Population, Energy Consumption, Global Climate Change

Current global power consumption: 12 TW (10^{12}), 85% fossil fueled
Atmospheric CO_2: 1900 - 270 ppm, 2000 - 377 ppm, 2100 - 550 ppm
To stabilize at 550 ppm, 15 TW of emission free power needed by 2050

"Advance Technology Paths to Global Climate Stability: Energy for a Greenhouse Planet"
M. J. Hoffert et al. Science 298, 981 (2002)

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Chemical and Engineering News, March 15, 2004
Editor's Page: A Challenge We Must Meet I, Rudy M. Baum

Reviewed "Out of Gas: The End of the Age of Oil" by David Goodstein and Frank J. Gilloon characterizing the book as "a simultaneously brilliant polemic and a clear examination of the chemistry and physics of global energy issues"

The book opens with the apocalyptic vision from the authors: "The world will soon start to run out of conventionally produced, cheap oil. If we manage to overcome that shock by shifting the burden to coal or natural gas, life may go on more or less as it has been until we run out of all fossil fuels by the end of the century. And by the time we have burned up that fuel, we may well have rendered the planet unfit for human life. Even if human life does go on, civilization as we know it will not survive unless we can find a way to live without fossil fuels.

Chemical and Engineering News, March 22, 2004
Editor's Page: A Challenge We Must Meet II, Rudy M. Baum

Followed his review of "Out of Gas: The End of the Age of Oil" by David Goodstein and Frank J. Gilloon with the following observations...

"Nuclear Energy will be an essential component of any strategy for weaning humanity from fossil fuels. While fissile uranium-235 is also a limited resource, breeder reactor technologies exist for converting ^{238}U to fissile plutonium-239 and thorium-232 to fissile ^{233}U. Breeder reactors can extend the supply of the earth's fissile material several hundred fold, enough to last at least several centuries."

He continues ...."(Problems of spent reactor fuel and ^{239}Pu) ...do not compare to the economic and environmental crises that our continued dependence on fossil fuels is guaranteed to engender."

Chemical Separations in Nuclear Waste Management (Choppin, Khankhasayev, Plendl) DOE/EM-0591

- New separations technologies must minimize wastes
  - Improved efficiency in partitioning processes
  - Integrate waste considerations into process
  - Consider environmental consequences
- Economic incentives for partitioning do not support deployment (Harvard study - Does not take into account future financial consequences of energy dependence, global competition for resources and global climate change)
- Transmutation as an alternative to repository disposition
- Surplus weapons material and MOX fuel
- World-wide loss of faculty positions
- Public acceptance
- Existing waste
- Give up single waste form concept
- International cooperation is essential
- Weapons proliferation

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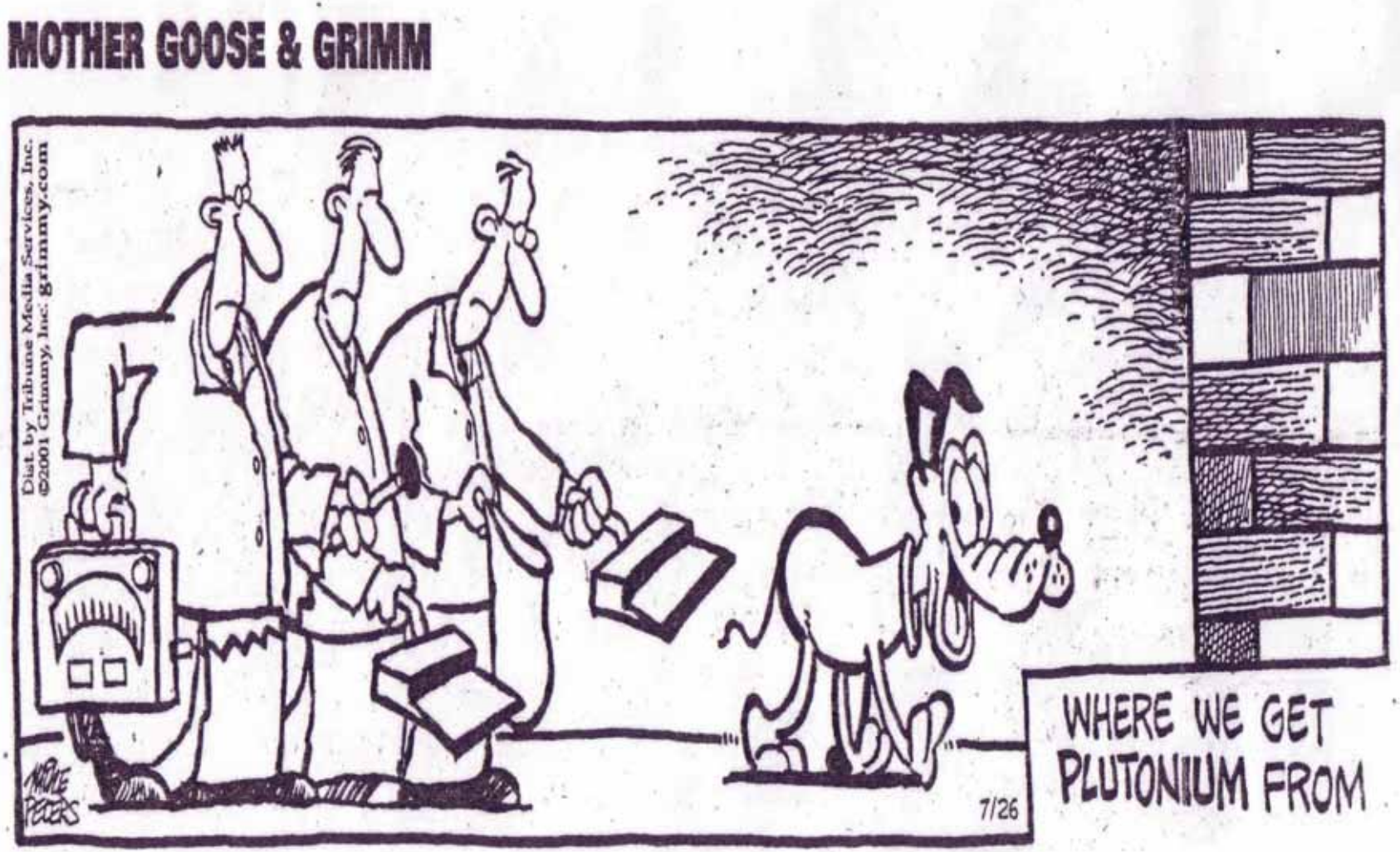
We must transform public opinion



21st Century Approaches to Actinide Partitioning

Kenneth L. Nash
Chemistry Department
Washington State University
Pullman, Washington 99164

The 1st COE-INES International Symposium, INES-1
October 31-November 4, 2004
Tokyo, Japan

Actinide Chemistry

5f	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
III	✎			✎	✎	✎	✎	✎	✎	✎	✎	✎	✎	(II)	✎
IV		✎	✎	✎	✎	✎	✎	✎	✎						
V			✎	✎	✎	✎	✎								
VI				✎	✎	✎	✎								
VII					✎	✎									

4f	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
II						✎	✎							✎	
III	✎	✎	✎	✎	✎	✎	✎	✎	✎	✎	✎	✎	✎	✎	✎
IV		✎	✎	✎						✎					

Reactor Charge:

967kg ^{238}U

33kg ^{235}U

0.26kg ^{234}U

irradiated for 33,000 MWd/t U burnup at a power density of 30MW/t U and neutron flux of 2.92×10^{13} $Ncm^{-2}s^{-1}$

(Choppin & Rydberg, Nuclear Chemistry)

50 kg $^{235, 238}U$ consumed (950 kg remain)

14 kg ^{236}U and transuranics produced

36 kg of fission products (10 kg Ln)

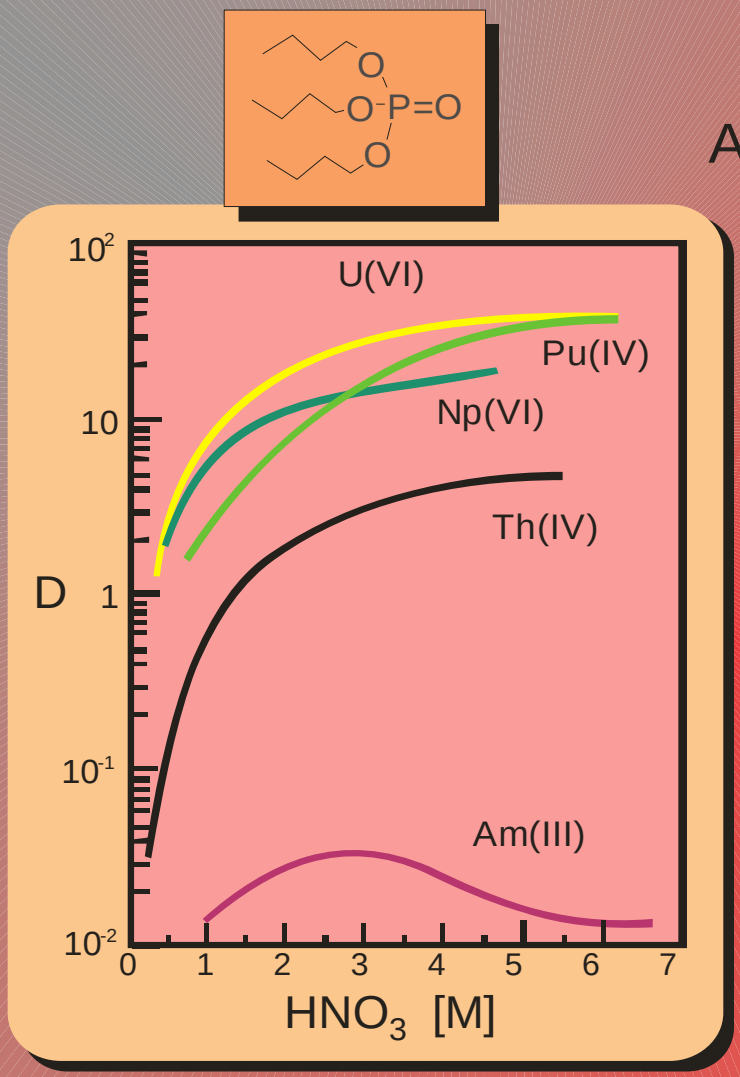
Actinides:

