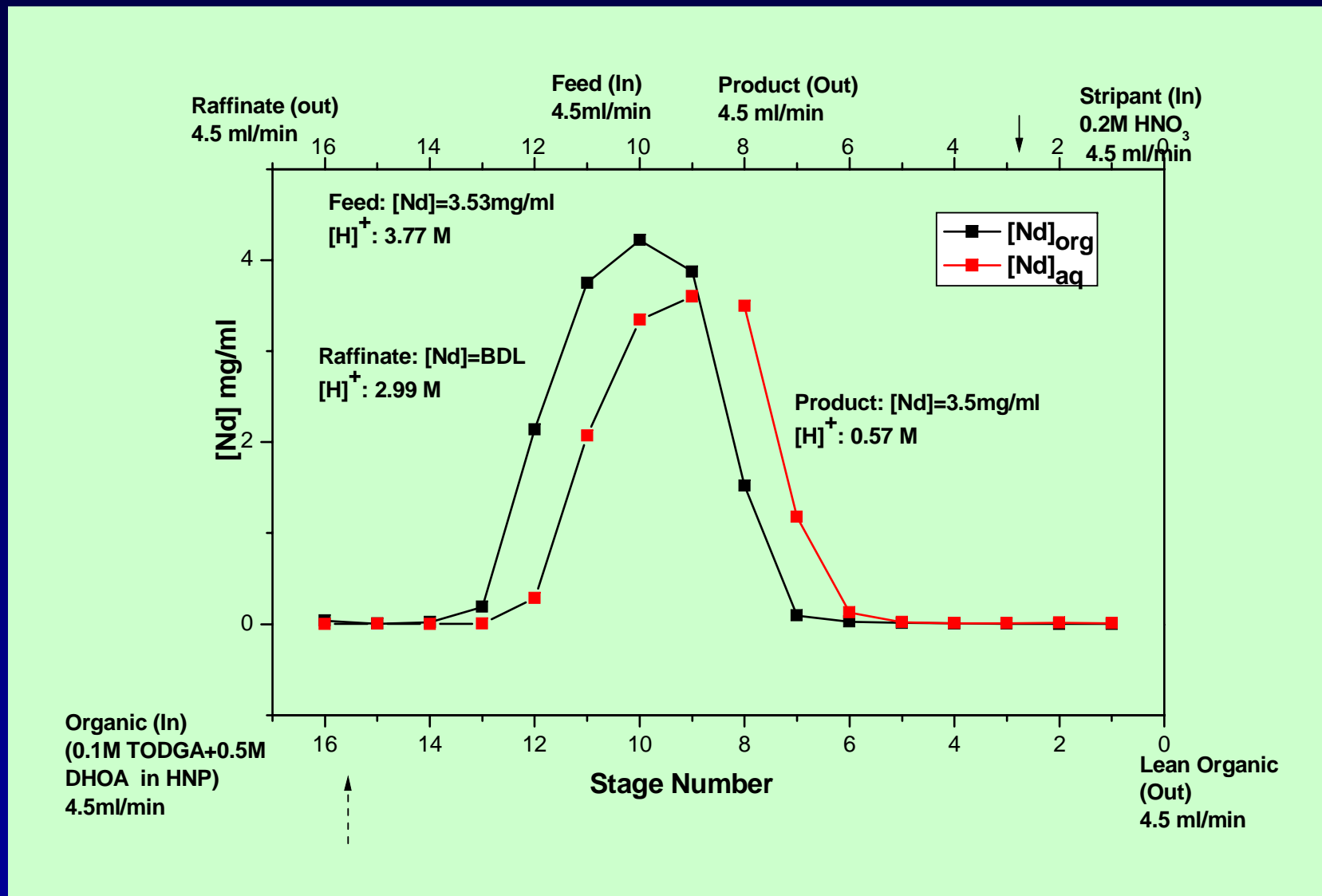
- Extensive batch and counter current liquid-liquid extraction runs with actual and simulated HLWs typically generated by different reprocessing operations with $O\Phi$ CMPO, Malonamide, and diglycol amides (TODGA and T2EHDGA)
- Extraction chromatographic studies
- Studies on third phase formation
- Studies on Actinide/Lanthanide separation



Effect of Tri n-Amyl phosphate on third phase formation
in TAP-CMPO/n-DD-Nd(NO₃)₃ system, T=25°C



Stage profiles for Nd³⁺ run with CMPO



Stage profiles for Nd³⁺ run with TODGA/DHOA

Russian TRU Extraction Process

- ❖ Uses Diphenyl-N,N-di-n-butyl CMPO (DΦDBCMPPO)
- ❖ Insufficient solubility in paraffinic hydrocarbon diluents, even in the presence of excess TBP, to be of practical use
- ❖ Strong tendency towards third phase formation
- ❖ Solubility and Third phase formation problems overcame using a fluoroether, called Fluoropol-732, as diluent
- ❖ The process uses a 0.1 M DΦDBCMPPO/Fluoropol-732
- ❖ An 18-stage bank of centrifugal contractors was used to test the flow sheet
- ❖ Feed solution consisted of a HLW simulant, 5 M in HNO_3 , containing more than 13 g/L of lanthanides and actinides
- ❖ The flow sheet uses acetohydroxamic acid (AHA) to strip Fe(III), Zr(IV) and Mo(W), which co-extract with the transplutonium elements (TPEs)

- ❖ A solution of 2 M HNO_3 -10 g/L AHA was employed for this purpose
- ❖ TPEs and Lanthanides were stripped from the process solvent using 0.01 M HNO_3
- ❖ Greater than 99.5% of the actinides and lanthanides were recovered and concentrated by a factor of four to six
- ❖ The reduction of Fe, Zr and Mo from the TPE fraction was > 50
- ❖ The Russian TRU process has the added advantage of using a lower concentration of a less expensive easy to synthesise extractant
- ❖ Radiolytic and hydrolytic degradation is probably less with the D Φ DBCMPPO -Fluoropol system than with TRUEX process solvent due to the absence of TBP
- ❖ Major concerns
 - ❖ Use of Fluoropol diluent
 - ❖ Its radiolytic stability, corrosive properties in high radiation fields
 - ❖ Cleanup techniques and environmental issues with spent solvent
 - ❖ Back extraction demands low acidity



Thank You

R & D in Partitioning

Part II

USA

The situation in the USA is peculiar because partitioning processes developed concern the treatment of defence wastes in particular those accumulated at DOE's Hanford site during the cold war

Several processes were developed for the partitioning of radionuclides from the wastes:

- (i) TRUEX process for transuranic extraction,
- (ii) SREX process for Sr removal and
- (iii) CSEX process for Cs extraction

DOE has published a report named "*A Roadmap for Developing Accelerator Transmutation of Wastes (ATW) Technology*" which considers the possible treatment of the LWR spent fuels accumulated in the USA in order to separate :

- (i) U for final disposition as low level waste and
- (ii) TRUs for burning in ATW systems using,
 - (i) the UREX process (a modified PUREX process aiming to only extract U
 - (ii) pyrometallurgical partitioning process for TRU separation from the UREX wastes and for the ATW fuel cycle.

ANL Experience

- ❑ Initial development studies on TRU EX, using a dissolved sludge waste that simulated the insoluble HLW sludge from a Hanford storage tank
- ❑ All additional studies with real waste solutions of TRU analytical waste generated at ANL and the New Brunswick Laboratory
- ❑ A total of 118 L of TRU nitric acid waste solutions were treated in four process runs
- ❑ A 20-stage bank of 4 cm centrifugal contractors housed in a plutonium glovebox was used to process the wastes
- ❑ The nitric acid concentration in the feed varied from 1.7 to 4.5 M
- ❑ Various amounts of other acids, such as HCl, H₂SO₄ and H₃PO₄, were also present in some of the solutions and H₃PO₄ was as high as 1.3 M in one of the waste solutions
- ❑ The flowsheets utilized in each of the four processing runs were designed using the GTM

ANL Experience.....

