UREX+ Process Overview

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Topical Seminar Series on Nuclear Fuel Separation Processes
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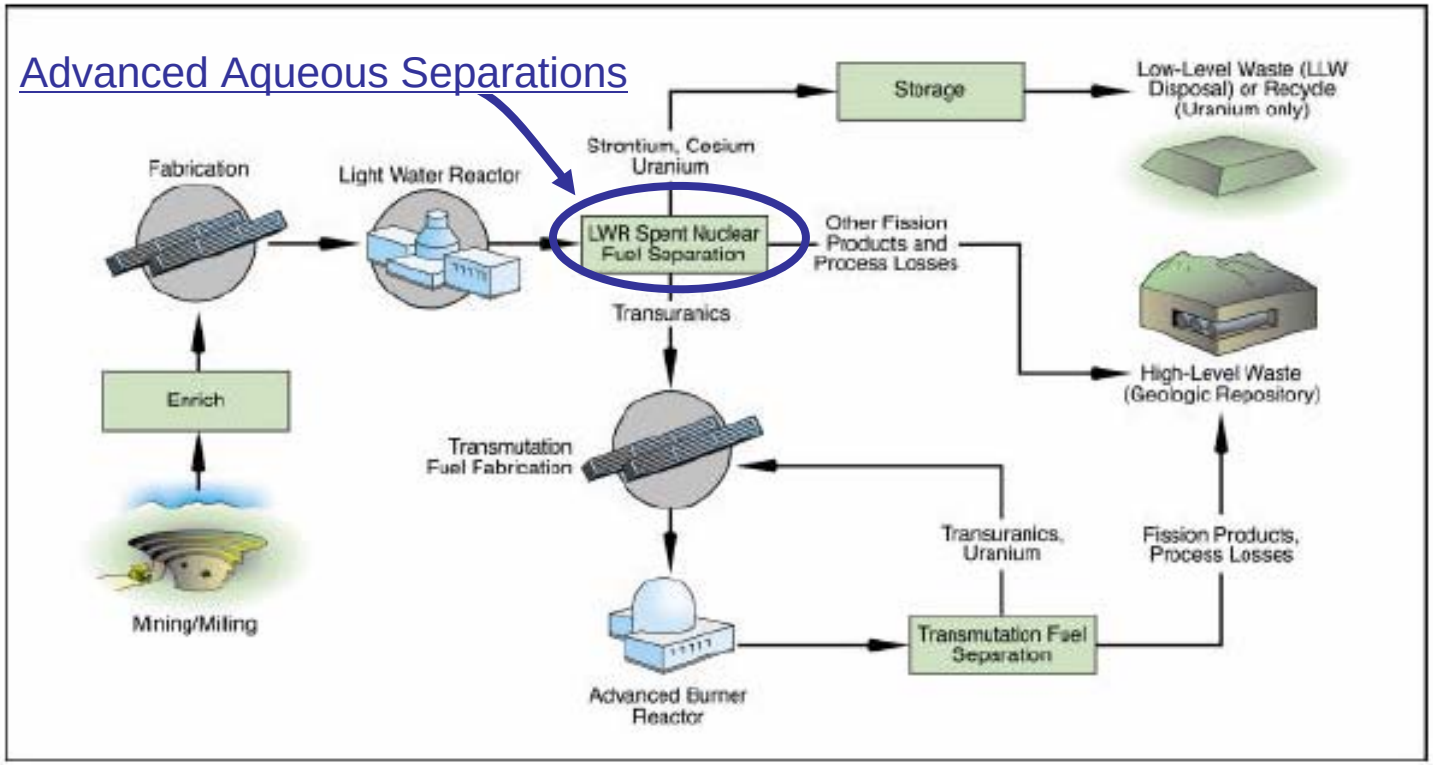
Outline

- Separations Overview
- Solvent Extraction
- Process Modeling and Simulation
- Processing Options
- Demonstration of UREX+ Processes

Separations are a central component of the GNEP scheme and implementation of an advanced fuel cycle in the U.S.



Separations Can Potentially Reduce the Volume, Activity and Toxicity of the Waste Bound for the Repository

Radionuclide	Oxide Fuel %	Significance
U	**~95**	**Hazard comparable to ore.**
Cs and Sr	**0.3**	**~30 yr half-life. Significant heat source.**
Pu and Np	**~1**	**Isotopes have long half-lives. Recycle.**
Am and Cm	**0.1**	**Isotopes have long half-lives and high toxicity. Can be recycled to fast reactors.**
I and Tc	**0.1**	**>10^5 yr half-life. Mobile in groundwater. Separate and stabilize for long-term disposal.**
Other Fission Products	**~3.5**	**Low heat and toxicity. Stabilize for disposal.**

Examples of Some Potential Aqueous Processing Options Meeting GNEP Objectives: UREX+

Process	Product #1	Product #2	Product #3	Product #4	Product #5	Product #6	Product #7
UREX+1	U	Tc	Cs/Sr	TRU/Ln	FP		
UREX+1a	U	Tc	Cs/Sr	TRU	FP/Ln		
UREX+1b	U	Tc	Cs/Sr	U/TRU	FP/Ln		
UREX+2	U	Tc	Cs/Sr	Pu/Np	Am/Cm/Ln	FP	
UREX+2a	U	Tc	Cs/Sr	U/Pu/Np	Am/Cm/Ln	FP	
UREX+3	U	Tc	Cs/Sr	Pu/Np	Am/Cm	FP/Ln	
UREX+3a	U	Tc	Cs/Sr	U/Pu/Np	Am/Cm	FP/Ln	
UREX+4	U	Tc	Cs/Sr	Pu/Np	Am	Cm	FP/Ln
UREX+4a	U	Tc	Cs/Sr	U/Pu/Np	Am	Cm	FP/Ln

Notes: (1) in all cases, iodine is removed as an off-gas from the dissolution process.
(2) processes are designed for the generation of no liquid high-level wastes

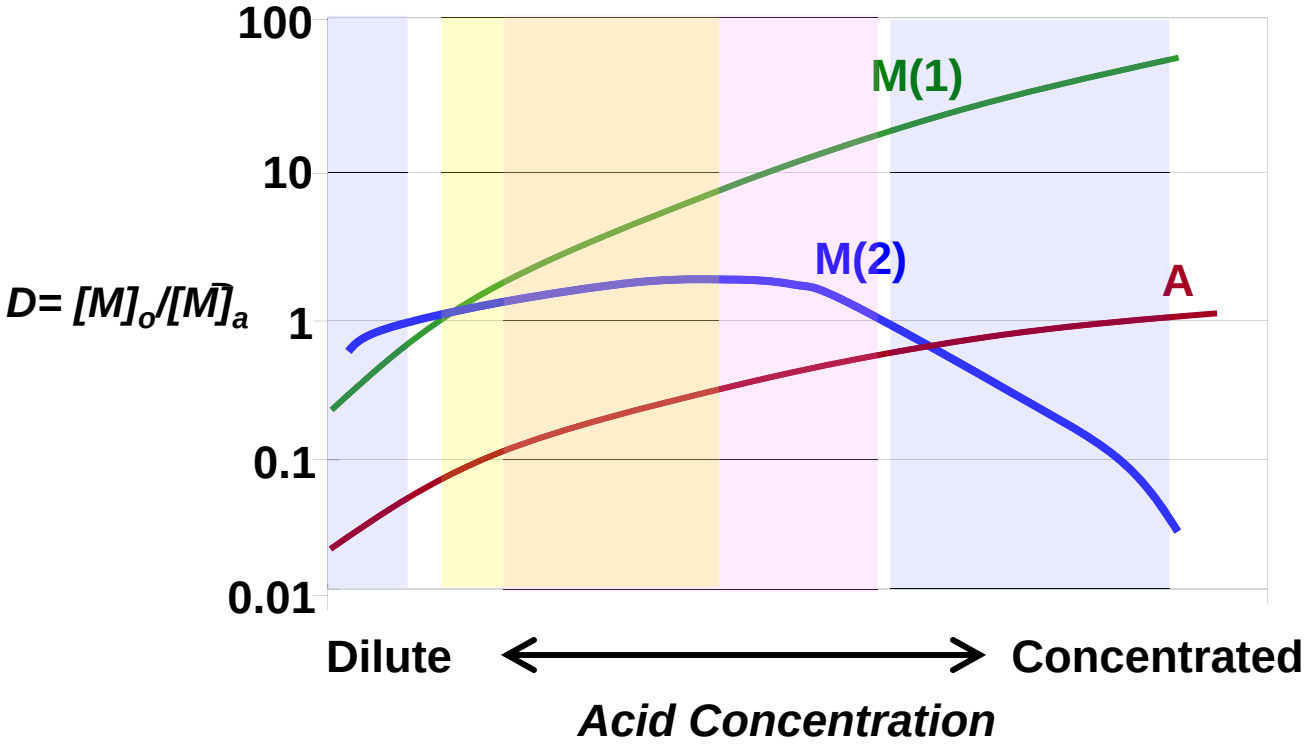
U: uranium (contributor to dose rate, and the mass and volume of high-level waste)
Tc: technetium (long-lived fission product, minor contributor to long-term dose)
Cs/Sr: cesium and strontium (primary short-term heat generators, affect waste form loading and repository drift loading)
TRU: transuranic elements: Pu - plutonium, Np - neptunium, Am - americium, Cm - curium (primary long-term dose rate contributors)
Ln: lanthanide (rare earth) fission products
FP: fission products other than cesium, strontium, technetium, iodine, and the lanthanides