^{238}U(942kg), ^{236}U(4.5kg), ^{235}U(8kg), ^{234}U(120g), ^{237}Np(482g), ^{238}Pu(168g), ^{239}Pu(5,260g), ^{240}Pu(2,160g), ^{241}Pu(1,008g), ^{242}Pu(352g), ^{241}Am(44.1g), ^{242m}Am(0.4g), ^{243}Am(91.2g), ^{242}Cm(5.82g), ^{243}Cm(0.12g), ^{244}Cm(31.1g), ^{245}Cm(1.76g)

The PUREX Process

The extractant: Tributyl phosphate in kerosine

Aqueous medium: Nitric acid



- Extracts $Pu(NO_3)_4(TBP)_2$ and $UO_2(NO_3)_2(TBP)_2$ but not trivalent (Am, Cm) or pentavalent (Np) actinides also rejects most fission products
- Plutonium is removed from the extractant phase by contact with a reducing nitric acid solution (Fe^{2+} or U^{4+}) as Pu^{3+}
- UO_2^{2+} stripped with dilute HNO_3 and excess scrubbed with Na_2CO_3
- Modifications and improvements of PUREX continue - it remains the only large-scale fuel recycling process in operation

Developed in the 1950's, PUREX remains the state of the art for U and Pu recycle today

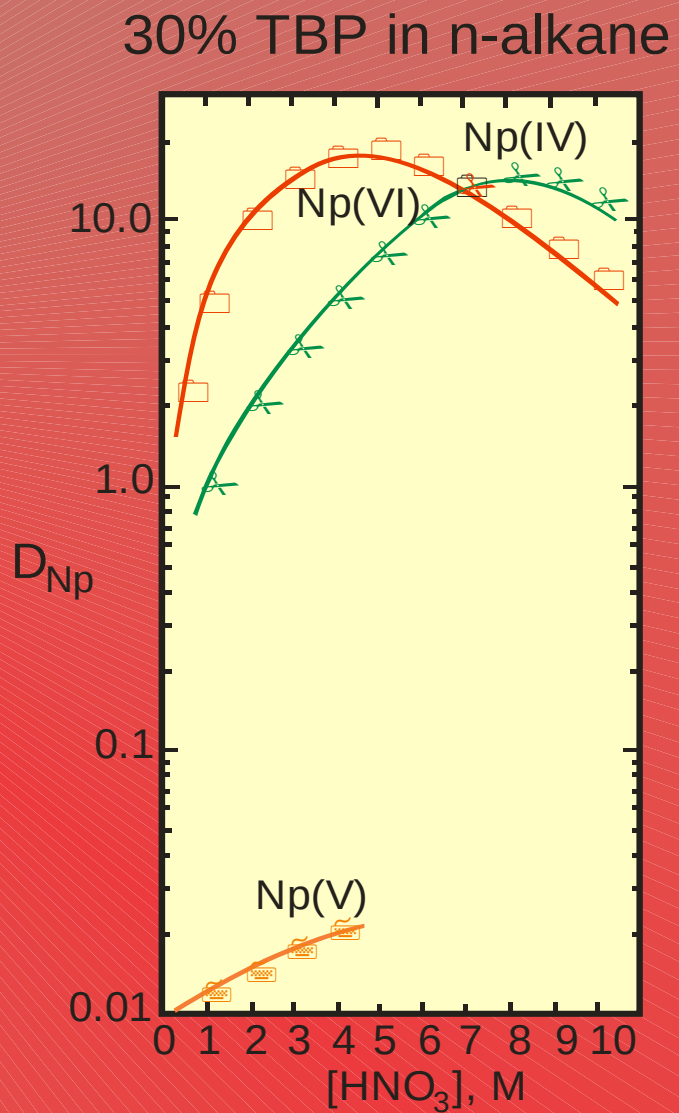
The Challenge of Neptunium?

- About 500g Np/ton of fuel
- Distribution among streams in PUREX impacts waste disposal
- From refluxing HNO_3 used to dissolve fuel, a mix of Np(V) and Np(VI) emerges
- Preadjustment of oxidation states helps but complexity of interactions hinders effectiveness of adjustment
- Np redox chemistry:
  - Np(V) disproportionates
  - Np(V) is oxidized by HNO_3 with HNO_2 catalysis

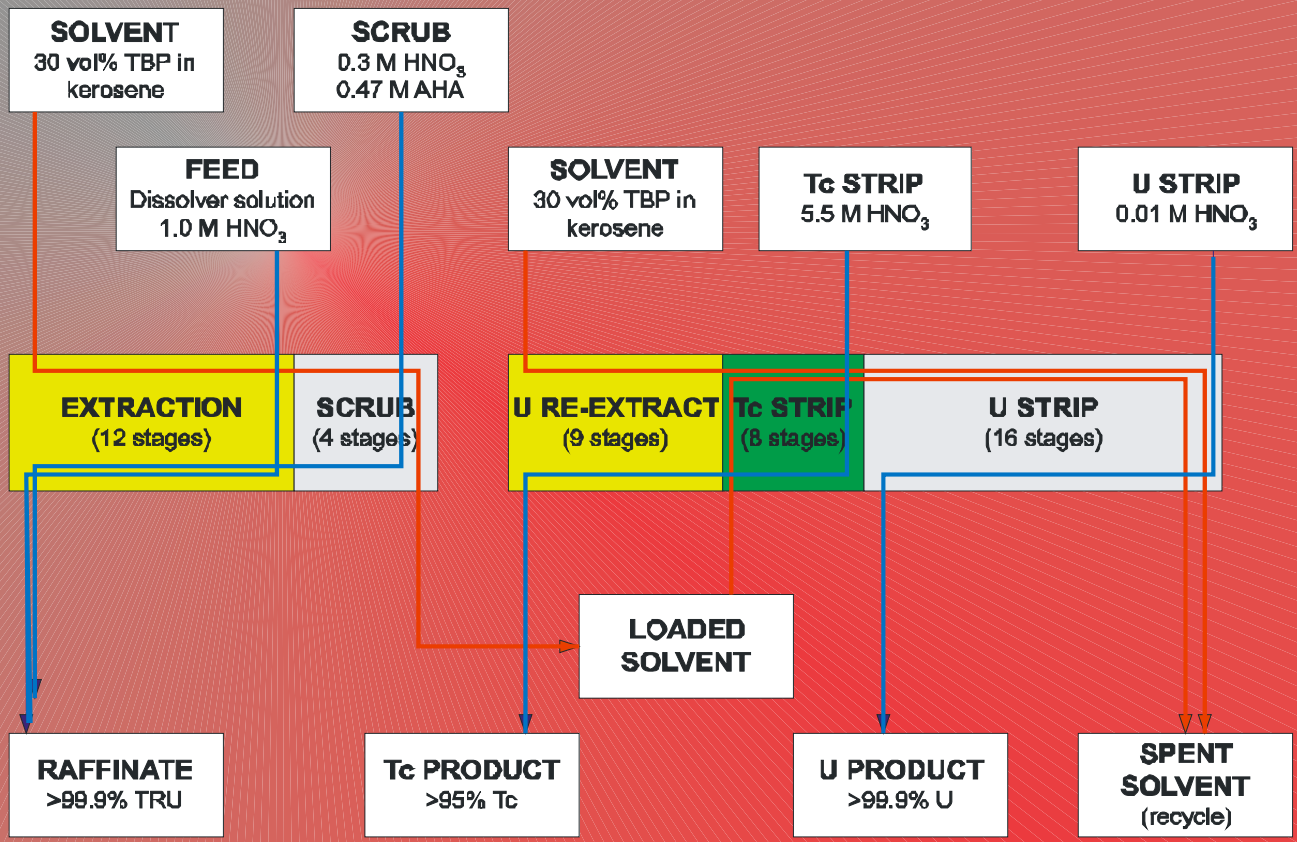
Advanced PUREX Enhancements

Kolarik (1980), Uchiyama (1992) - *n*-butyraldehyde reduces Np(VI) and Pu(IV), isobutyraldehyde only Np(VI)

Taylor et al (1997) - hydroxamates complex and selectively adjust oxidation state of Np