- ❑ The TRUEX process solvent used was 0.2 M CMPO - 1.4 M TBP/n-DD
- ❑ Alpha decontamination factors, D.F.s, of the waste solutions ranged from $4.0 \cdot 10^3$ to $6.5 \cdot 10^4$, which allowed disposal of the process raffinates as low-level wastes
- ❑ Approximately 18 g of U, 84 g of Pu and 200 mg of Am were recovered
- ❑ In addition to the high alpha DFs were achieved

LMITCO Experience

- ❖ The TRUEX process was evaluated at the Lockheed Martin Idaho Technologies Co. (LMITCO) for the separation of the actinides from acidic HLW
- ❖ Several TRUEX demonstration runs have been performed on Sodium Bearing Waste (SBW)
- ❖ The SBW is a secondary acidic HLW (1.5 to 1.7 M HNO₃) containing twelve inert constituents, including Pb and Hg, and ⁹⁰Sr, ⁹⁹Tc, ¹³⁷Cs, ^{235,238}U, ^{238,239}Pu and ²⁴¹Am
- ❖ Flow sheet was tested in shielded hot cells at the ICPP Remote Analytical Laboratory using a 20-stage bank of 2 cm diameter centrifugal contractors
- ❖ The flowsheet, designed using the *Generic Truex Model*, consisted of six stages of extraction (O/A=0.33), four 0.01 M HNO₃ scrub stages (O/A= 1.5), six 0.01 M 1-hydroxyethane-1,1 -diphosphonic acid (HEDPA) strip stages (O/A= 1.0), two 0.25 M Na₂CO₃ solvent wash stages (O/A= 1.0) and two 0.1 M HNO₃ rinse stages (O/A=6.0)
- ❖ HEDPA is a powerful completing agent that will effectively remove actinides (III, IV, VI) from TRUEX process solvent
- ❖ The solvent formulation was 0.2 M CMPO -1.4 M TBP/Isopar-L (Isopar-L is a mixture of isoparaffinic hydrocarbons with an average of 12 carbons per molecule)

ORNL Experience

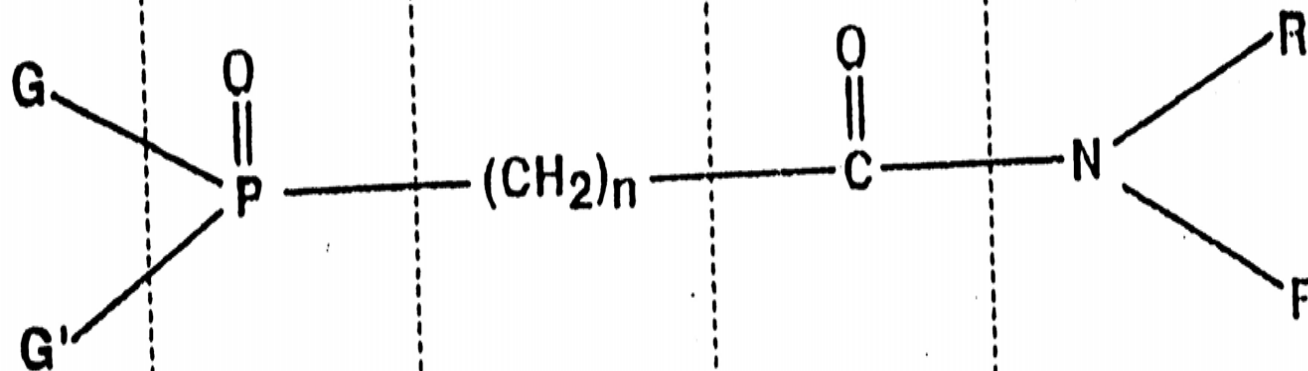
- ❖ The Radiochemical Engineering Development Center (REDC) at ORNL tested TRUEX for separation and recovery of macroquantities of Am and Cm from highly irradiated (>87% fission), Mark 42 PuO₂ targets
- ❖ Three banks of 16-stage mixer-settler contractors in a shielded hot cell were used to conduct three test runs using TRUEX
- ❖ The objectives of the test runs were twofold:
 - (1) to test the performance of the TRUEX process
 - (2) to verify the GTM using gram quantities of Am and Cm and dekagram quantities of Pu
- ❖ Solvent composition was 0.2 M CMPO -1.2 M TBP/Norpar-12
- ❖ In general, the design criteria for the process flowsheet were met
- ❖ The major problem area revolved around the stripping section for Pu
- ❖ In all three test runs, a significant Pu concentration remained in the lean solvent
- ❖ It is believed that the unstripped Pu is most likely retained by acidic degradation products formed in the process solvent

PNNL/WHC Experience

- ❑ The first TRUEX demonstration done outside ANL at the Plutonium Reclamation Facility (PRF) located at the Hanford Site, with plutonium Finishing Plant (PFP) waste, generated at the PRF
- ❑ The PFP waste consisted primarily of aqueous raffinate from a SX process using TBP/CCl₄, to recover Pu from scrap materials, with Al (0.5 M), Na (0.05 M), Mg (0.3 M), Ca (0.2 M), Fe (0.05 M) and F (0.4 M)
- ❑ The nitric acid concentration ranged from 1.5 to 4.0 M
- ❑ Typical Pu and Am concentrations in PFP were 0.1g/L (7,500 pCi/L) and 0.05 g/L (170,000 nCi/L), Respectively
- ❑ Due to ban on flammable solvents use in the PRF plant, the TRUEX process solvent formulation consisted of 0.25 M CMPO-0.75 M TBP/C₂Cl₄
- ❑ Four centimeter centrifugal contactors housed in a GB train were used
- ❑ A total of 40 L of clarified PFP waste was treated in four separate runs. In each of the runs, 10 liters of clarified feed were processed through the centrifugal contactors in about 40 minutes. The TRU content of all aqueous raffinates was reduced to well below the 100 nCi/g goal

TRUEX Process





- Affects basicity of phosphoryl group

- Selectivity

- Solubility

- Primary donor group

- Affects interaction between donor groups

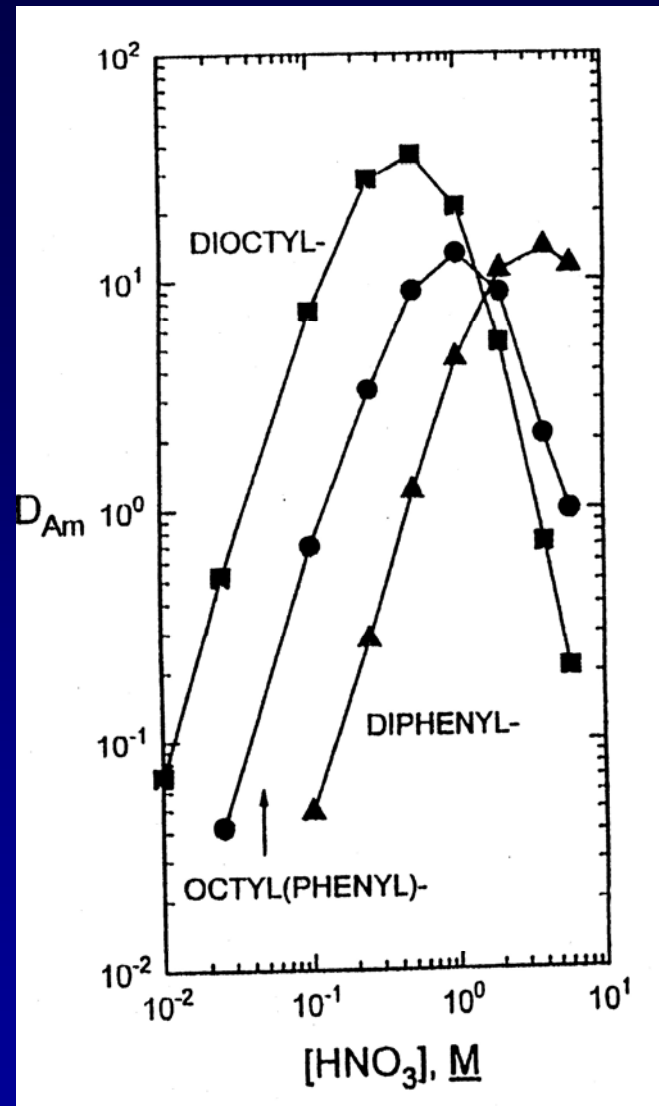
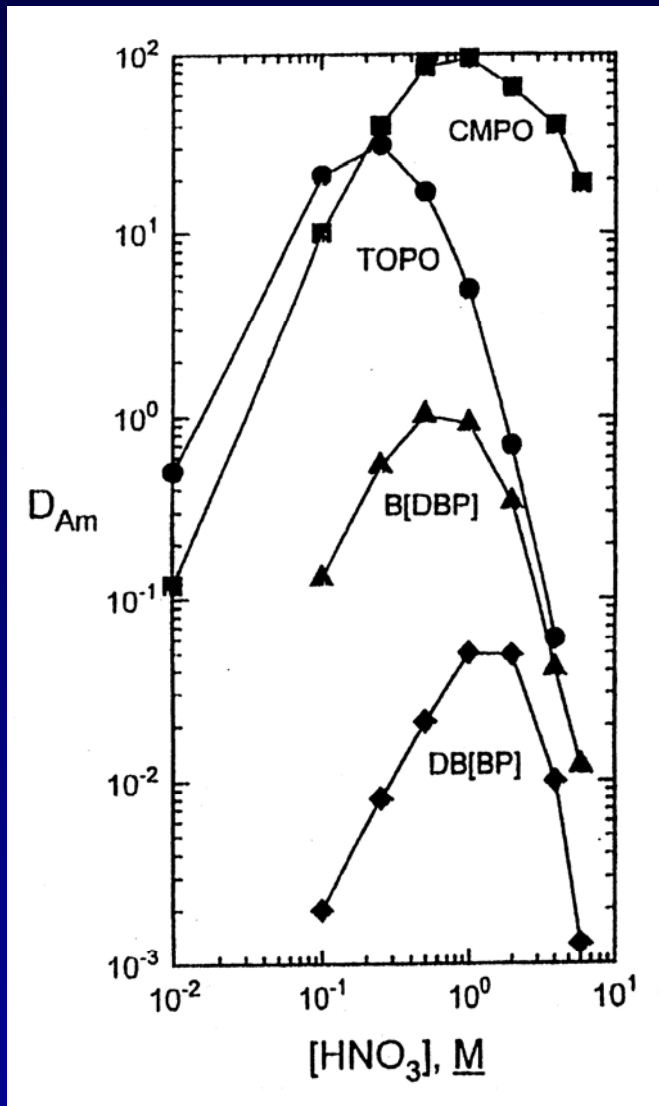
- Intramolecular buffer