Solvent Extraction

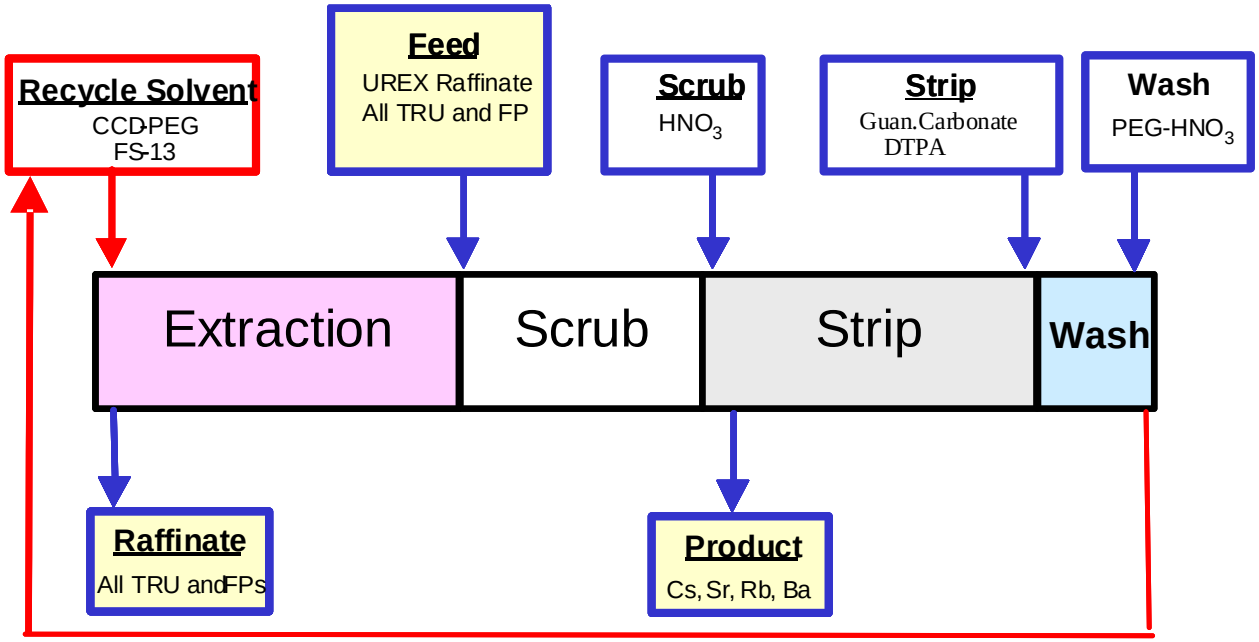
Advanced Aqueous Processing of LWR Spent Fuel

- **Aqueous solvent extraction processes are the reference methods under GNEP for treatment of LWR spent fuel**
  - High degree of technological maturity; industrial practice in France, the United Kingdom, Russia, and Japan
  - Capable of achieving high decontamination factors for separated products
    - *For thermal recycle, must eliminate high cross section fission products nearly completely (DF>10,000 required)*
    - *For fast reactor recycle, must reduce the rare earth content (DF>250 for separation of lanthanides from transuranics)*
  - Provides flexibility in degree of partitioning of radionuclides present in spent fuel
    - *Suite of process variants under development*

Example of Process Flowsheet Design

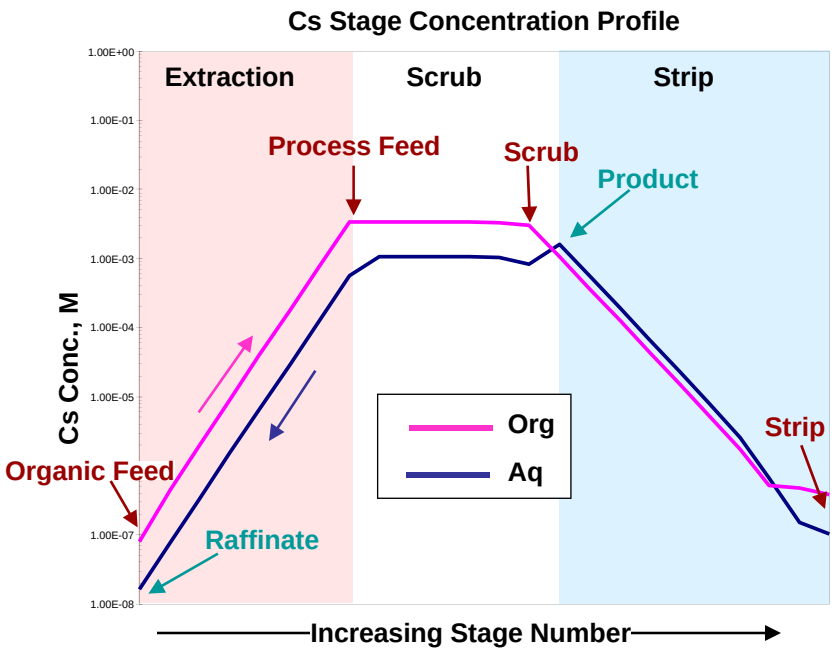


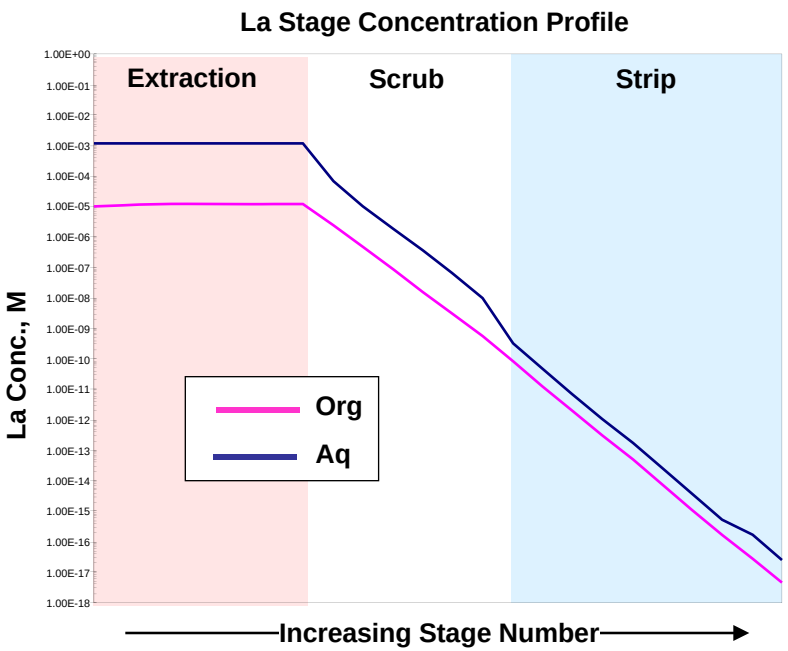
CCD-PEG Process from 2006 UREX+ Demonstration