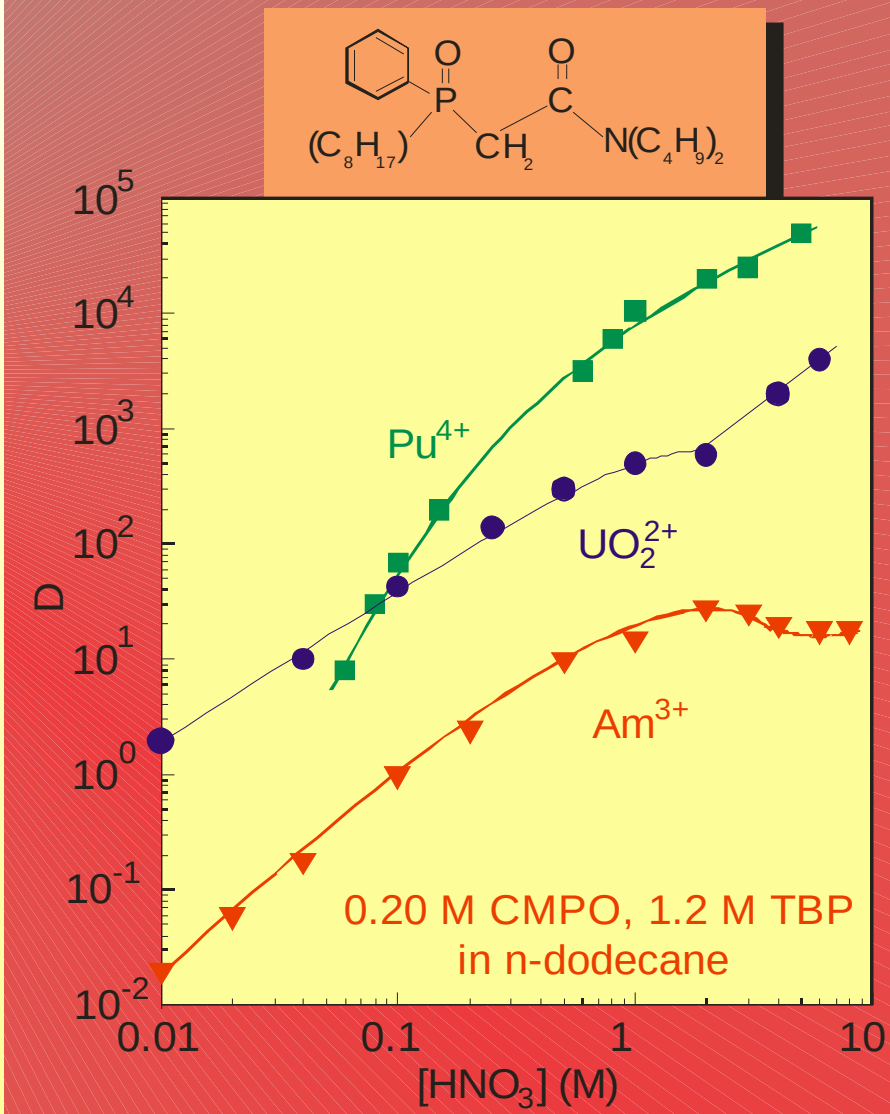
UREX Process Flowsheet



Argonne National Laboratory

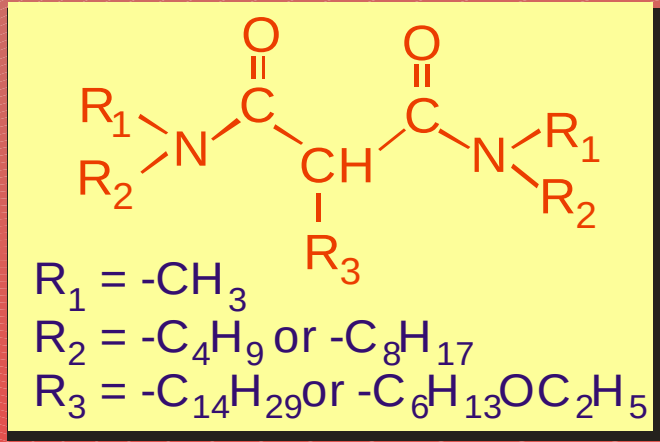
The TRUEX Process Extractant CMPO

- Bifunctional reagent CMPO designed at ANL for its ability to extract An(III), (IV) and (VI) and to allow their selective partitioning
- Process for its use (TRUEX) uses TBP as a phase modifier and is directly compatible with PUREX raffinates
- At high concentrations of metals (e.g. U(VI)), **third phase formation** can be a problem
- Degradation products can be problematic but solvent cleanup procedures are known
- UREX and UREX+ Processes use CMPO's (UREX + employs DΦDBCMPO in a fluorinated sulfone diluent) designed for waste processing



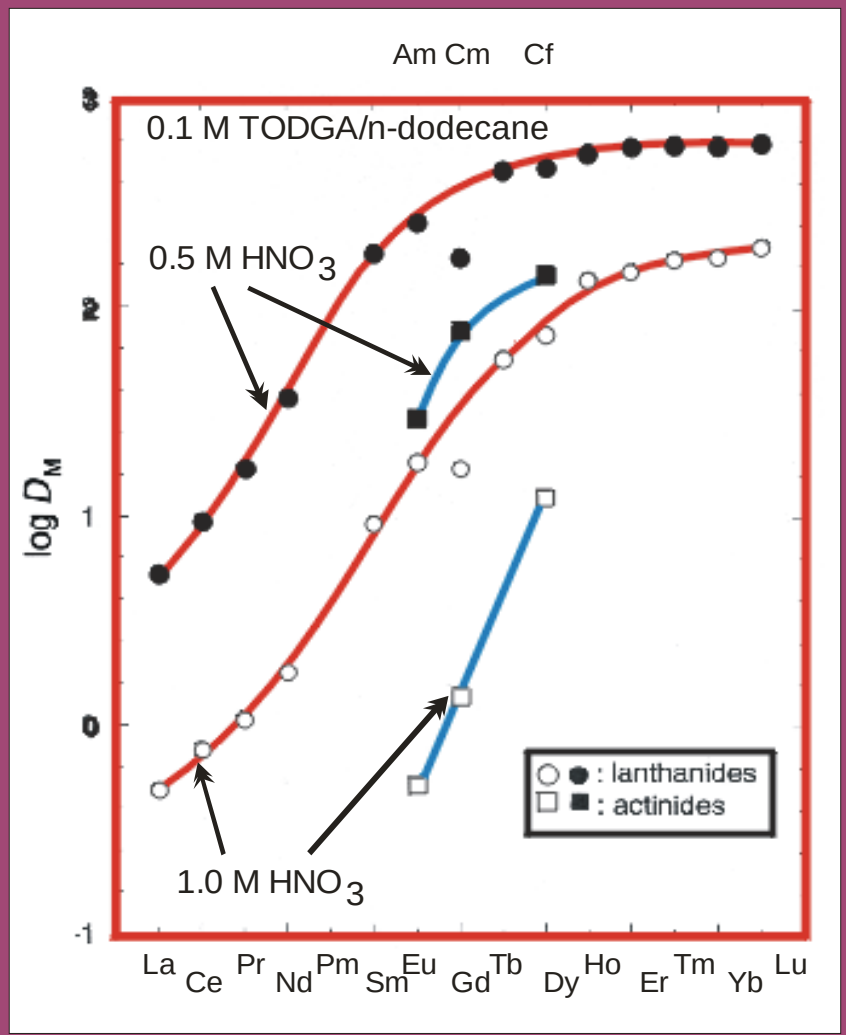
Malonamides and the CHON principle

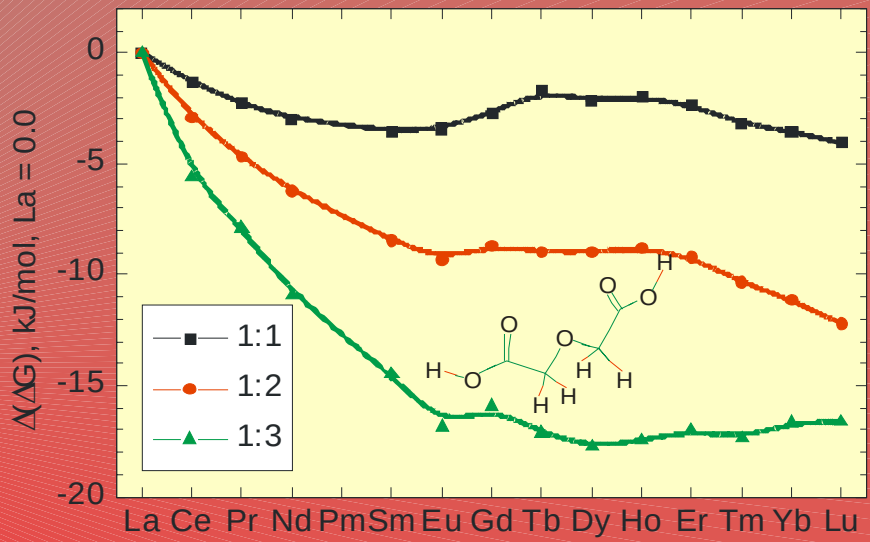
- **The first CHON reagent** - compounds containing only carbon, hydrogen, oxygen, and nitrogen are employed. Upon incineration when the reagent has reached the end of its useful life, only innocuous species are produced
- Amide extractants favored for minor actinide recovery (malonamide in particular - bears structural relationship to CMPO and the parent acid is a well-known water-soluble complexant)



- Degradation products do not interfere with stripping of actinides
- Higher concentrations of HNO_3 are needed for efficient extraction than are needed for CMPO or TBP
- Large pilot-scale studies in plant-style contacting equipment have proven successful
- Shares some phase compatibility characteristics of CMPO, i.e., **third phase formation can be a challenge** - highly branched hydrocarbon solvent used in process applications
- Lumetta et al. have noted 10^7 sronger extraction in a structurally hindered analog

TODGA - Lanthanide & Trivalent Actinide Extraction
The Artist Process

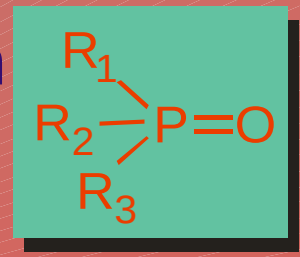


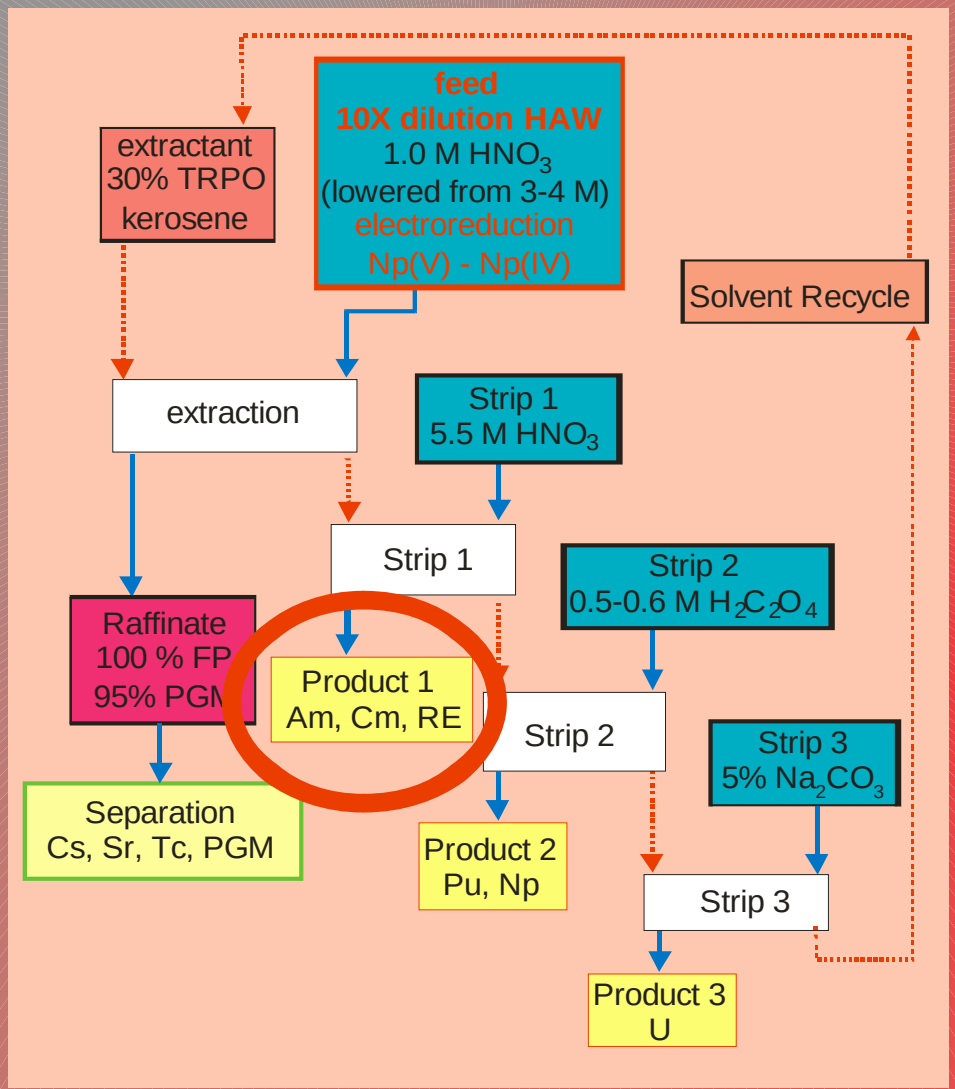


- Pattern consistent with relative stability of aqueous complexes of diglycolic acid
- Very steep extractant dependencies under some conditions appear to indicate large scale aggregation of extractant