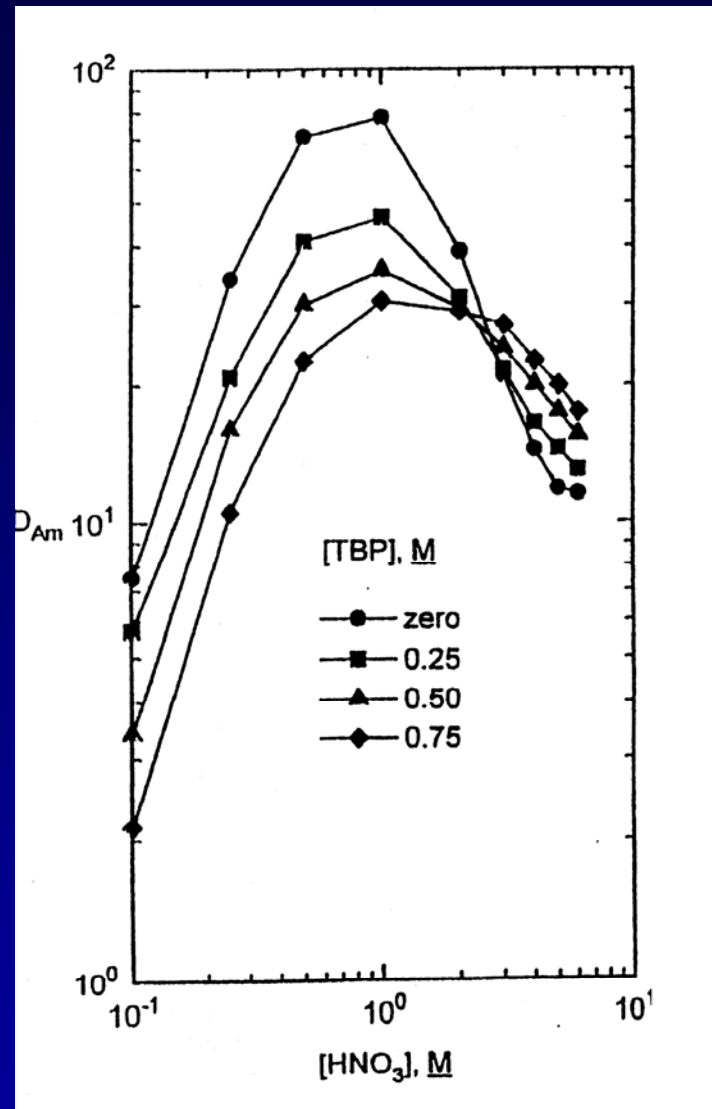
- Secondary donor group

- Affects basicity of carbonyl

- Affects third phase formation

- Solubility





CMPO - Metal ion extraction characteristics

Table 1 Extractabilities of Elements from 1 to 3 M HNO₃ Using 0.2 M CMPO–1.4 M TBP in C₁₂ to C₁₄-NPH

Distribution ranges				
<5 × 10 ⁻²	10 ⁻² to 1	1 to 20	>20	
Na–Cs	Ni	Zr ^a	La–Eu	Th
Be–Ba	Cu	Mo(VI) ^a	Y	U(VI)
Al	Zn	Ru	Tc	Np(IV)
Cr(III)	Rh	Pd ^a		Pu(IV)
Mn(II)	Ag		Am	
Fe(III)	Cd		Cm	
Co(II)	In			
	Sb			
	Tc			

^a Ds lowered by oxalate ion.

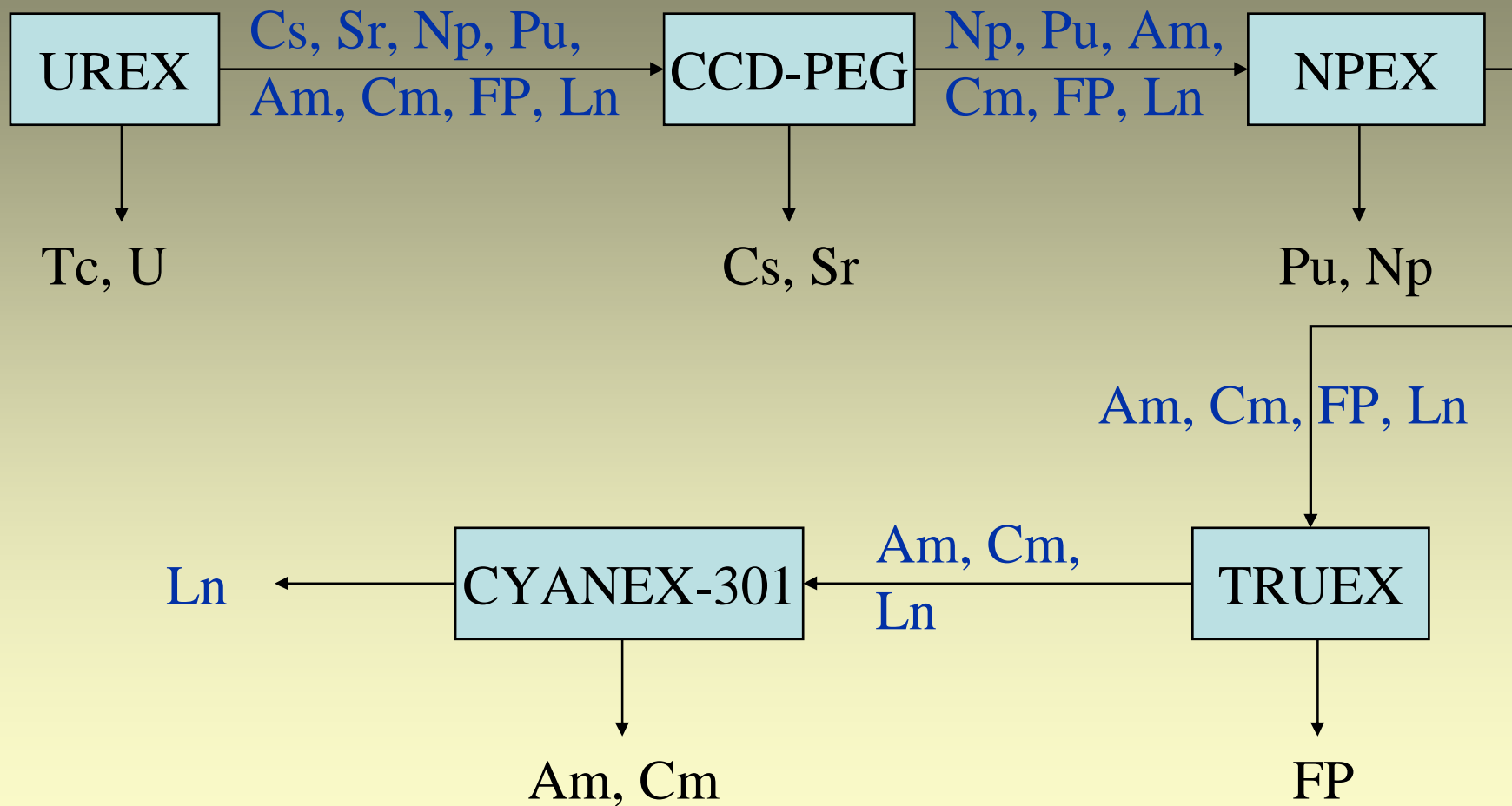
Table 2 Extractabilities of Elements from 6 M HCl Using 0.5 M CMPO in TCE