Typical Profiles for Extraction Processes

AMUSE Simulation of Cs and La in CCD-PEG Process



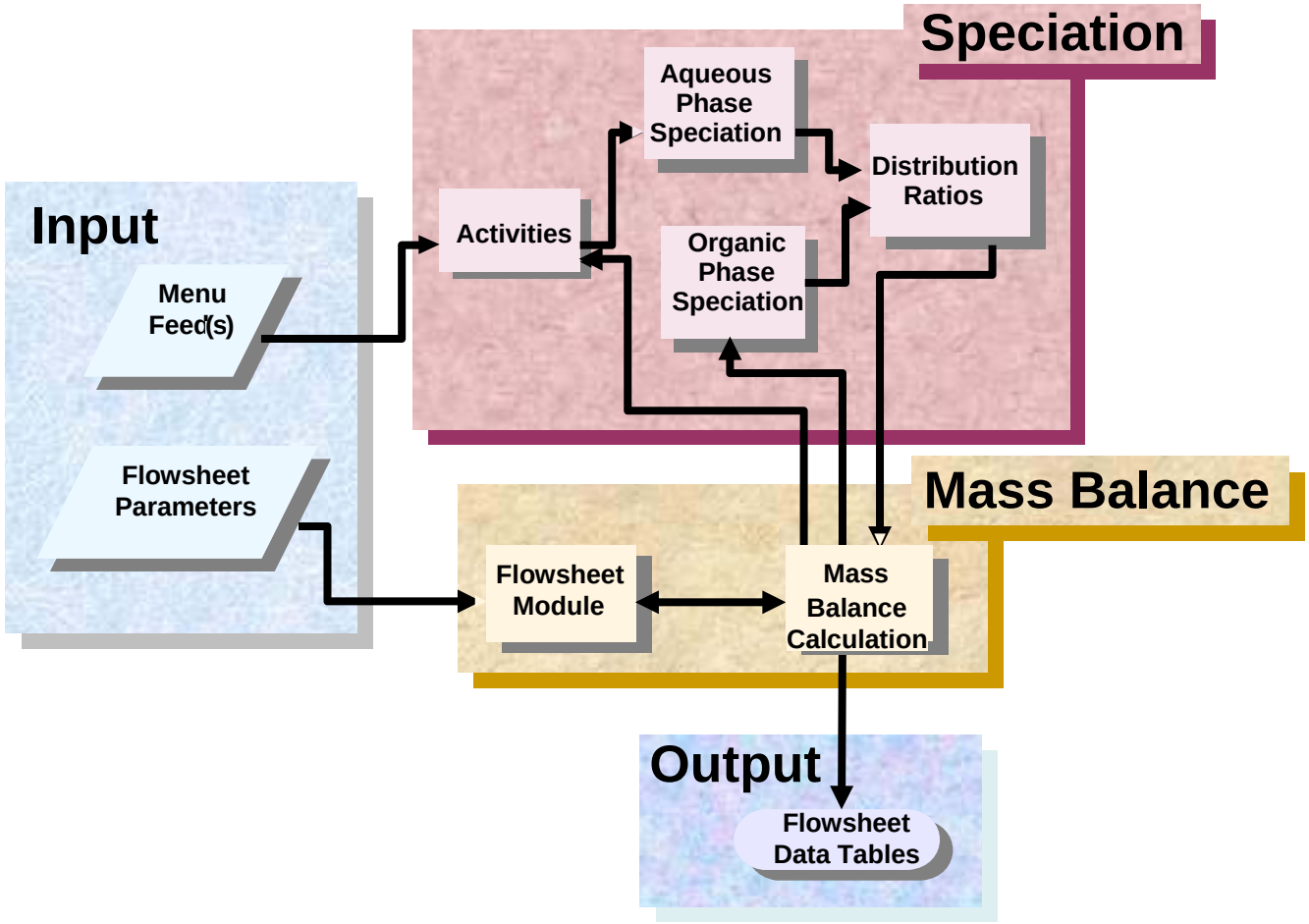


Process Modeling and Simulation

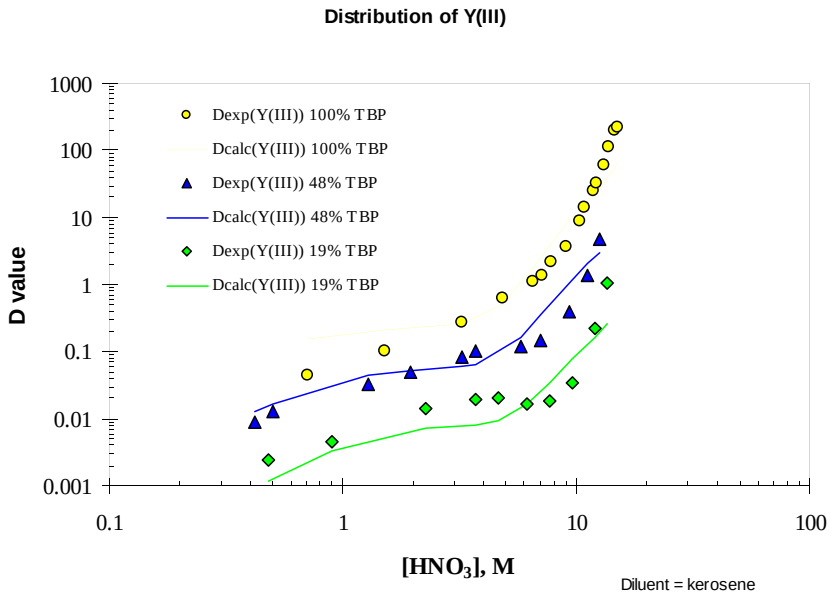
Process Design and Modeling for UREX+ is Done With AMUSE

- **The Argonne Model for Universal Solvent Extraction—AMUSE is used to:**
  - Design and optimize solvent extraction flowsheets
    - *PUREX, UREX, NPEX, TRUEX, CCD-PEG, SREX*
    - *TALSPEAK module is under development*
  - Perform sensitivity analysis to determine key process variables and their control bound
    - *Flow rates, number of stages, concentration of feed components, concentration of solvent, temperature*

Structure of AMUSE code



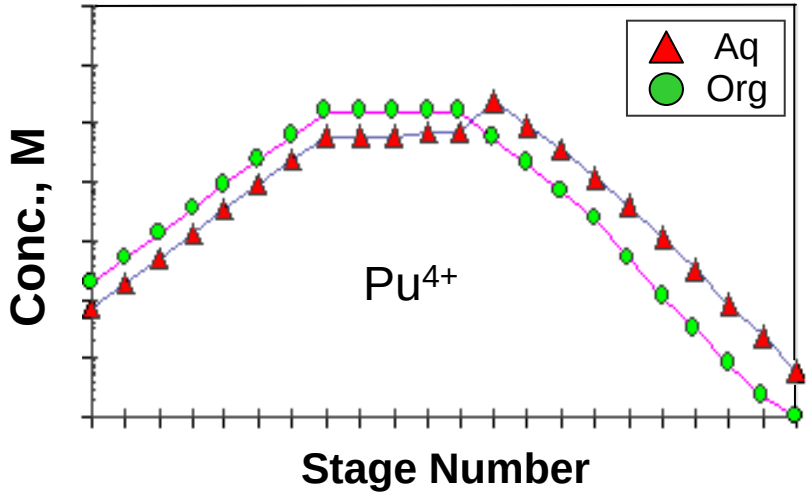
Extraction Model Derived from Literature Data