Y. Sasaki, Y. Sugo, S. Suzuki, S. Tachimori, *SX&IX* **19**, 91-103 (2001)

Trialkylphosphine Oxide (TRPO) Extraction Actinide Processing in China





Feed from fuel dissolution must be **diluted ten fold** to reduce metal concentration and acidity (because of competing extraction of HNO_3)

Neptunium is reduced electrolytically

Separation of potentially valuable fission products incorporated

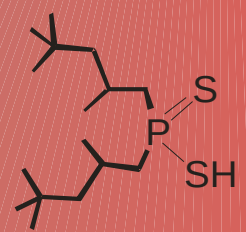
Trivalent actinides and rare earths stripped using concentrated nitric acid

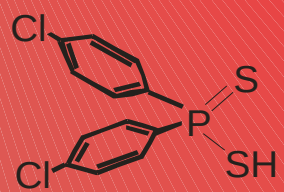
Oxalic acid strips Np, Pu

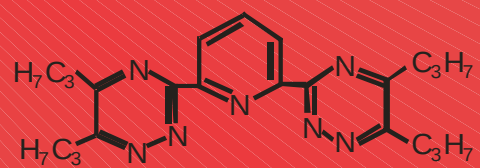
Zhu, Jiao, *Nucl. Technol. 108,* 361 **1994**

Trivalent Actinide-Lanthanide Separation A Key to Actinide Burnup

- Several lanthanides interfere with neutron physics, hence must be removed (for thermal reactor-based approach)
- An-Ln chemistries nearly identical except for slightly stronger interaction strength of actinides for soft (S, Cl^-) or less-hard (N) donor atoms
- TALSPEAK, Reverse TALSPEAK, Cl^- Ion exchange, Cl^- SX with amines are the classic methods
- Newest reagents: Cyanex 301 (dialkyldithiophosphinic acid)
- Di(*p*-chlorophenyl)dithiophosphinic acid plus TBP (ALINA)
- Polyaza (BTP) compounds synthesized in Europe (CHON principle)

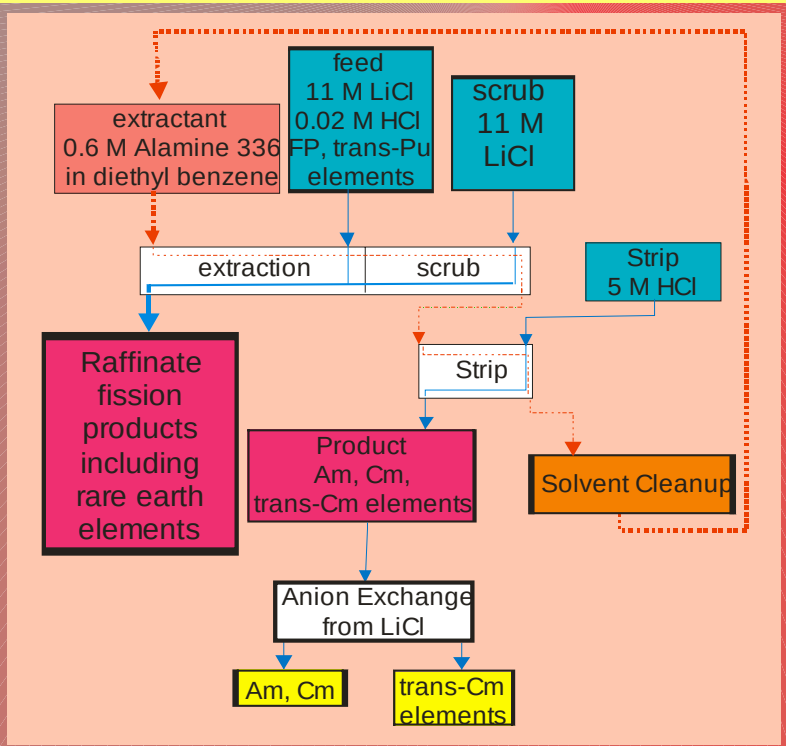




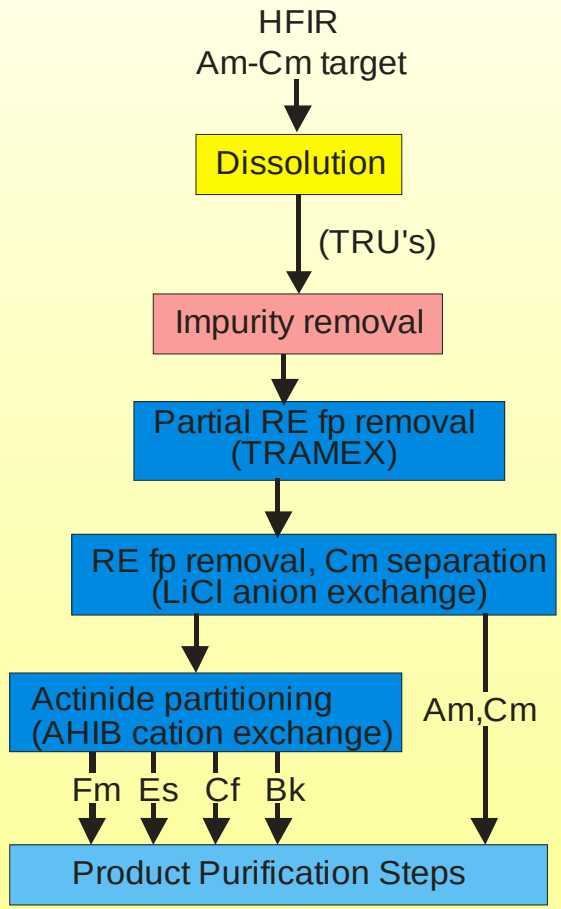


TRAMEX

- Developed at ORNL in mid 1960's
- Achieves An(III)/Ln(III) separation factor of about 100
- Tertiary amines give better separation than quaternary amines



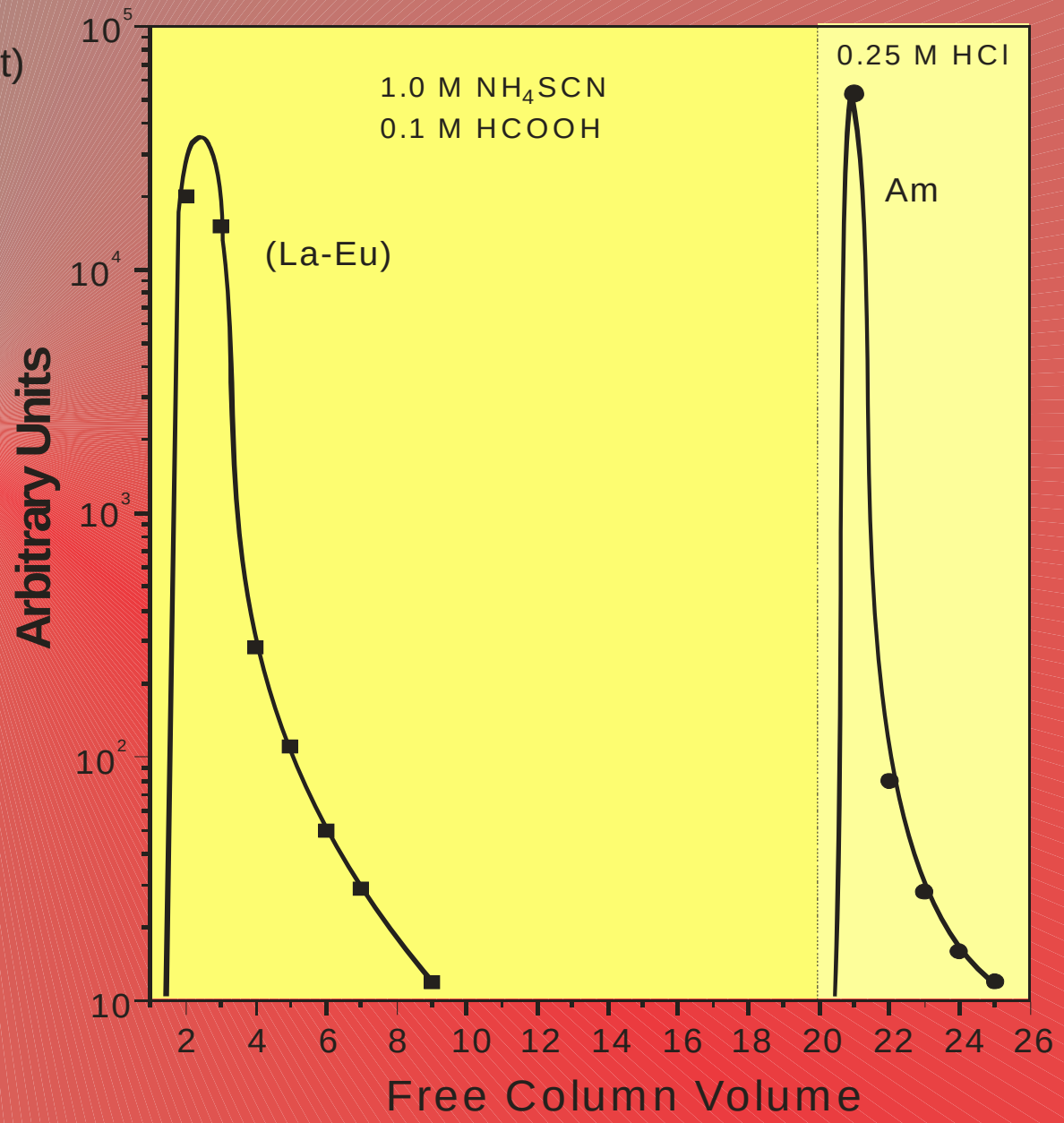
Transuranium Processing Plant (TRU) and High Flux Isotope Reactor (HFIR) at ORNL produce transuranium elements for research