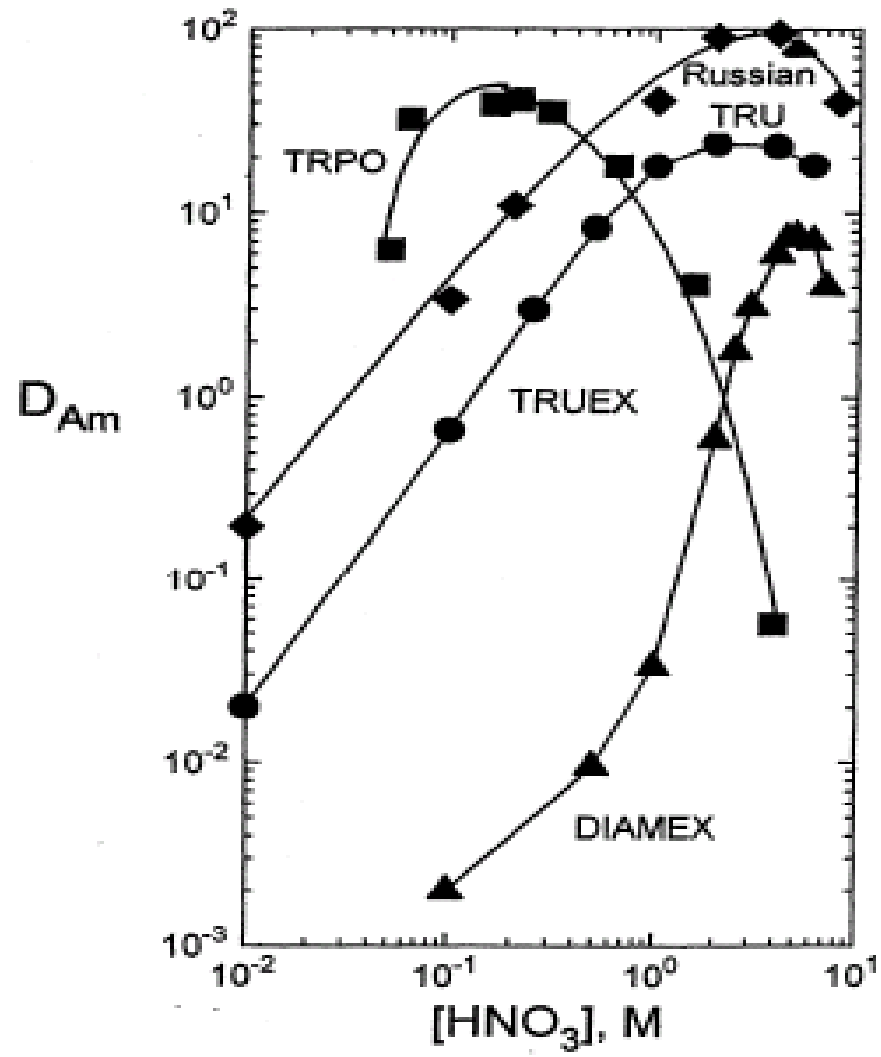
Distribution ranges			
<10 ⁻²	10 ⁻² to 1	1 to 10 ²	>10 ²
Li–Cs	Mn(II)	V	Fe
Be–Ba	Co(II)	Zn	Ga
Al	Ni	Cd	Zr
Cr(III)	Pb	Sn	Mo
		Am	Th
		Cm	U(VI)
			Np(IV)
			Pu(IV)

Current Extraction Scheme, Courtesy : Univ. of Nevada

- UREX
 - PUREX modification
 - addition of the acetohydroxamic acid (AHA) reduces Pu
 - Tetravalent Np and Pu forms aqueous phase AHA complexes
 - U and Tc extracted
- CCD-PEG
 - Cs and Sr extracted with chlorinated cobalt dicarbollide/polyethylene glycol (CCD/PEG-400)
- NPEX
 - Np, Pu
 - Nitric acid, acetohydroxamic acid, CH_3COOH
- TRUEX
 - Remaining fission products except lanthanides
 - TBP with Diphenyl-N,N-dibutylcarbamoyl phosphine oxide (CMPO), oxalic acid
- CYANEX-301 (Bis (2,4,4 -trimethylpentyl) dithiophosphinic acid)
 - Am and Cm

Separation flowsheet, Courtesy : Univ. of Nevada





Trialkyl phosphine oxide (TRPO) process

- ❑ The TRPO process, developed by Zhu, Song *et al.* in Tsinghua University (China), is based on the use of liquid mixtures of TRPO soluble in aliphatic hydrocarbon diluent (kerosene)
- ❑ The affinity of the TRPO extractant for trivalent actinides and lanthanides is high for moderate aqueous nitric acid concentration (1 M) and low for high acidity (5 M), respectively
- ❑ An+Ln extraction is performed after adjustment of the HNO₃ to 1 M, though in principle the method can operate in 1 - 2 M HNO₃ and the An+Ln mixture is stripped from the solvent using a 5.5 M nitric acid
- ❑ The process was also successfully tested at the ITU, Karlsruhe with diluted HLLW solution
- ❑ The decontamination factors for TRUs range from 10³ to 10⁴ in 1 M HNO₃

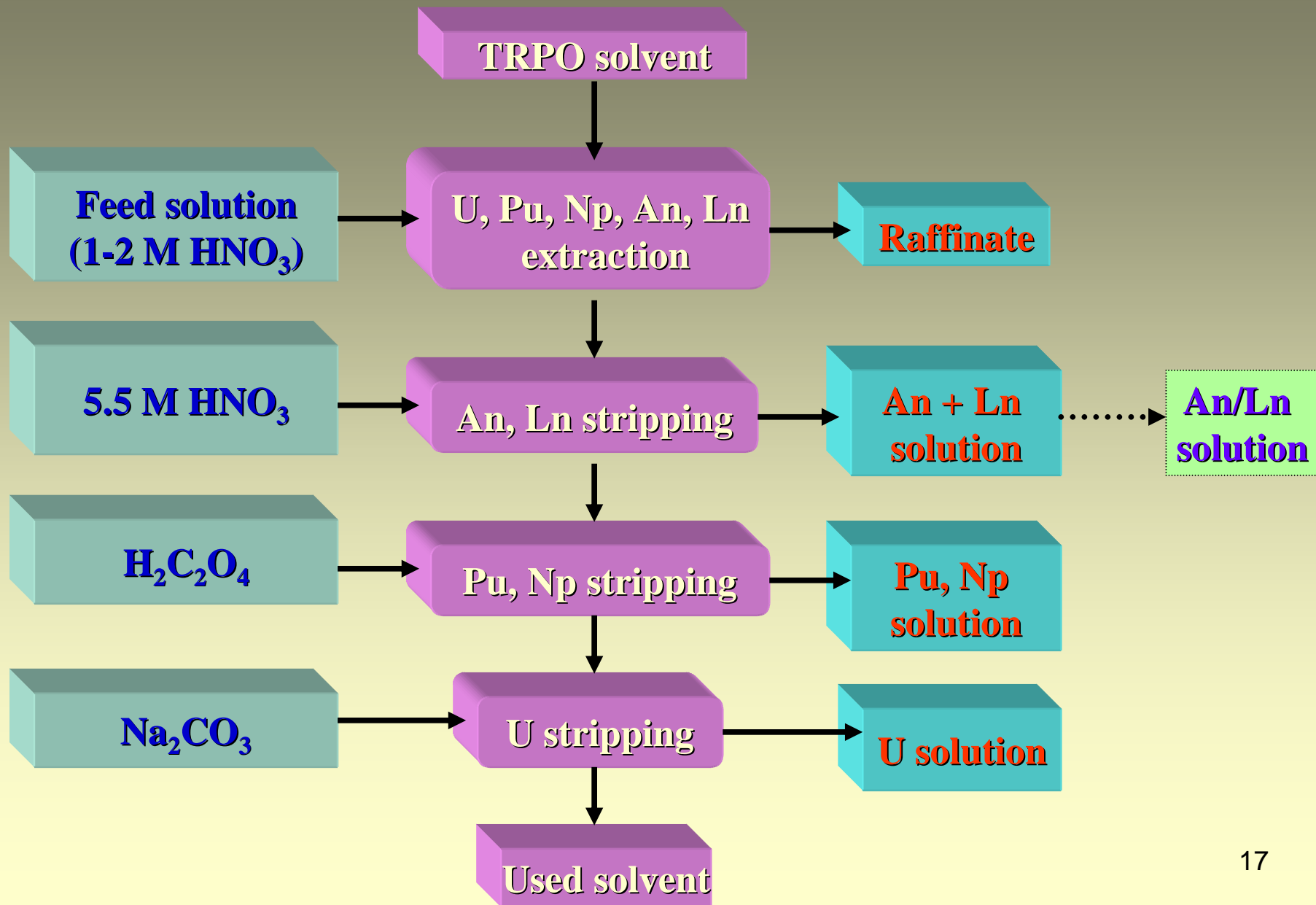
The great advantages are

reversibility in extraction and stripping
solvent miscibility with TBP and loading capacity

Drawbacks

Fission products such as Zr, Mo, Ru and Tc interfere with the separation
High acidity strip interferes with An/Ln separation

TRPO Process



Actinide - Lanthanide Separation

TALSPEAK and CTH processes

Trivalent Actinide Lanthanide Separation by Phosphorous reagent
Extraction from Aqueous Komplexes