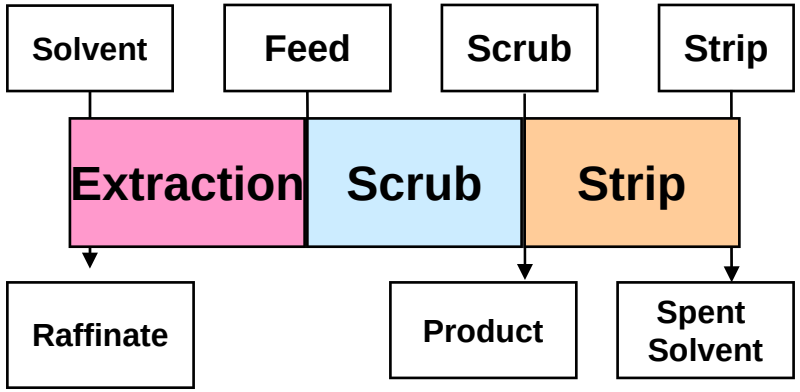


- **Model of extraction behavior for Yttrium (III)**
  - Nitric acid (0.4-15 M)
  - TBP in Kerosene
- **D value data from SCARGILL (1957)**

Examples of AMUSE Outputs

GRAPHICAL



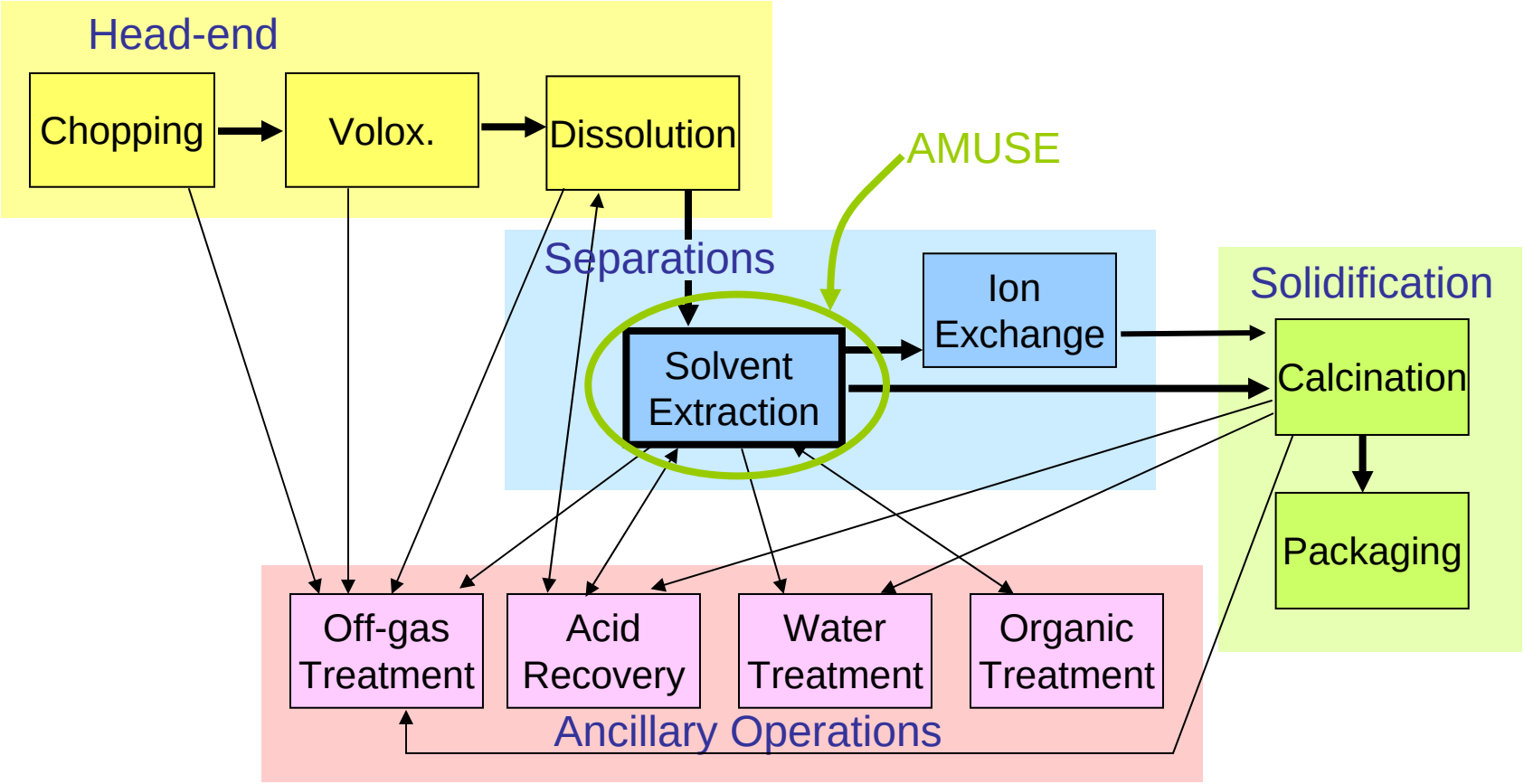


TABULAR

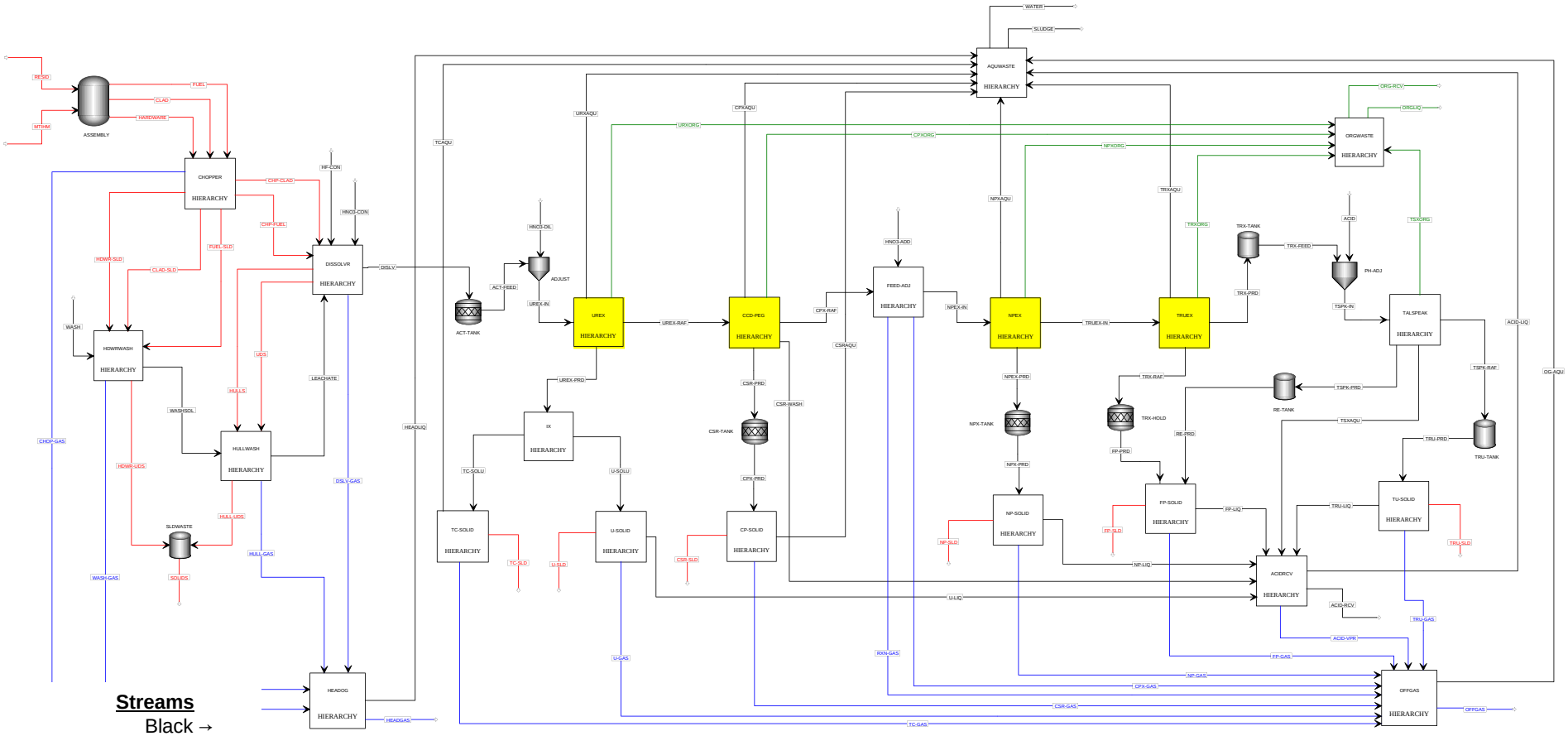
- **Tabular reports are created for**
  - Influent and effluent compositions and flow rates
  - Stage profiles that include
    - *Distribution ratios*
    - *Component concentrations in organic and aqueous phases*