Extraction Chromatography

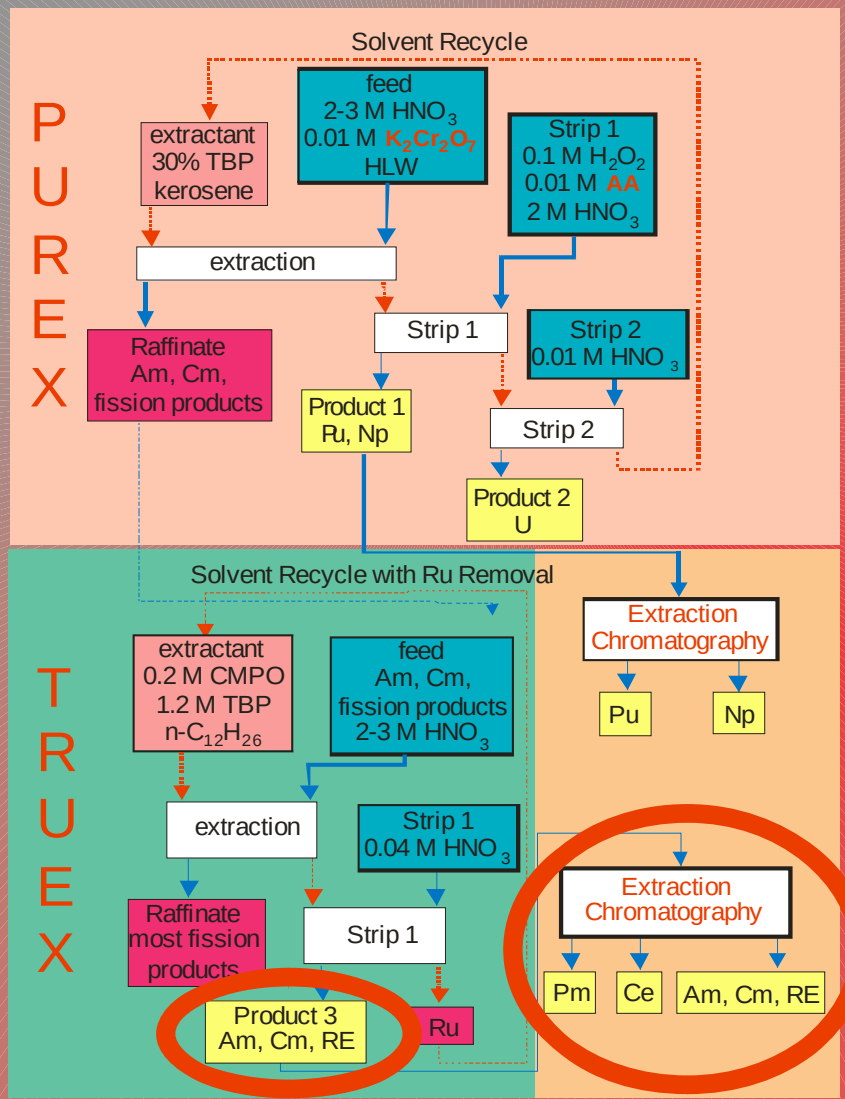
TEVA Resin
(Aliquat 336 onXAD-7 support)
Column -
Ln/An Separation
using NH_4SCN
Eluant
Horwitz and coworkers

- Soft donor SCN^- accounts for Am(III) sorption on "resin"
- Use of more than one complexant in the same solution can alter performance characteristics
- EC offers performance enhancement in the right circumstance
- NH_4^+ salts reduce waste



PUREX-TRUEX in India

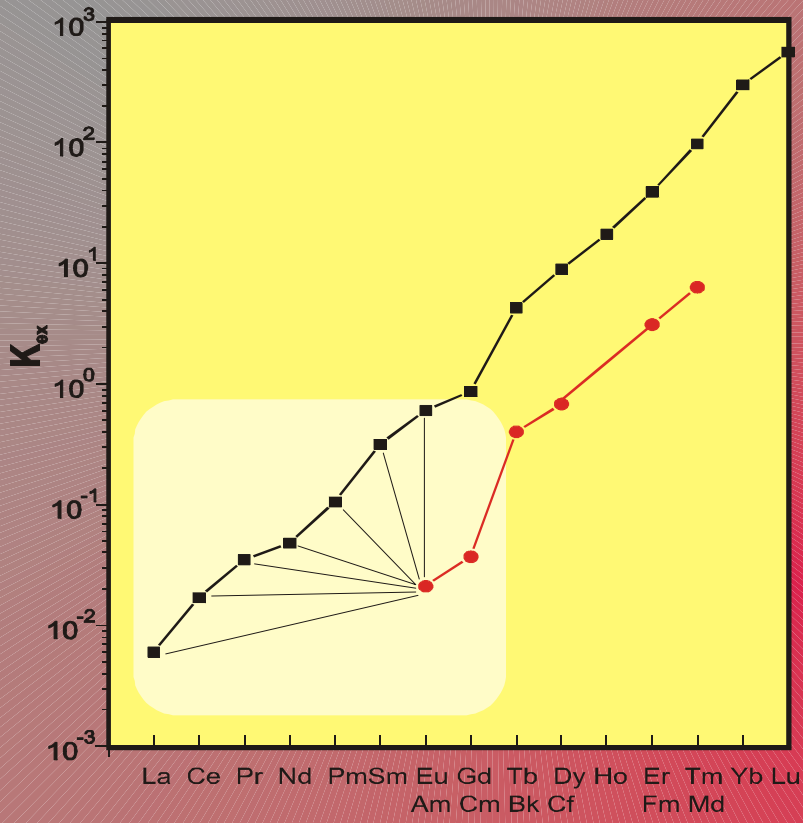
Bhabha Atomic Research Centre Plan for Fuel Treatment



- Pu, Np oxidized to the hexavalent state then extracted in preliminary stage with TBP
- Reductive stripping of Np and Pu with H_2O_2 and ascorbic acid
- Np, Pu fractions isolated using extraction chromatography
- TRUEX stage for concentration of Am, Cm and rare earths from most fission products
- Rare earth, Am, Cm processing by extraction chromatography

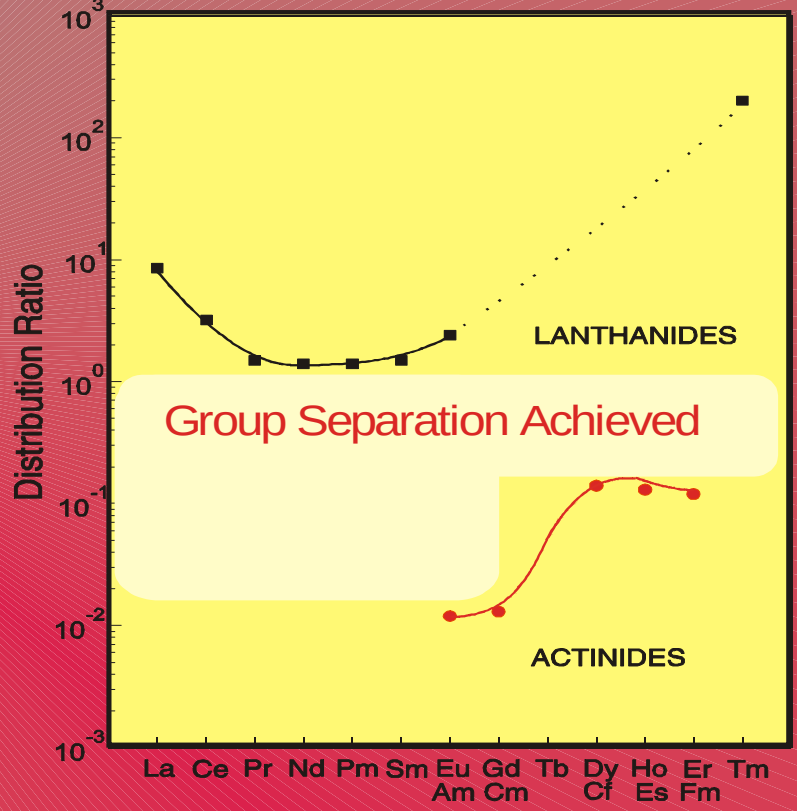
Mathur, Murali, Natarajan, Badheka, Banerji, *Talanta 39,* 493 **1992**

TALSPEAK Trivalent Actinide/Lanthanide Separation by Phosphorus Reagent Extraction from Aqueous Komplexes
Weaver, Kappelmann (1968)



HDEHP (HL) Extraction from mineral acid solution

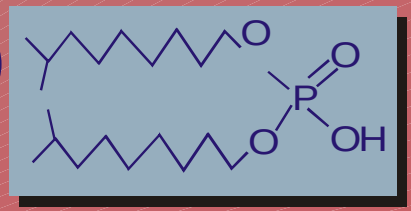
$$D = ([ML_3]_{org}/[M]_{aq}) = K_{ex} \bullet [HL]^3/[H^+]^3$$