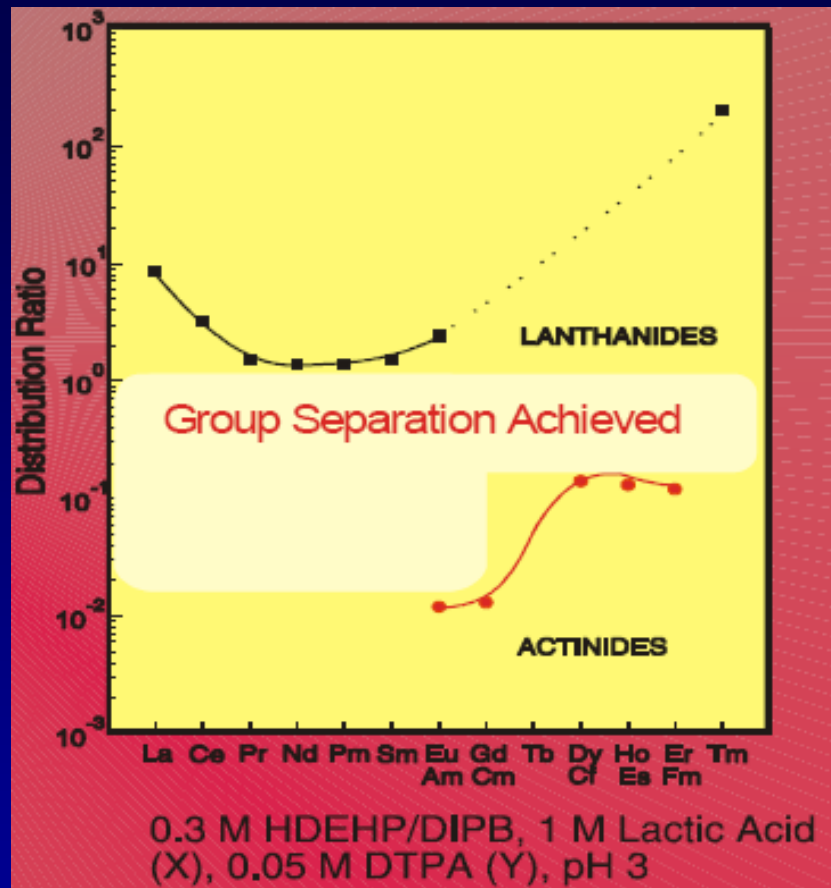
- The TALSPEAK process, developed at ORNL (USA) in the sixties and then adapted (CTH process) at Chalmers University, Göteborg, Sweden, can be considered as the reference process for An(III)/Ln(III) group separation
- It is based on the use of HDEHP as extractant and DTPA as the selective An(III) complexing agent
- The An(III)/Ln(III) separation is performed by the selective stripping of An(III) from the HDEHP solvent loaded with the mixture of An(III)+Ln(III) under the action of an aqueous solution containing DTPA and an hydroxocarboxylic acid, like lactic, glycolic or citric acids

The advantages of this process are

- (i) the large experience gained worldwide,
- (ii) good efficiency

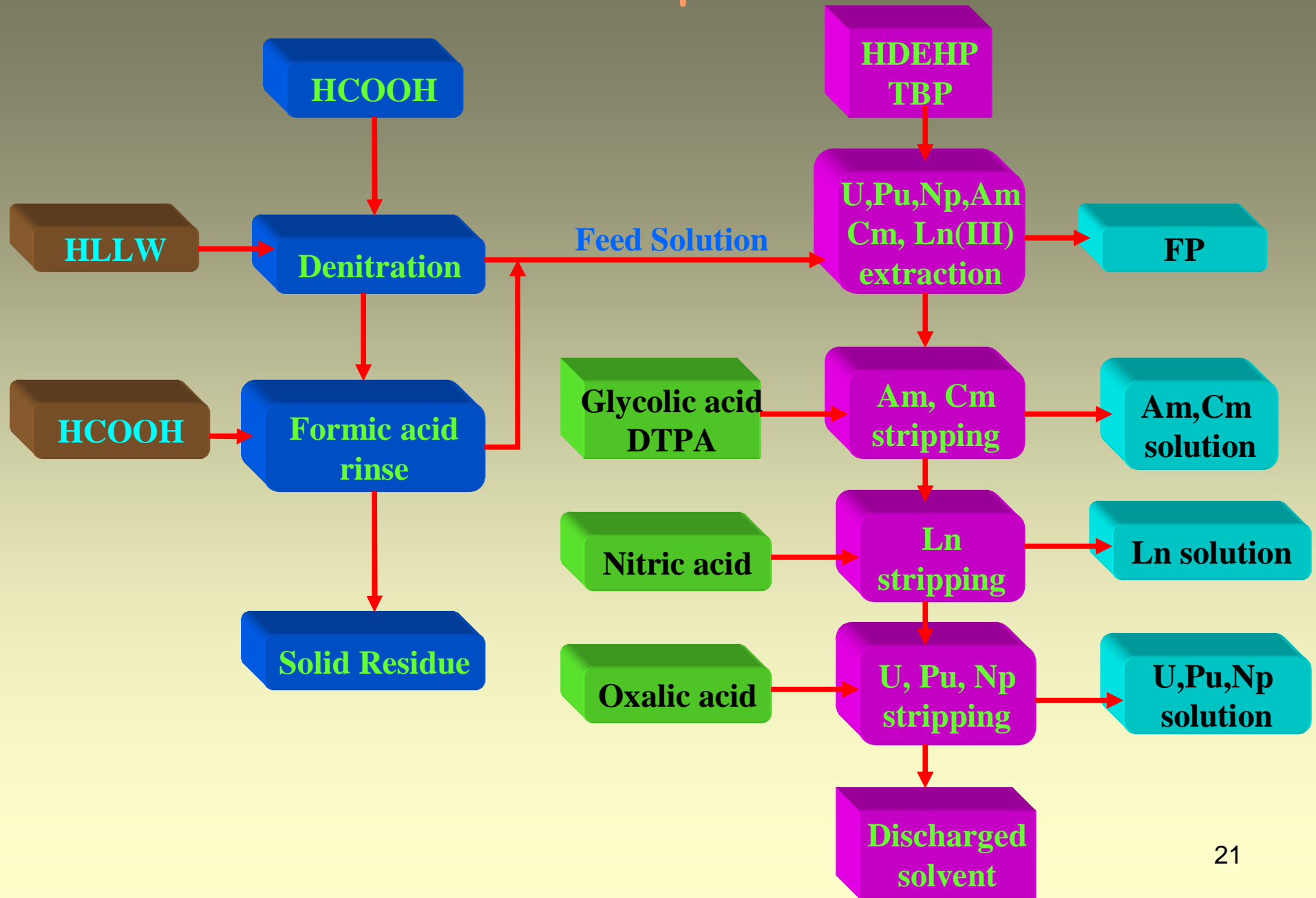
Among the main drawbacks

- (i) the necessity to adjust the pH of the feed
- (ii) the limited solvent loading of metal ions
- (iii) the difficult solvent clean-up



TALSPEAK with Lactic Acid and DTPA complexants
 Courtesy : Ken Nash, WSU, USA

TALSPEAK process



SANEX concept (acidic S-bearing extractants)
- CYANEX 301 process (China, USA, Germany)

- ❑ The CYANEX 301 extractant consists in a dialkyldithiophosphinic acid (R_2PSSH , with R = an alkyl group)
- ❑ Its use for An(III)/Ln(III) was first proposed by Zhu at Beijing (China) in 1995
- ❑ The main interest of the process relies in:
 - (i) the large efficiency for An(III)/Ln(III) separation
 - (ii) the fact that the process has been tested with genuine An(III)+Ln(III) Mixtures
- ❑ Nevertheless, for an efficient use, the feed solution should be adjusted to pH 3 to 5, which is not so easy to carried out industrially
- ❑ Moreover, the solvent clean-up is also a weak point

ALINA process (Germany)

Actinide(III)-Lanthanide **IN**tergroup separation from Acidic medium)

- ❑ To cope with the main drawbacks of the *CYANEX 301* process mentioned above, Odoj and Modolo at Jülich (Germany) proposed the use of a synergistic mixture made of $(\text{Cl}\Phi)_2\text{PSSH}$ + TOPO for An/Ln group separation
- ❑ The separation factors between An(III) and Ln(III) are less than those observed with *CYANEX 301*, but the concentration of HNO_3 in the feed can be as high as 1.5 mol/L, which makes the ALINA process more attractive
- ❑ The ALINA process was successfully tested with genuine wastes
- ❑ The possible drawbacks of this process are:
 - (i) the solvent clean-up process not yet defined
 - (ii) the generation of P- and S-bearing wastes (from the degraded extractants) which should be managed

SANEX concept (neutral N-bearing extractants)
BTPs (Germany, France, Europe)

- ❑ After the discovery by Kolarik at FZ Karlsruhe (Germany) of the astonishing properties of the bis-triazinyl-1,2,4-pyridines (BTPs) for An(III)/Ln(III) separation, a process was readily developed and tested in the frame of the European NEWPART project
- ❑ Successful hot tests were achieved both at the CEA/Marcoule and at the ITU in Karlsruhe using the n-propyl-BTP
- ❑ Large efficiency of the BTP process was obtained
- ❑ The feed of the n-propyl-BTP process can be high in acidity ~ 1 mol/L

Drawbacks

- ❑ Instability of the n-propyl-BTP extractant

SANEX concept (neutral N-bearing extractants)

BTPs (Germany, France, Europe)

TMAHDPTZ + Octanoic acid (CEA, France)

- ❖ A synergistic mixture made of the terdentate N-ligand, 2-(3,5,5-trimethylhexanoylamino)-4,6-di-(pyridin-2-yl)-1,3,5-triazine (TMAHDPTZ) and octanoic acid was developed at CEA/Marcoule
- ❖ A process flowsheet was defined and successfully tested with genuine effluent with good efficiency
- ❖ The main drawbacks of this process are:
 - ❖ the required pH (>1)
 - ❖ adjustment of the feed,
 - ❖ the management of secondary wastes not yet defined