Stream Identity	Flow Rate	Ag	Am	Ba	Cd
DX	2.50E+01	0.00E+00	0.00E+00	0.00E+00	0.00E+0
DX	1.00E-03	0.00E+00	0.00E+00	0.00E+00	0.00E+0
DF	1.00E+01	3.50E-06	6.80E-04	5.40E-03	2.40E-0
DS	4.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+0
DW	1.00E+00	2.33E-06	4.53E-04	3.60E-03	1.60E-0
DP	2.50E+01	9.45E-20	1.35E-16	1.46E-16	6.48E-1

Aqueous Spent Fuel Processing Involves A Number Of Key Operations in Addition Solvent Extraction



UREX+3a Process Plant Worksheet



Streams

Black → aqueous

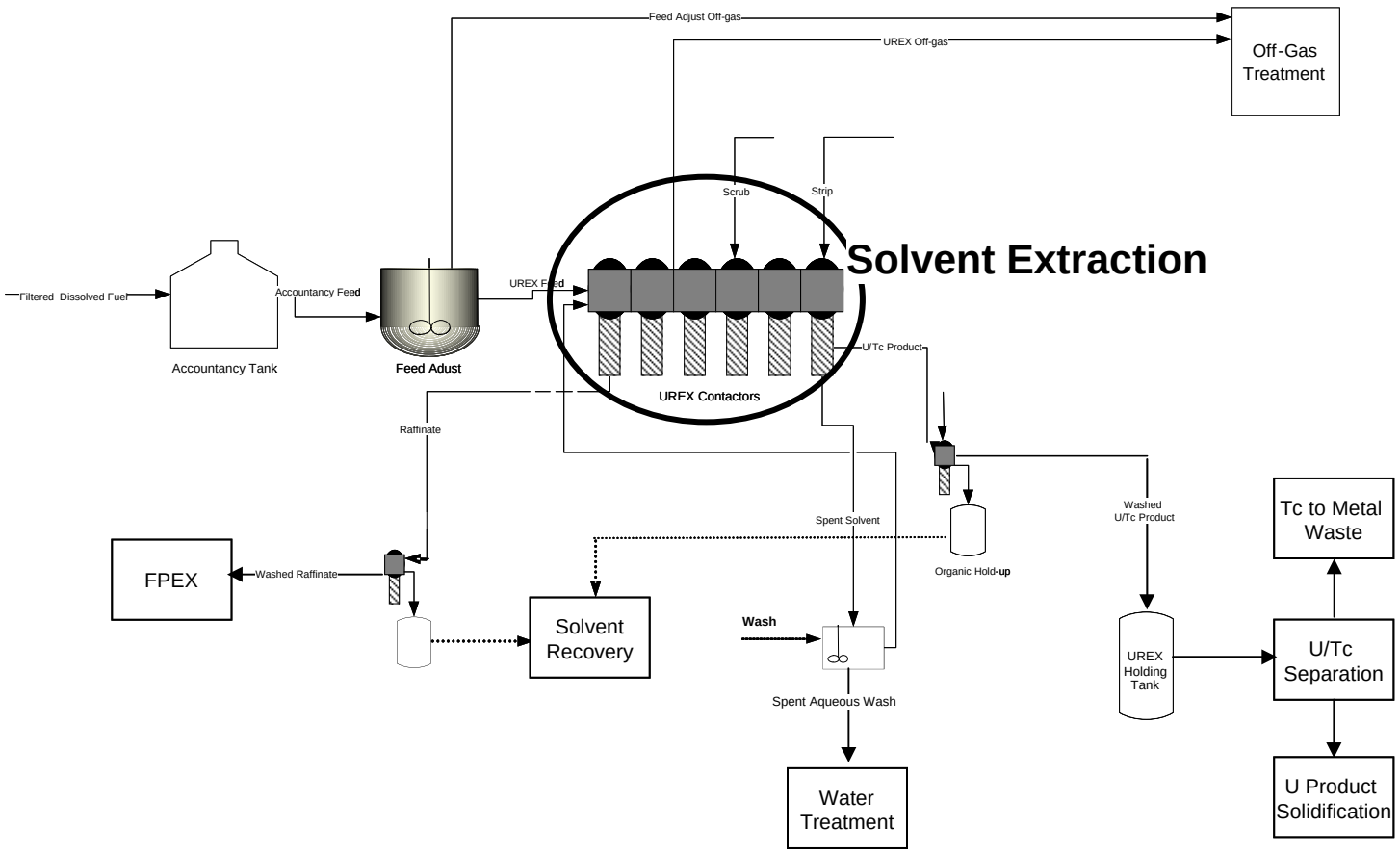
Green → organic

Red → solids

Blue → gas

Aspen/AMUSE UREX+3a Flowsheet Version 1.1

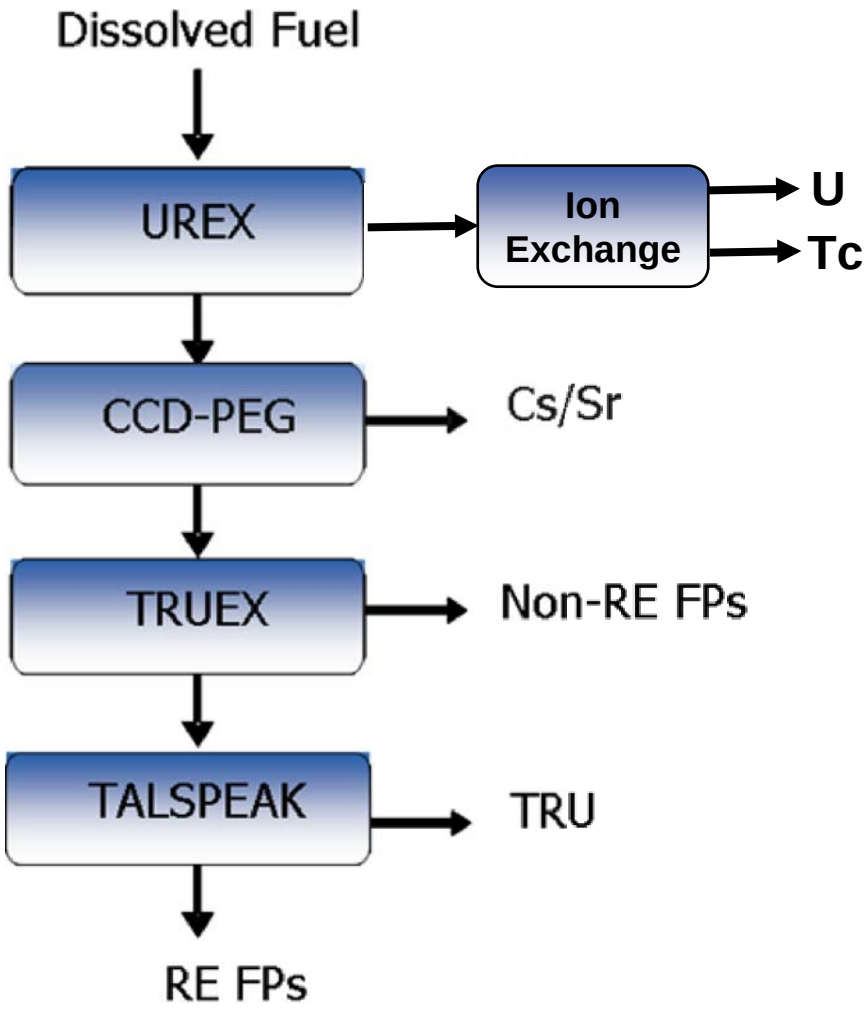
Top-level Modeling of Aqueous Separations Operations: UREX