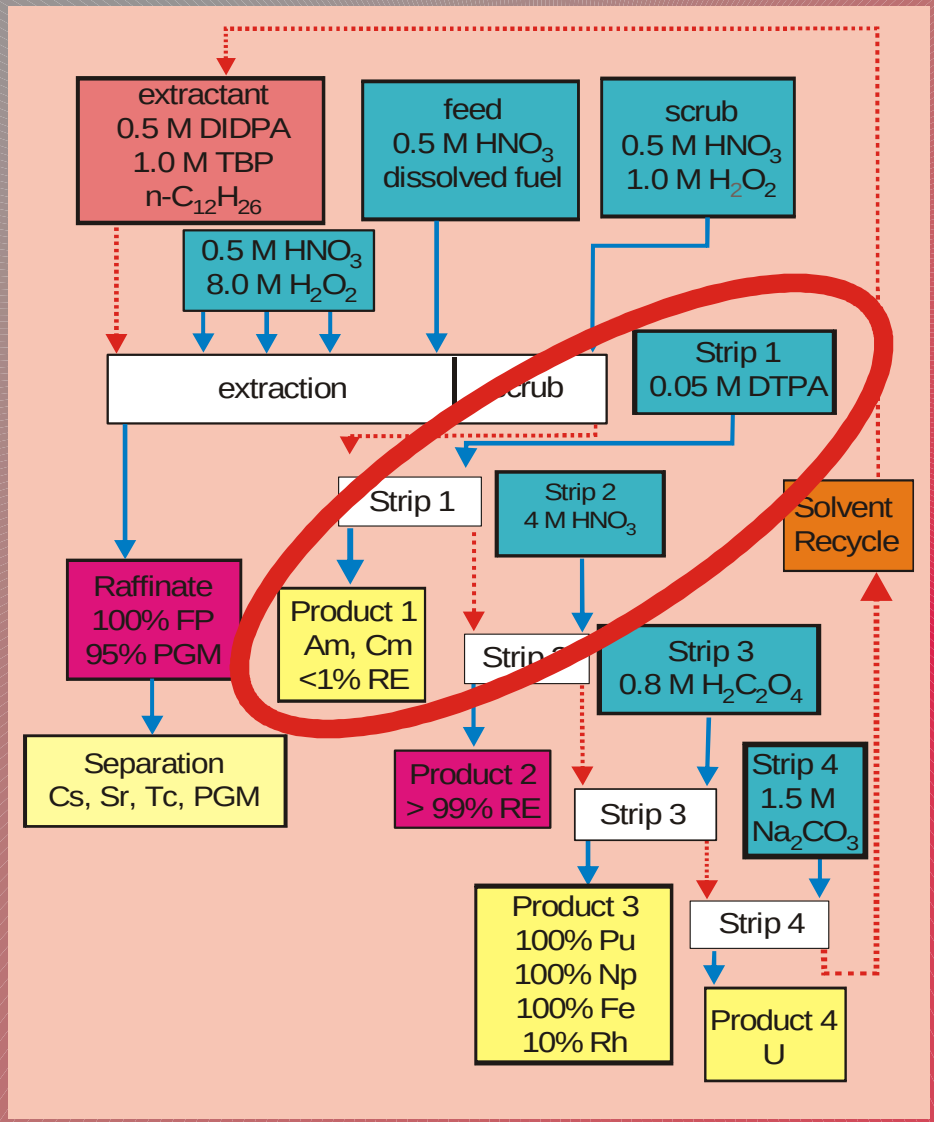


0.3 M HDEHP/DIPB, 1 M Lactic Acid (X), 0.05 M DTPA (Y), pH 3

$$D = \frac{[ML_2X]_{org}}{[M]_{aq}} = \frac{K_{ex} \bullet [HL]^2[X^-]/[H^+]^2}{1+\beta_1^x [X^-]+\beta_2^x [X^-]^2+\beta_1^y [Y^{5-}]}$$

Japan Atomic Energy Research Institute (JAERI)
Actinide Recycle Using Acidic Extractants

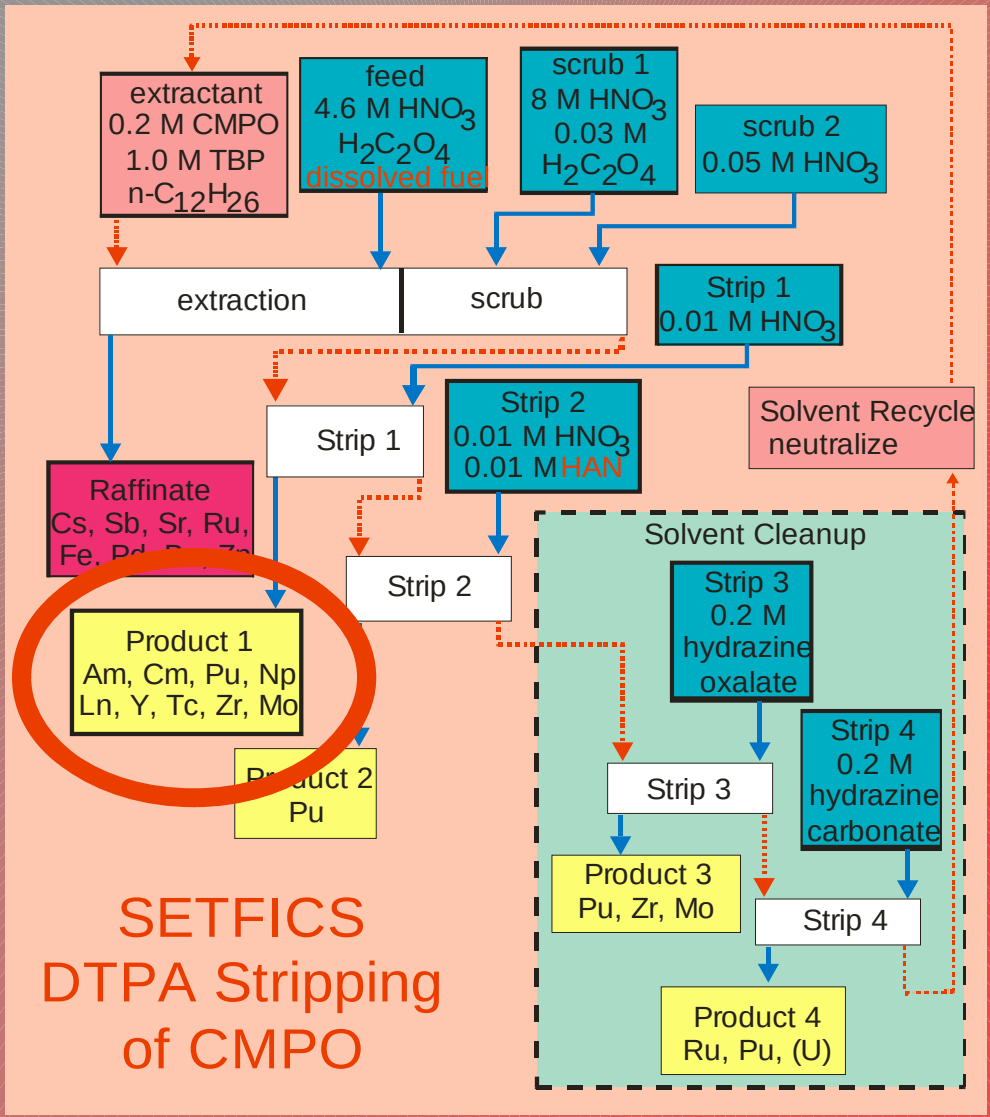




- Primary extractant is DIDPA, an acidic organophosphorus reagent - extraction is most favored from dilute acid media
- Dissolved fuel must be denitrated prior to extraction (done with formaldehyde)
- Separations of long-lived fission products and PGM's incorporated
- Reverse TALSPEAK-type selective separation of Am, Cm from Ln with DTPA
- Oxalate strip for Np, Pu recovery (Fe and Rh follow)

Morita, Kubota, *J. Nucl. Sci. Technol. 24,* 227 **1987**

TRUEX in Japan
JNC Approach for Fuel Treatment



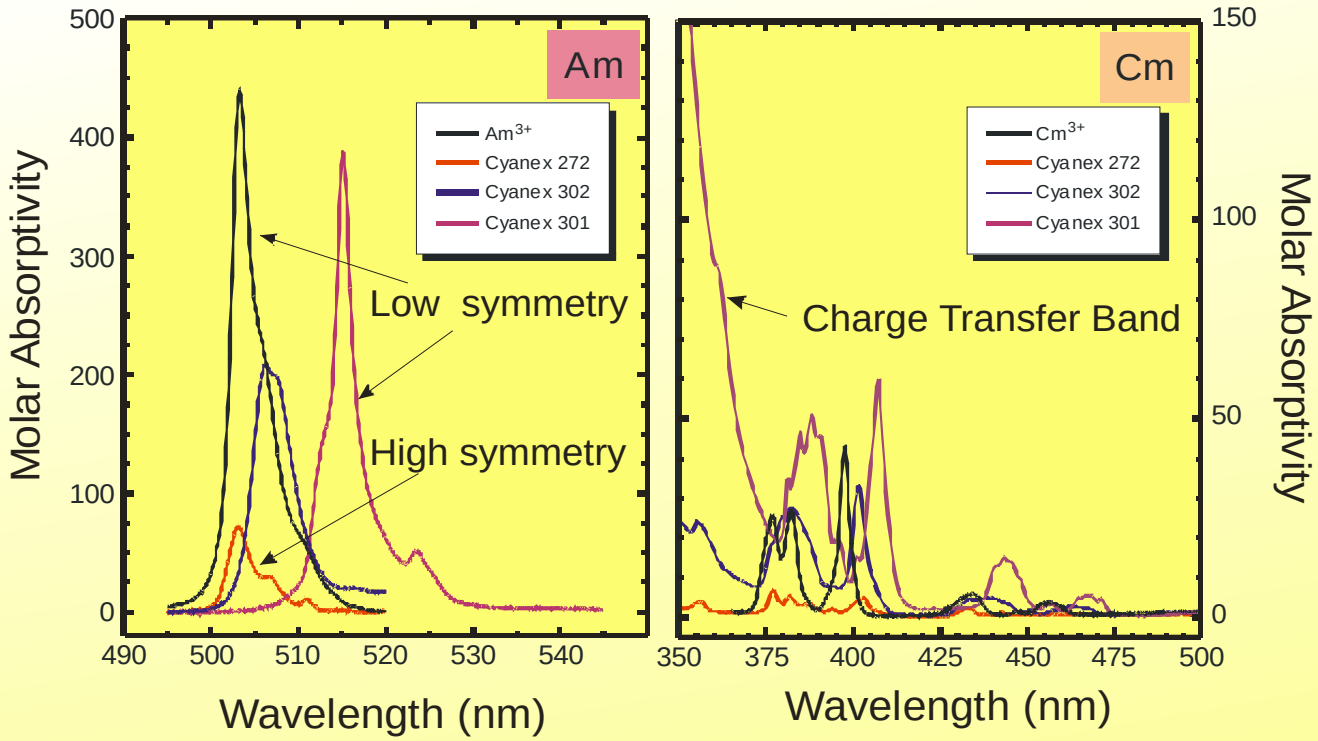
SETFICS
DTPA Stripping
of CMPO

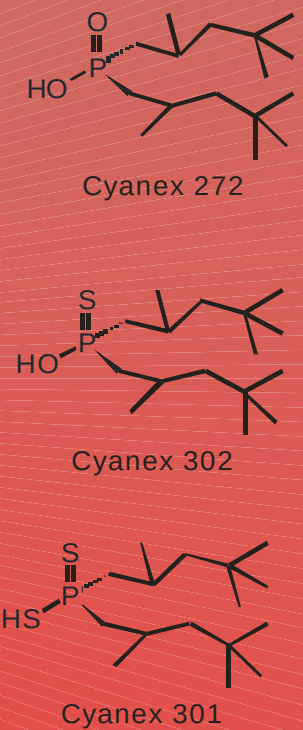
- Uranium removed in preconcentration step (**PUREX**)
- Pu recovery with reducing agent (HAN)
- Incomplete removal of Pu, Ru, Zr, Mo demands reducing scrub (hydrazine) before solvent recycle