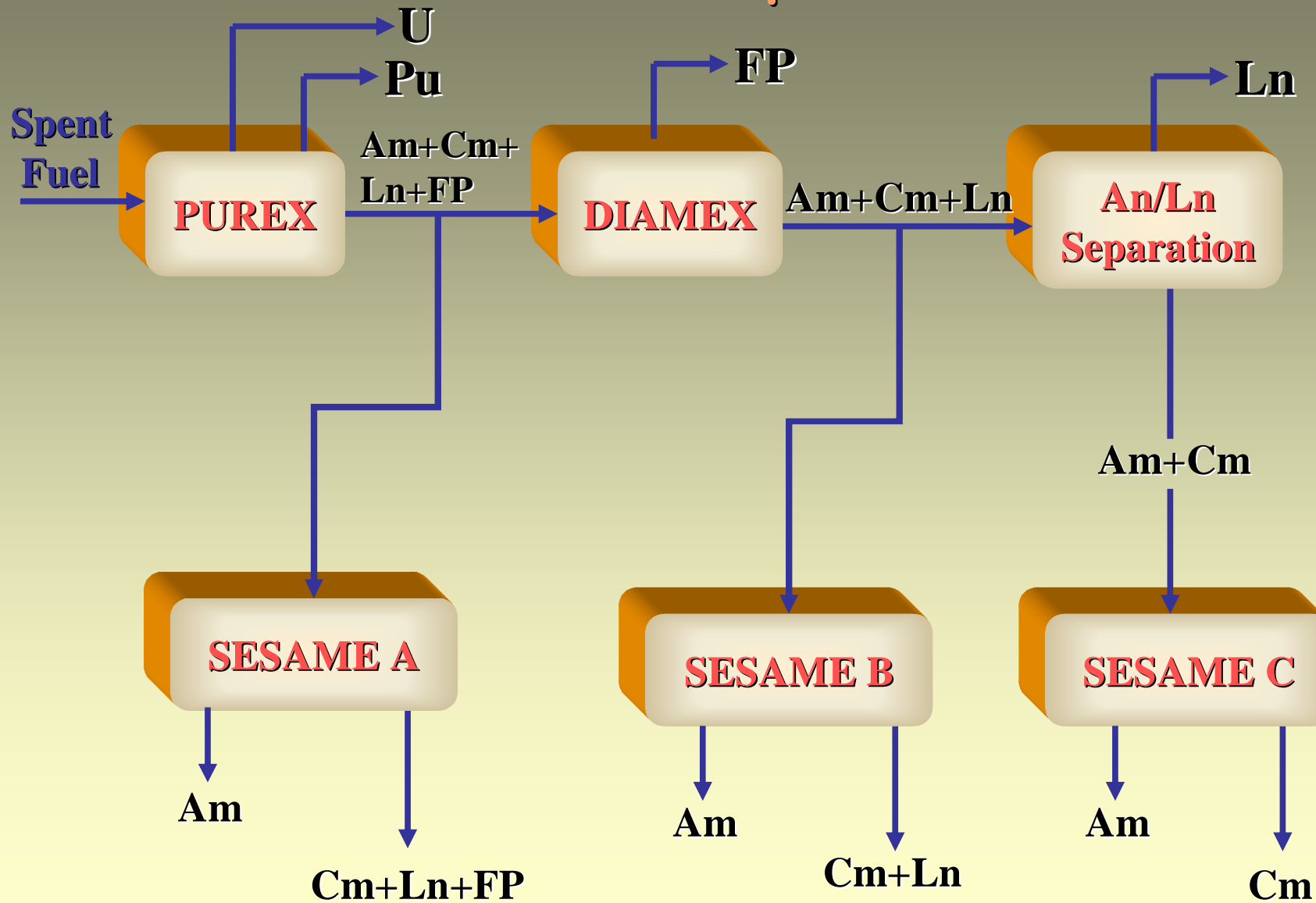
SESAME process (CEA, France, Hitachi, Japan)

- ❖ In the SESAME process Am(III) is oxidised to Am(VI) by electrolysis in the presence of heteropolyanions (HPA) acting as catalyst and Am(VI) is separated from Cm(III) by extraction by TBP
- ❖ This is the principle of the so-called SESAME process developed at CEA/Marcoule and kg amounts of ^{241}Am were purified on pilot scale during the last twenty years
- ❖ At Hitachi (Hitachi city, Japan), oxidation of Am to Am(VI) is done using ammonium persulphate, and Am(VI) is extracted by TBP
- ❖ The SESAME process exhibits a great efficiency for Am/Cm separation

Drawbacks

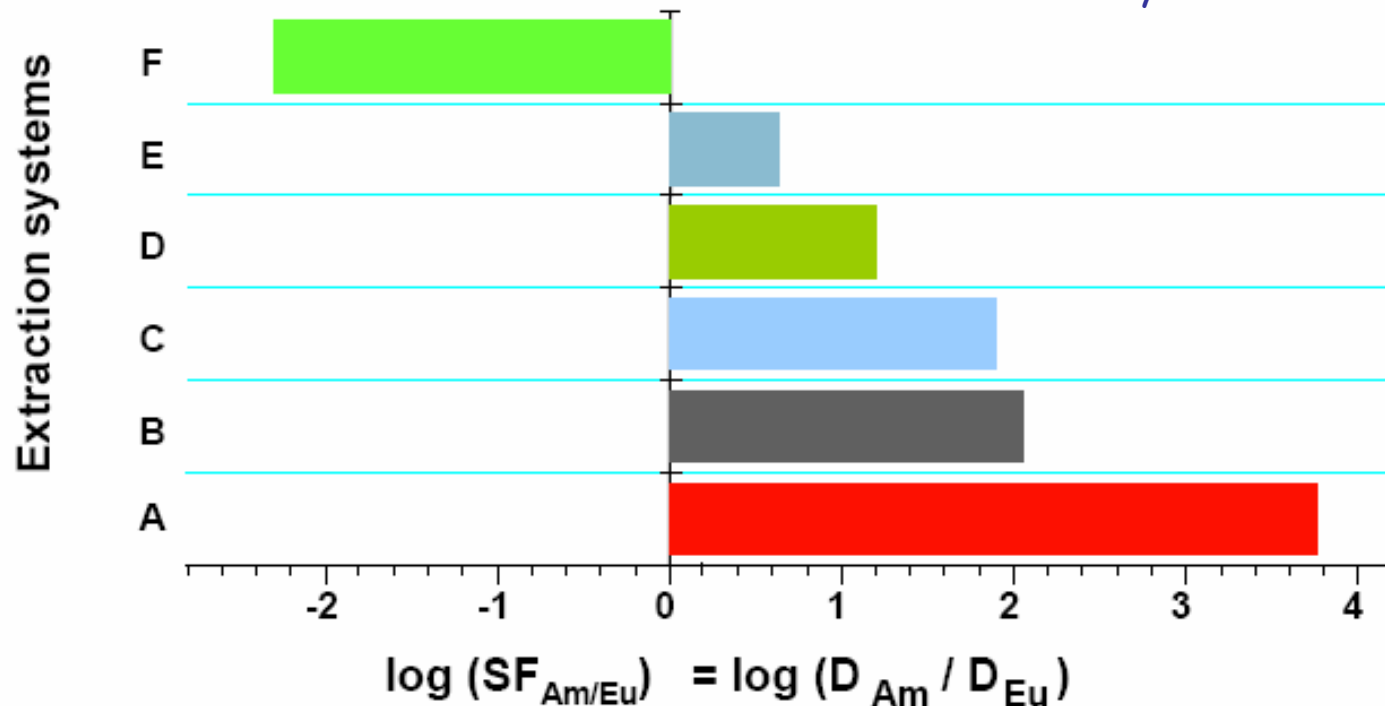
- ❖ instability of Am(VI),
- ❖ the non-easiness to develop a multi-stage process
- ❖ use of HPA results in secondary solid waste generation

Possible separation schemes related to SESAME process



COMPARISON BETWEEN SEPARATION SYSTEMS (Ken Nash, ANL)

Courtesy : Bernard Boullis, CEA



A : Cyanex 301 (0.5 M) / kerozene / NaNO_3 (1 M); pH 3.5

B : *i*Pr-BTP (0.01 M) / « *n*-octanol/[DMDOHEMA] = 0.5 M" / HNO_3 (0.5 M)

C : Alamine 336 (30%) / xylene / LiCl (11 M)