Demonstration of the UREX+ Processes

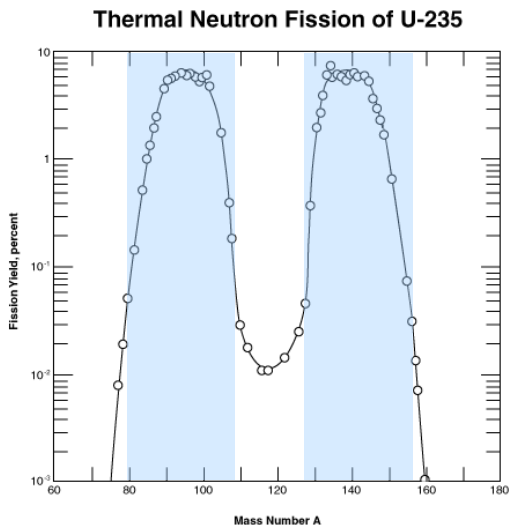
UREX+1a Process

- **A baseline process for LWR treatment**
- **Demonstrated with dissolved spent fuel**
  - Flowsheets developed using the AMUSE code



Fission Products and Actinides Are Separated Based on Chemical Differences: UREX+1a Example

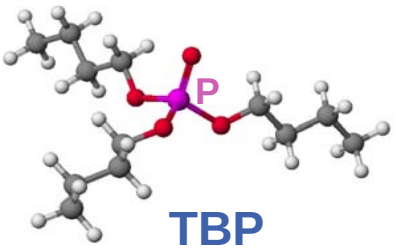
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	A															



La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

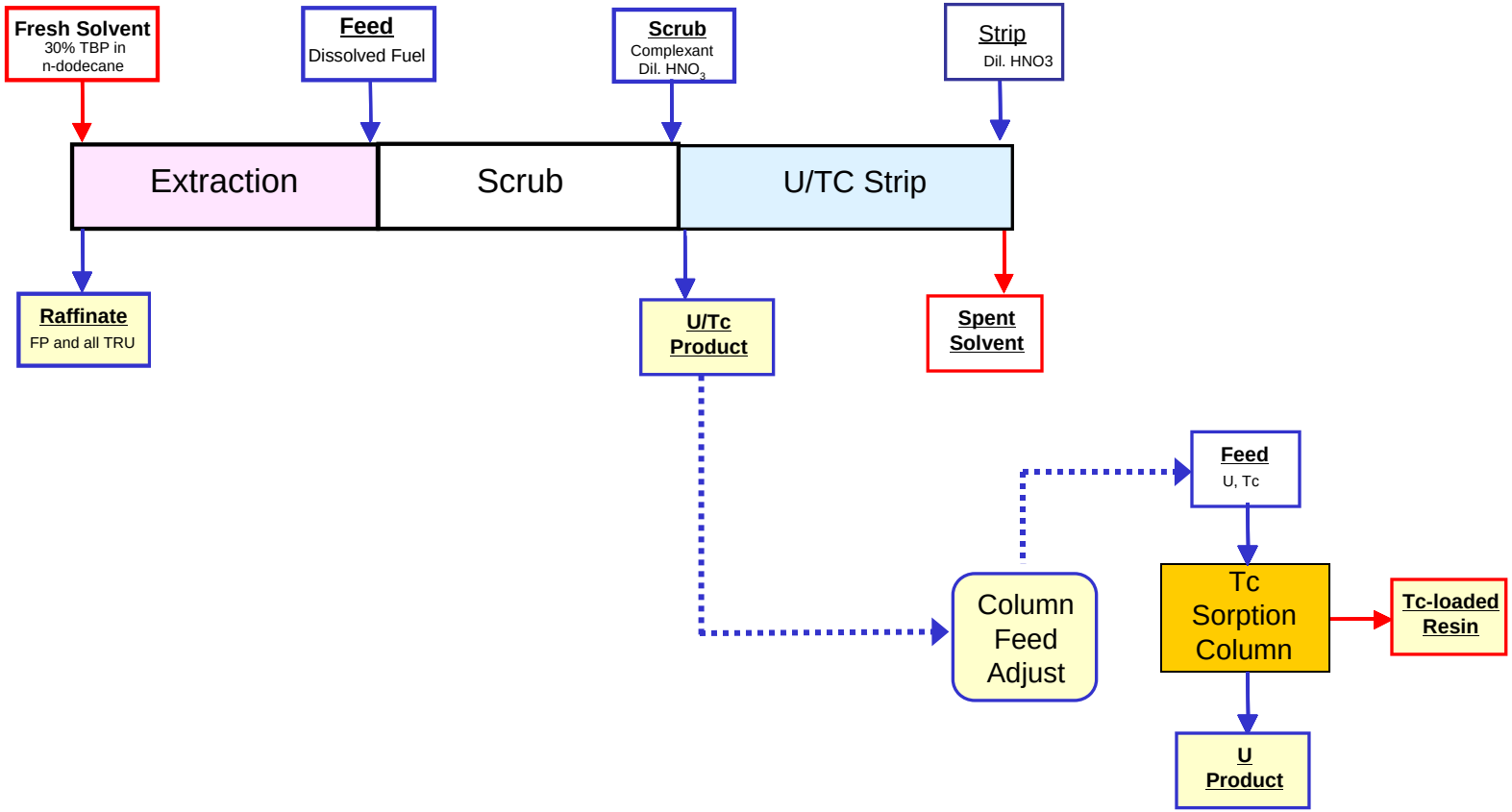
Processing Options for Recovery of U, Pu, Np

- **UREX**
  - Uses same solvent as PUREX (TBP in n-dodecane)
  - Recovers high purity U while leaving Pu with fission products
  - Recovers Tc in high yield
- **NPEX**
  - Uses same solvent as PUREX
  - Recovers mixed Pu and Np
  - Can generate a U/Pu/Np product in a predictable ratio
  - Requires UREX be run first to remove U from feed
- **Co-Extraction**
  - Uses same solvent as PUREX
  - Recovers U and Np/Pu or U/Pu/Np mixture
  - Likely requires multiple cycles to control U:Pu/Np ratio
  - Tc not targeted; recovery complicates processing