Ozawa, Nemoto, Togashi, Kawata, Onishi, *Solvent Extraction & Ion Exchange 10,* 829 **1992,**

Ozawa, Koma, Nomura, Tanaka, *J. Alloys and Compounds 271-273,* 538 **1998**

Hard- and Soft-donor Cyanex Extractants





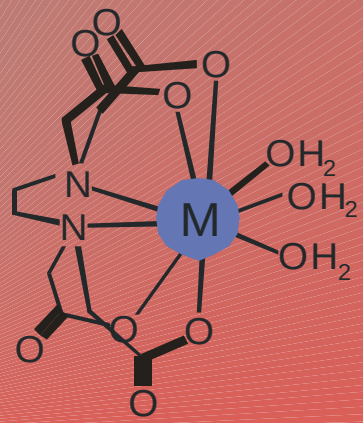
Jensen and Bond, *Inorg. Chem., JACS* (2002)

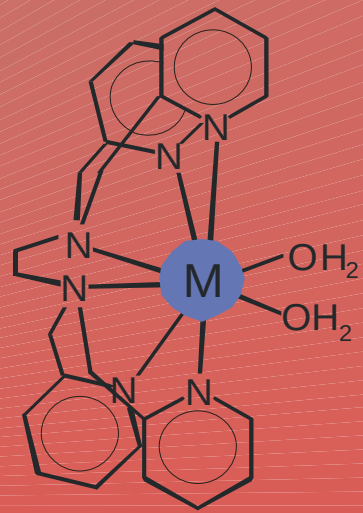
Zhu, Chen, Jiao, *SX&IX* (1996) Am^{3+}/Eu^{3+} separation factor 6000

	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol-K)
Eu	+66.3	+43.6	-66
Am	+44.8	+18.1	-87
Δ (Am-Eu)	-21.5	-25.1	-21

Actinide Interactions with Amine Donors

(Ln, Am Complexes with EDTA and TPEN)

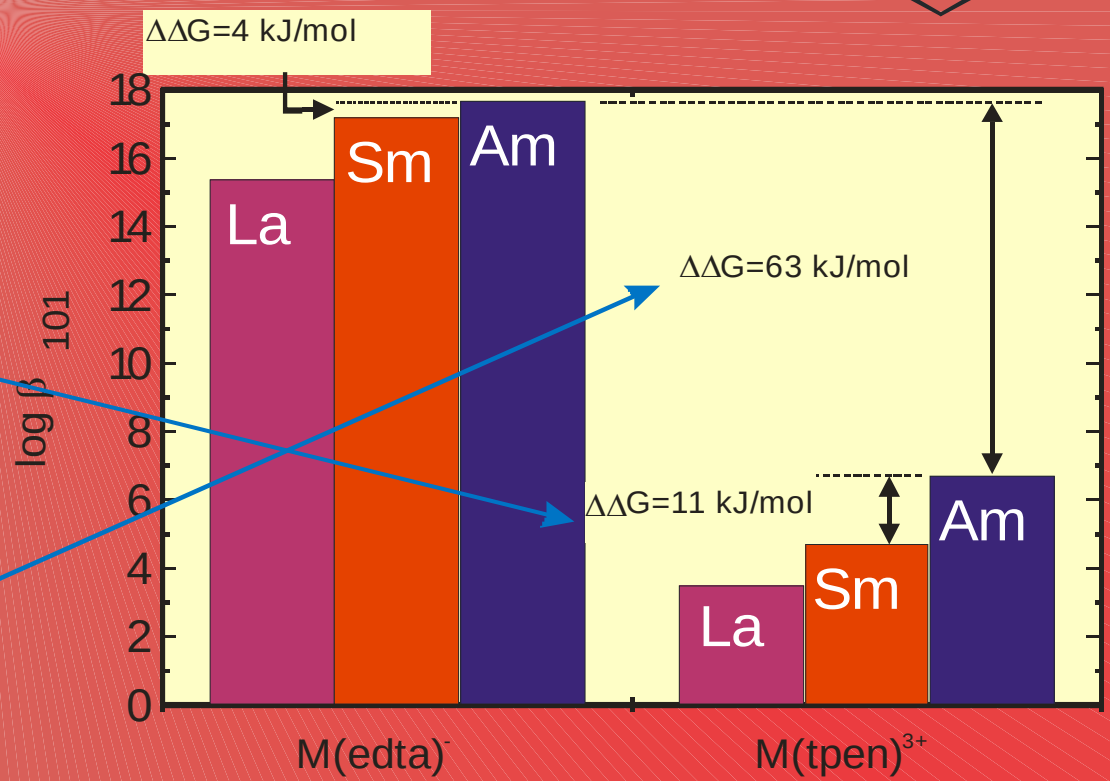




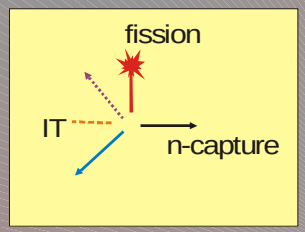
Soft Ligands are Selective but Complexes are Weak

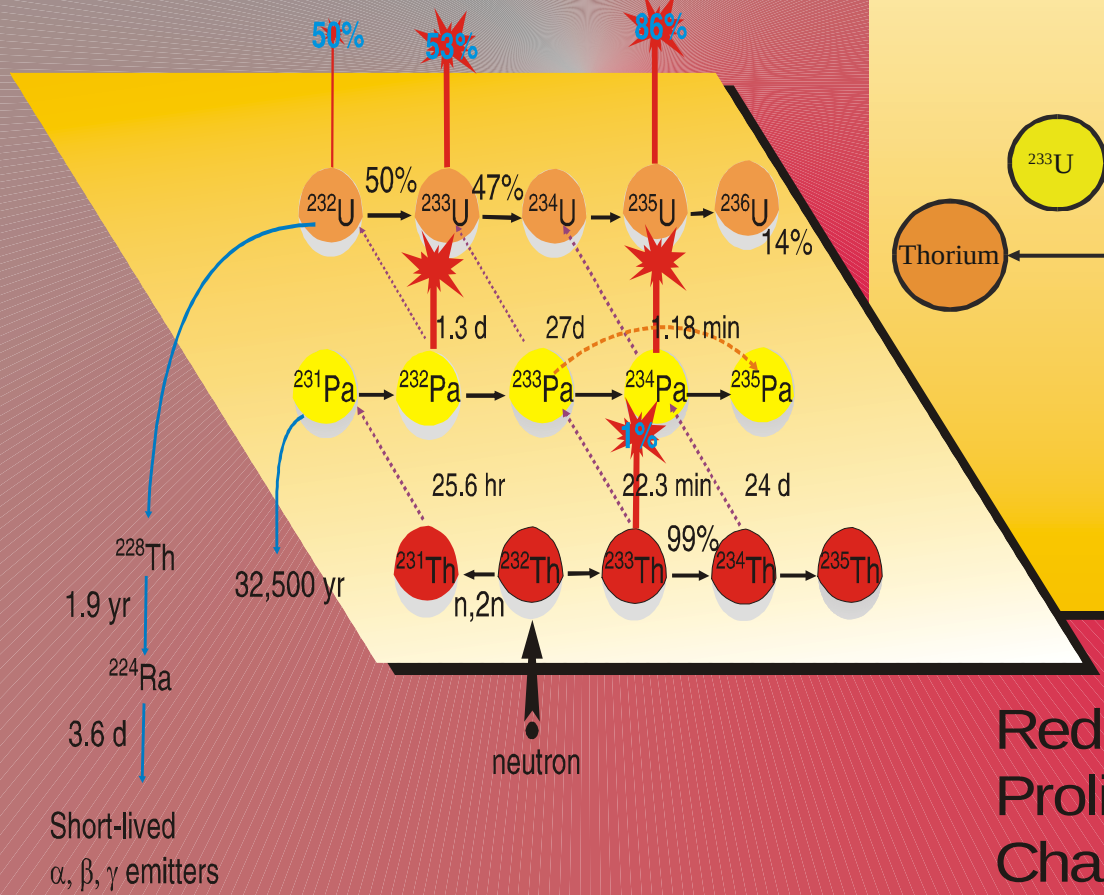
Represents a separation factor of about 100