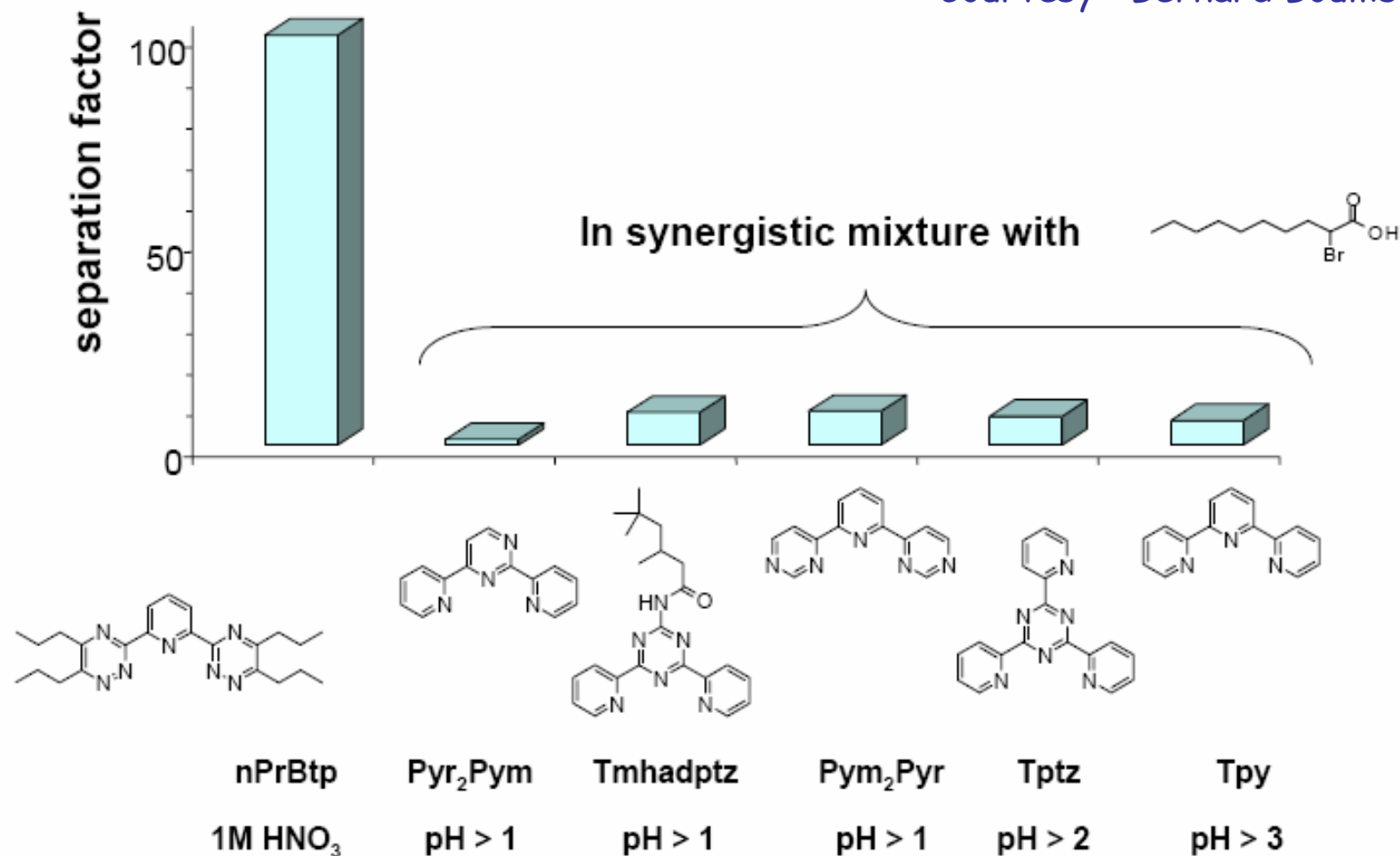
D : TPTZ, α -cyano-decanoic acid and malonamide / TPH / HNO_3 (0.2 M)

E : TBP (100%) / HNO_3 (13 M)

F : HDEHP (0.3 M) / diisopropylbenzene / lactic acid (1 M), DTPA (0.05 M); pH 3

An(III) / Ln(III) SEPARATION BY POLYAZINES

Courtesy : Bernard Boullis, CEA



Americium - Curium Separation

Am(V) precipitation (JNC, Japan)

- ❖ The selective precipitation of double carbonate of Am(V) and potassium is one of the oldest method for Am/Cm or Am/Ln separations, developed at the end of the 60's in the USA
- ❖ This method selectively removes Am(V) as $K_5AmO_2(CO_3)_3$ as a precipitate under oxidation of a mixture of Am(III) and Cm(III) in 2 M K_2CO_3 solution

Advantages

- (i) simple,
- (ii) selective for Am
- (iii) has been largely used worldwide

Drawbacks

- (i) high Am losses with Cm
- (ii) generation of large amounts of secondary wastes

Separation of Long Lived Fission Products

Inorganic sorbents

- ☆ AMP , AWP - Cesium Selective Sorbents

 - ☆ Limitation - powder

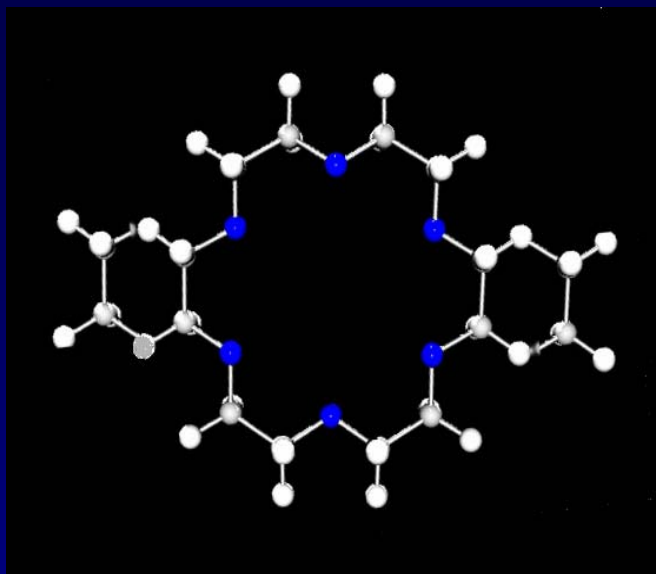
- ☆ Polyantimonic acid for strontium- Limitation - poor kinetics

- ☆ Titanates of alkali metals and Crystalline Silico Titanates -

 - ☆ Only R&D

- ☆ "Still, a better candidate for strontium removal from acidic medium is lacking" A. Clearfield, 2000

Crown Ethers



- ❖ Macrocyclic polyethers (crown ethers) act as ligands to form stable complexes with salts of numerous metals
- ❖
- ❖ Macro effect : The cyclic structure of the crown ethers create a circular cavity of oxygen atoms to which the cations coordinate
- ❖ Host -Guest Interaction: The diameter of this cavity - relative size of the cation determine the stable complex

Crown Ethers

- DCH18C6 in n-alkanols (1-Octanol) is well studied for the extraction of strontium in liquid - liquid separations
- Electroneutrality to be maintained during the extraction of metal ion from aqueous solution into organic solvent - achieved by aqueous phase anion co-extraction



Factors that facilitate extraction

- ❑ Presence of organophilic anions like picrates
- ❑ Increase in water content in organic phase (1-octanol is used as co-diluent)
- ❑ Limitations in HLLW waste treatment
 - ❑ non-compatible diluent
 - ❑ external addition of salts
 - ❑ chemical toxicity

Other Extraction systems

- ❖ Lariat Crown ethers
 - ❖ carboxyl group attached to crown ether that act as anion and encapsulates after extraction
- Calixarenes
 - Cavity is similar to crown ether
 - External anions are not required; phenolic moieties present in calix act as anion
- Both need to be demonstrated at higher levels