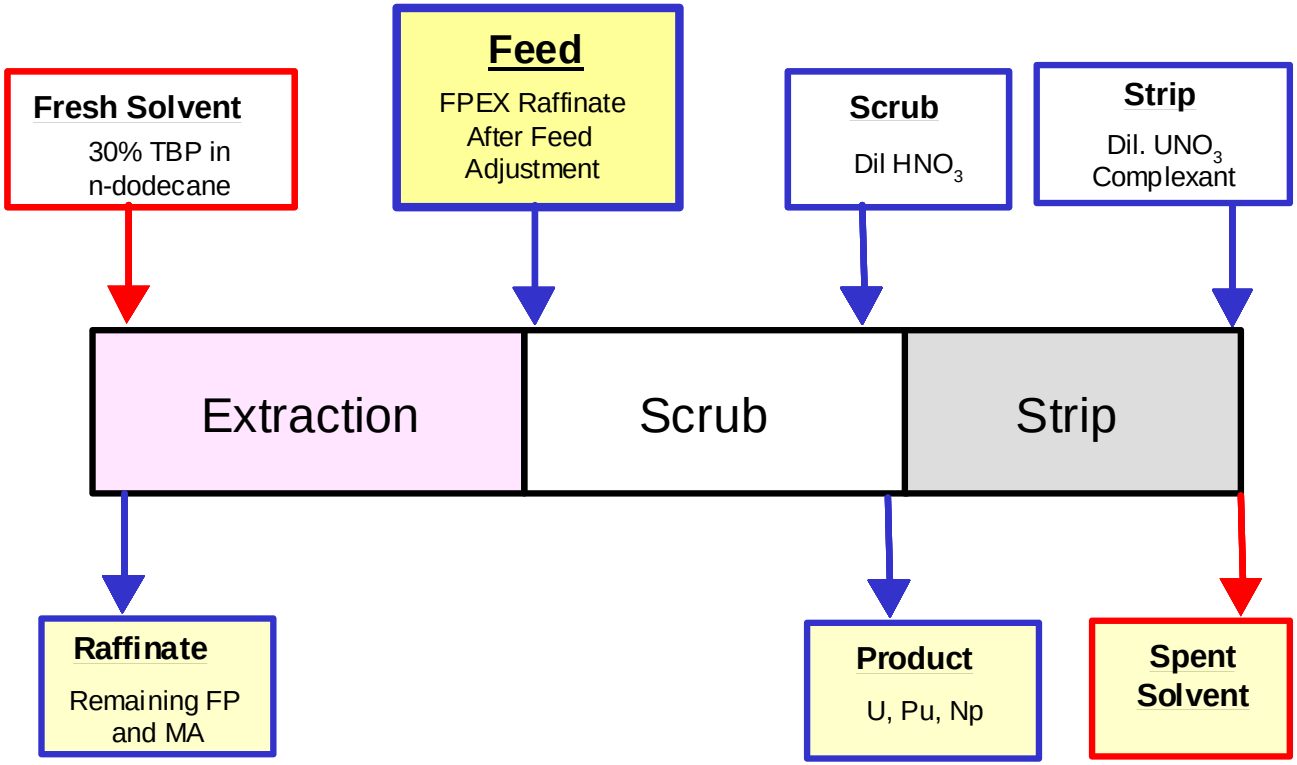


TBP

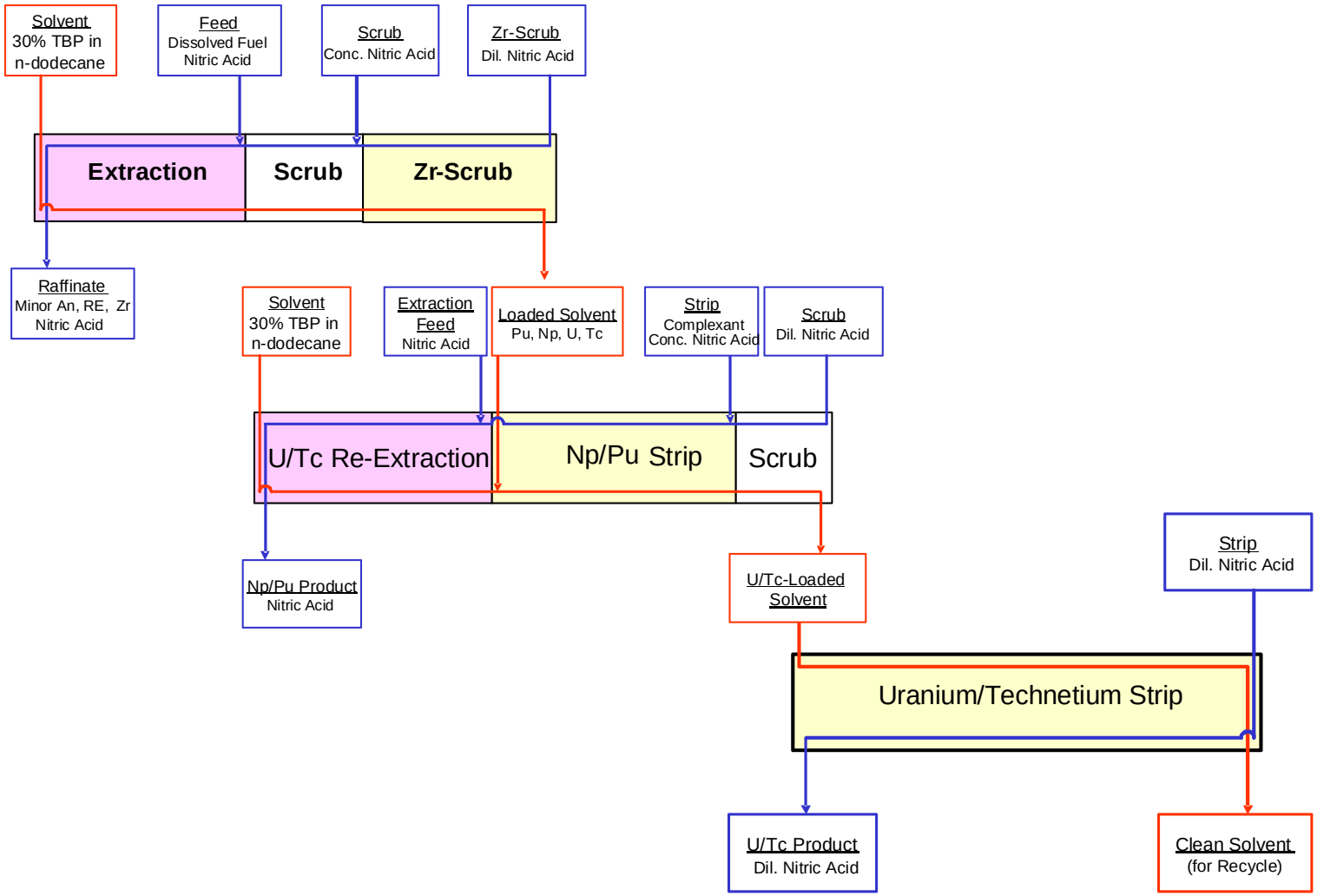
UREX Process for U and Tc Recovery



NPEX Process from 2007 UREX+ Demonstration

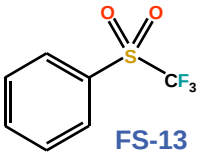


Co-Extraction Process from 2004 UREX+ Demonstration



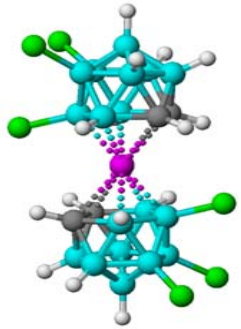
Processing Options for Cs and Sr Recovery

- **CCD-PEG**
  - Solvent is chlorinated dicarbollide and polyethylene glycol in FS-13
  - Recovers Cs and Sr in high yield
  - Solvent requires a dense sulfone diluent
  - PEG is partially soluble in aqueous phase
  - Acidity of feed is low
    - *Requires feed adjustment when run after NPEX, TRUEX, COEX*
    - *Degradation of complexants affects extraction*
  - Complexant required is used to strip solvent