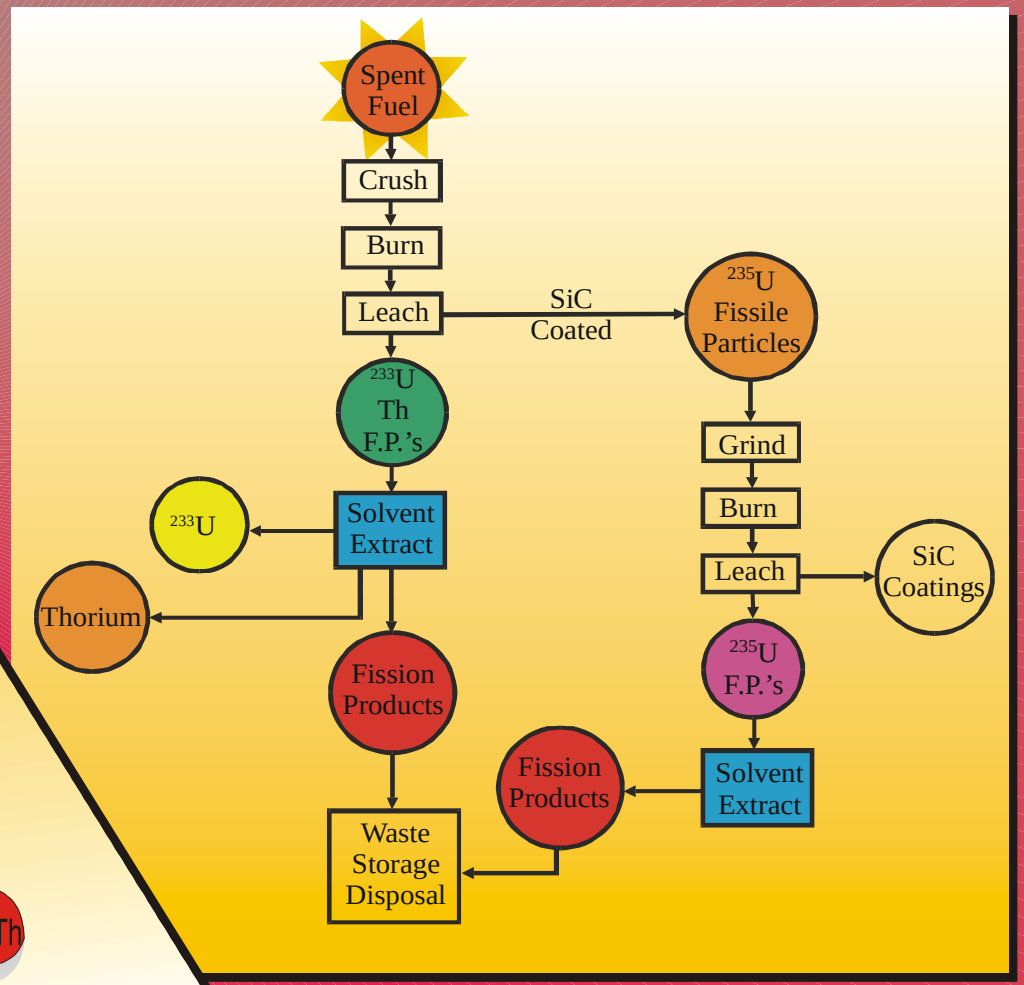
but at a cost of about 10^{11} in net bonding strength



Thorium-Uranium Fuel Cycle

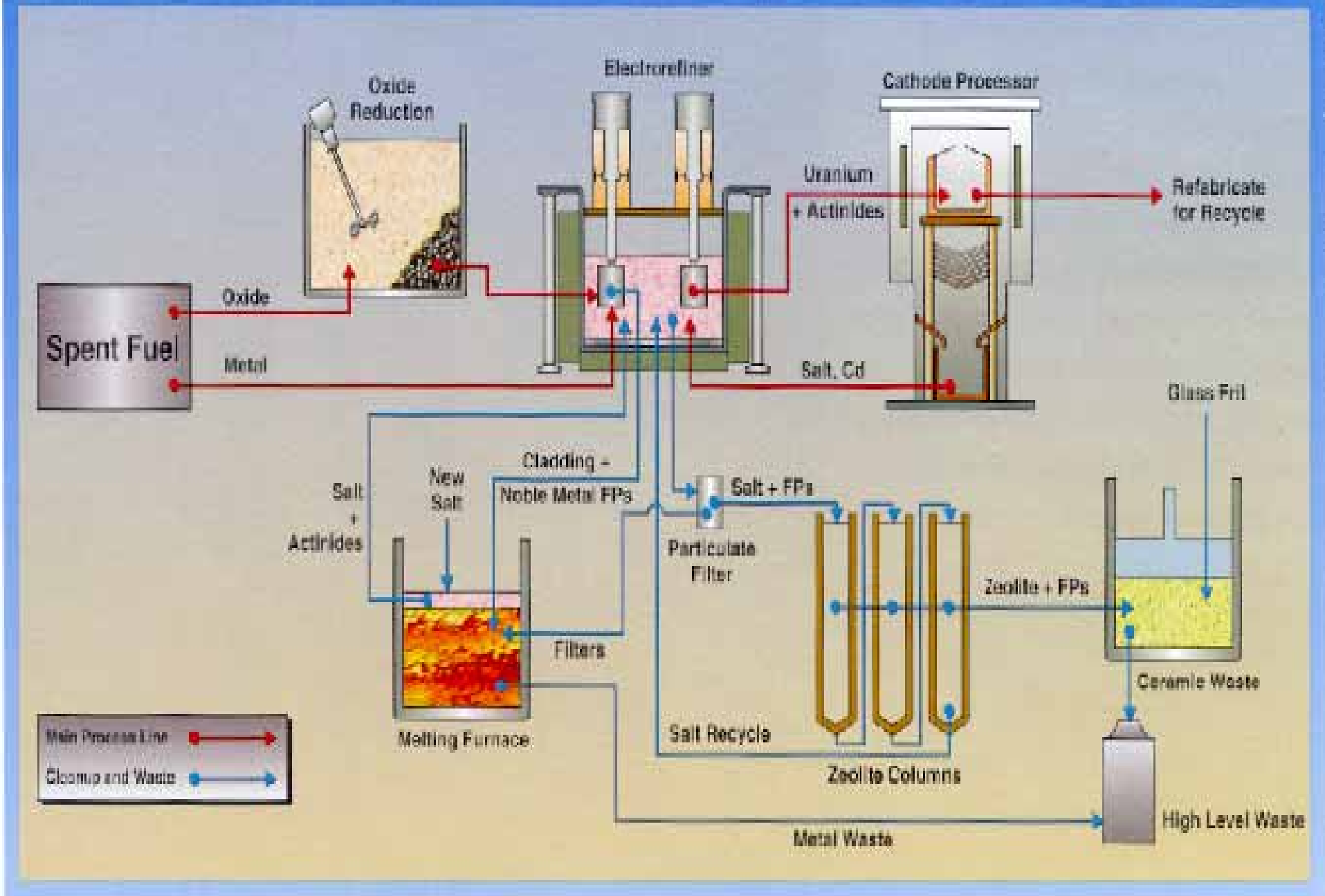




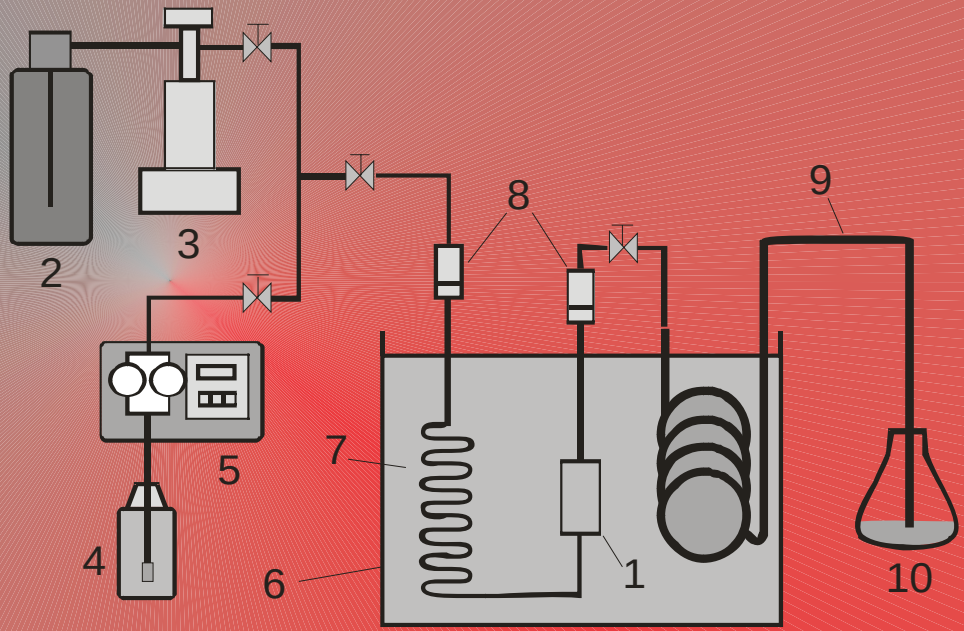


Reduced TRU production
Proliferation resistance
Challenging separations

Argonne's pyroprocessing technology



Dissolution of UO_2 Powder with Supercritical CO_2 Containing the HNO_3-TBP Complex



1: Reaction vessel 2: Liquid CO_2 cylinder 3: Syringe pump
4: Container for HNO_3-TBP reactant 5: Plunger-type pump
6: Thermostated water bath 7: Pre-heating coil 8: Filter
9: Restrictor 10: Collection vessel

Wai and coworkers, University of Idaho
Yoshida and coworkers, JAERI

Room Temperature Ionic Liquids in Actinide Separations

What: ionic salts of cationic organic compounds liquid at temperatures below 100 °C

- (methyl(alkyl) imidazolium, methyl pyridinium, tetraalkyl ammonium, tetraalkylphosphonium salts with a variety of different anions including Cl^-, PF_6^-, BF_4^-, $(CF_3SO_2)_2N$,...)
- Can be either lipophilic or hydrophilic depending on choice of anion
- Wide electrochemical window
- Tend to be viscous liquids, waxy solids at room temperature
- Low volatility

Obstacles to be overcome: Viscosity, chemical instability, expensive

Promise: hybrid process opportunities, unique solvation properties, electrometallurgical processing options

Unknowns: Many chemical features and properties remain unexplored, "Green"-ness

Conclusions

Future Directions for the Nuclear Fuel Cycle

- Aqueous-based technologies will likely continue to dominate the field for the next 20 years - opportunities exist for further improvements
- Legacy wastes will most likely have to be processed using aqueous technologies (Strongly alkaline solutions)
- Transmutation of actinides and long-lived fission products (best non-proliferation option but Am production increases with increased recycle of Pu)
- Lanthanide/actinide separations needed if actinides are transmuted
- Thorium-uranium breeder cycles have some attributes and some challenges
- Ionic liquids as solvents ? Supercritical Fluids ? Other unique materials ?
- Micelle-based separations (i.e., non-conventional aqueous processes)
- Aggregation and organization of solutes (e.g., third-phase formation)
- Non aqueous concepts (Pyro, volatility)
- Support for education of a next generation of experts

The overall objective should be to maximize the recovery of valuable (or potentially valuable) byproducts while minimizing both the volume of wastes produced (all types) and the long term environmental impacts