Separation of long-lived fission products

Titanic acid and Zeolites for Sr and Cs

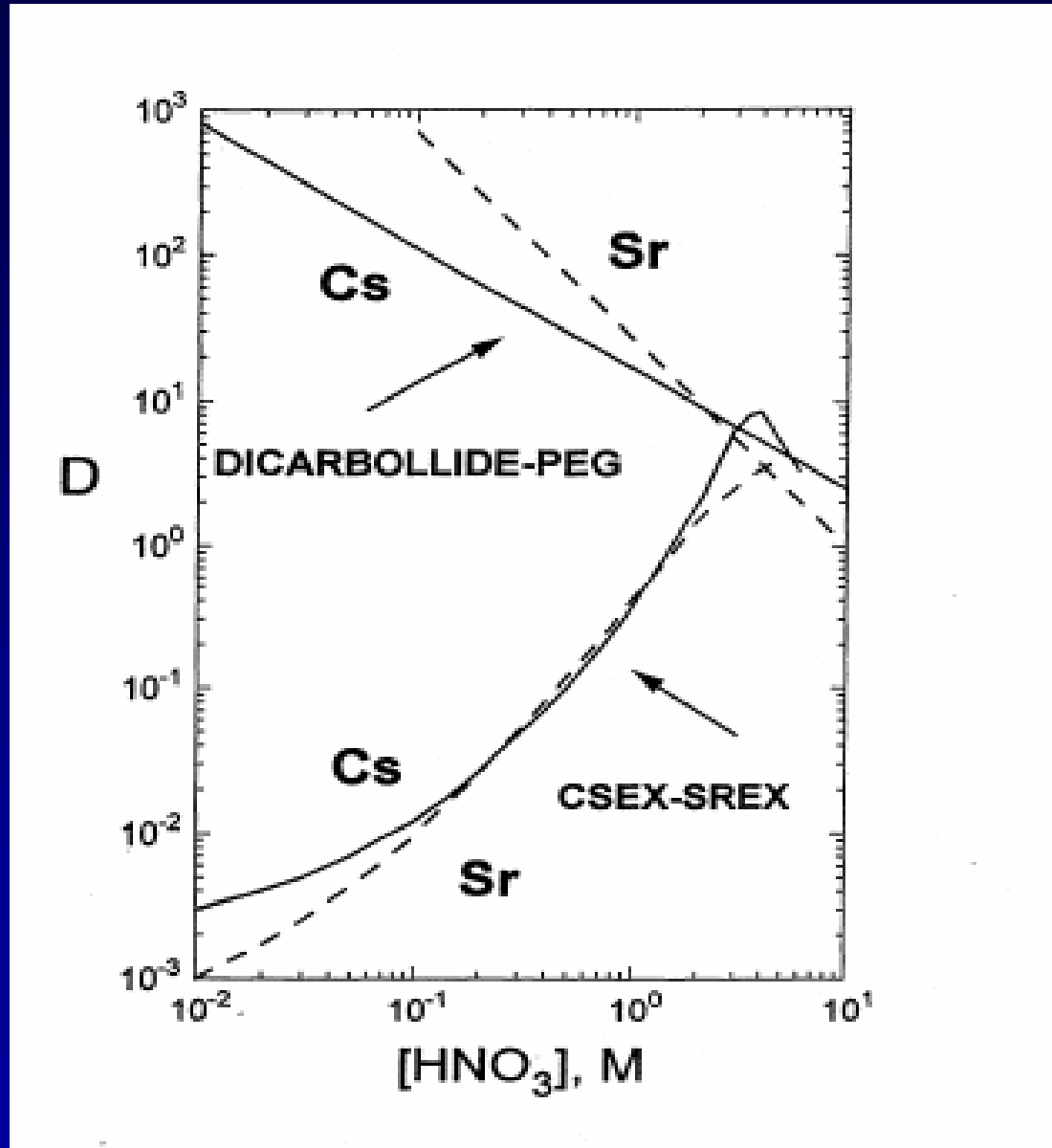
- The adsorption method with inorganic exchangers, titanic acid and zeolite developed for the separation of heat generating nuclides such as ^{90}Sr and ^{137}Cs in many countries during the sixties and the seventies, and recently reinvestigated by JAERI
- More than 99.9% recovery from real HLLW was successfully demonstrated
- This adsorption method adopted in the four group partitioning process greatly contributes to the reduction of the waste volume after the partitioning of HLLW because the inorganic exchangers loaded with Sr and Cs can be solidified into a very stable form by direct calcination at high temperature

Chlorinated Cobalt Dicarbolides

- ❖ Cobalt dicarbollides were first synthesised and produced in Czechoslovakia for application to caesium and strontium extraction
- ❖ From 600 kg of hexachloro derivative of dicarbollide, synthesised by KATCHEM (Prague), diluted in nitrobenzene, the extraction of strontium and caesium has been tested on a plant scale in the former USSR

Chlorinated Cobalt Dicarbolides

- ❑ The use of highly toxic nitrobenzene is a drawback for the use of dicarbollides
- ❖ The framework of a project supported by the European Commission, focused on the synthesis of dicarbollides soluble in diluents other than nitrobenzene
- ❑ Promising results were achieved with
 - ❑ bis-ylene cosan (BISPHECOSAN) diluted in
 - ❑ nitrophenyl-alkyl-ether (NPHE or NPOE) or in
 - ❑ diethylpropanesulfonamide (DEPSAM) or
 - ❑ dibutylmethanesulfonamide (DIBUMESAM)
- ❖ The presence of two phenyl groups enhances the caesium extraction from acidic media

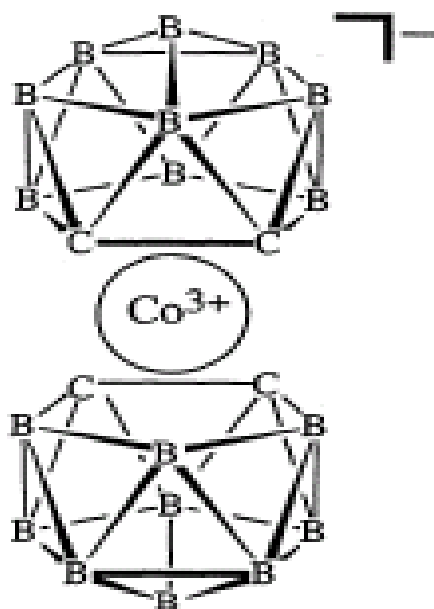


Separation of Cesium with Calix Crowns

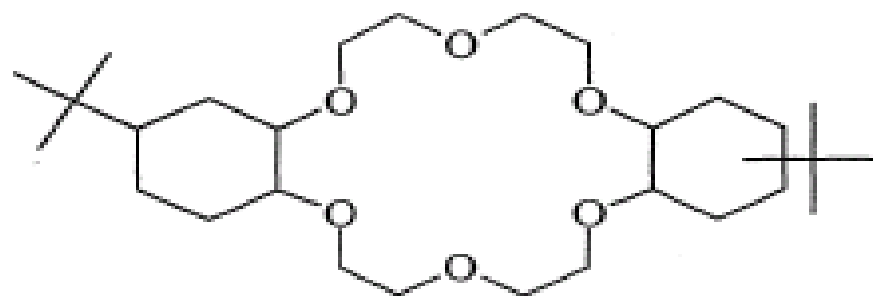
- ❖ Macrocycles of the calixarene type, functionalized by etheroxide chains are best suited for selective Cs extraction from large amount of Na
- ❑ Calixarenes are cyclic oligomers produced by the condensation of phenolic units on formaldehyde (the name is derived from their shape which resembles a calyx)
- ❖ They only display weak complexing properties, and must be functionalized, for example, by grafting one or two etheroxide chains on either side of the macrocycle cavity
- ❑ These compounds, called calix-crowns, thus display pre-organised co-ordination sites, which can be perfectly adjusted to the dimensions of the Cs⁺ ion, giving them strong affinity, outstanding selectivity in terms of cesium/sodium separation. Separation factors in the range of 30 000 in favour of cesium have been obtained
- ❑ In a real high-level effluent, the results obtained were highly satisfactory, in terms of selectivity, because no other fission product, actinide or chemical element, except for rubidium, was extracted in more than 1 to 2%

Separation of Strontium

- ❑ The SREX (Strontium Extraction) process complemented the TRUEX process for the strontium removal from acidic HA liquid waste
- ❑ Horwitz chose among the dicyclohexano 18-C-6 derivatives the lipophilic di-*t*-butylcyclohexano 18-C-6 (0.2 M) diluted in octanol
- ❑ Tests carried out on simulated waste show the selectivity of crown ether since only barium and technetium are appreciably extracted with strontium by the crown ether
- ❑ Subsequently Horwitz proposed as diluent a variety of phase modifier/paraffinic hydrocarbon mixtures, among them TBP (1.2 M) in Isopar L
- ❑ In Bhabha Atomic Research Centre (India), Kumar optimised the extraction of strontium by diluting dicyclohexano 18-C-6 in a mixture butanol (80%)-octanol (20%)



Cobalt(III) Dicarborollide Anion



Bis-4,4'(5')-(*t*-butylcyclohexano)-18-crown-6

Combined CSEX-SREX

- ❑ The key ingredient in the Cs extraction process (CSEX) is a dibenzo-18-crown-6 derivative of proprietary composition
- ❑ The Combined CSEX-SREX process solvent consists of 0.1 M Cs extractant -0.05 M Sr extractant -1.2 M TBP in Isopar-L
- ❑ Five volume percent of laurionitrile is added to the process solvent to solubilize precipitates that sometimes form from the interaction of macro concentrations of Sr and Ba with DtBuCH18C6
- ❑ Extraction occurs at high acidity and stripping at low acidity and extraction curves for both Cs and Sr are typical of situations in which metal nitrates extraction by neutral extractants
- ❑ The Combined CSEX-SREX process if performed first the radiation level for all subsequent processing steps (e.g., TRUEx) will be significantly reduced, enabling TRUex operation in a glovebox
- ❑ The recovered Cs-Sr fraction devoid of TRUs will decay to low-level waste after a few hundred years
- ❑ Combining Cs and Sr extraction into a single process will reduce the amount of equipment and space required to pretreat the waste and result in cost reduction

Separation of PGMs

- ❑ PGMs are not compatible with vitrification
- ❑ Wealth from waste !
- ❑ They are highly useful as catalysts
- ❑ Fission Pd is mostly inactive (stable) except ^{107}Pd
(Half life : $6.5 \cdot 10^6$ a , Emission : β^- 2.72 keV, γ 214.9 keV)
- ❑ Yield is 27 kg/te of fuel in fast reactor spent fuel !

Acknowledgements

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- ❑ Google
- ❑ Proceedings of OECD IEMs, Status Report
- ❑ IAEA Tecdocs on P&T
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Thank You