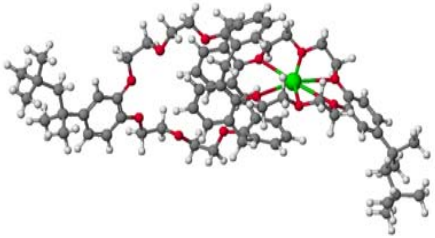
FS-13
Phenyltrifluoromethyl Sulfone

$HOCH_2CH_2(OCH_2CH_2)_7OCH_2CH_2OH$
Polyethylene Glycol (PEG-400)

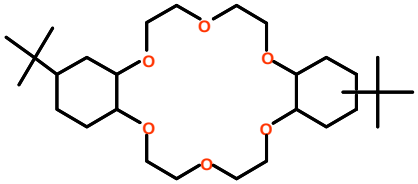


Chlorinated Cobalt Dicarbollide

- **FPEX**
  - Solvent contains a calixrene, crown ether, and modifier in Isopar-L®
  - Isopar-L is a refined kerocene and similar to that of other UREX+ processes
  - Derived from CSSX process being implemented at SRS
  - Less-developed than CCD-PEG process: composition not yet finalized
  - Cs and Sr D-values slightly lower than for CCD-PEG
  - Acidity of feed is low
    - *Requires feed adjustment when run after NPEX, TRUEX, COEX*
    - *Degradation of complexants affects extraction*

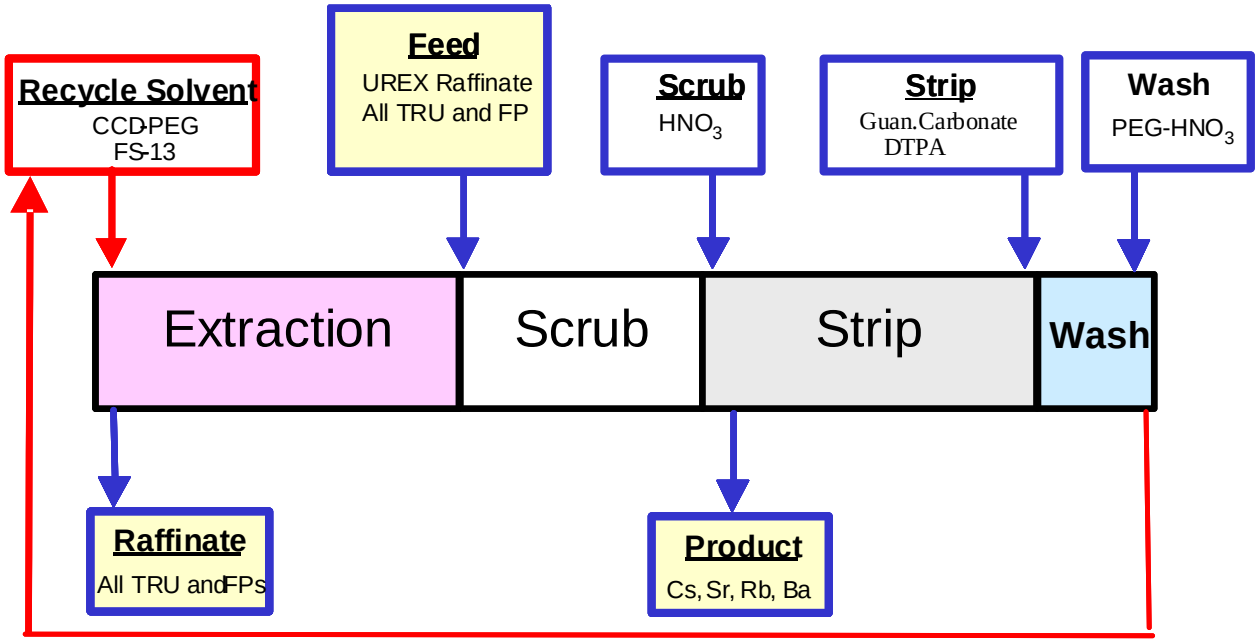


Calix[4]arene-bis(t-octylbenzo-crown-6) (complexed with Cs)

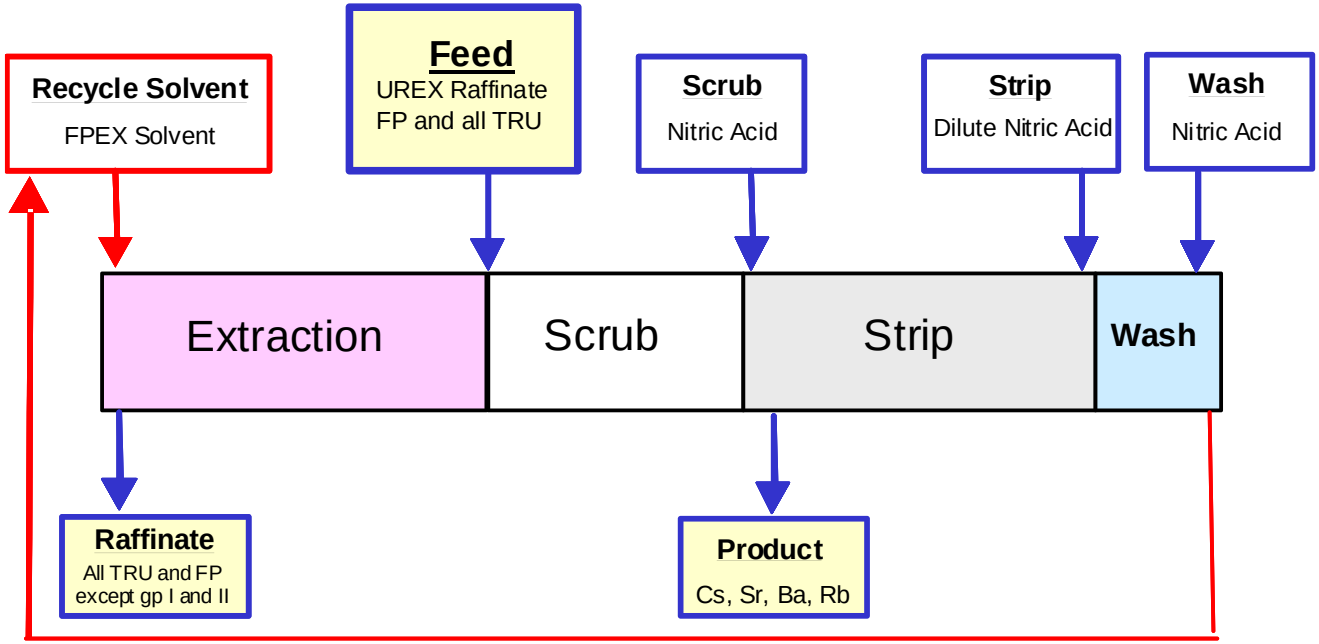


4,4'(5')-di-t-butylcyclohexano 18-crown-6

CCD-PEG Process from 2006 UREX+ Demonstration



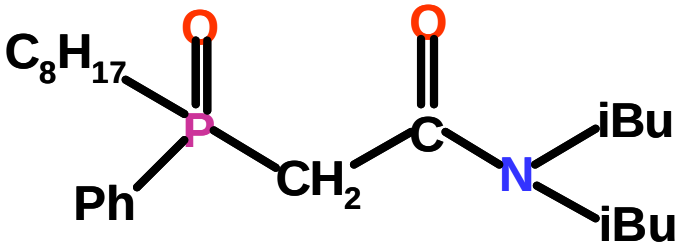
FPEX Process from 2007 UREX+ Demonstration



UREX+ Processing Options for An and Ln Recovery

- **TRUEX**
  - Solvent is CMPO and TBP in n-dodecane
  - Recovers rare earths and transuranics
  - Extensive database and development
  - Readily compatible with NPEX, COEX, UREX

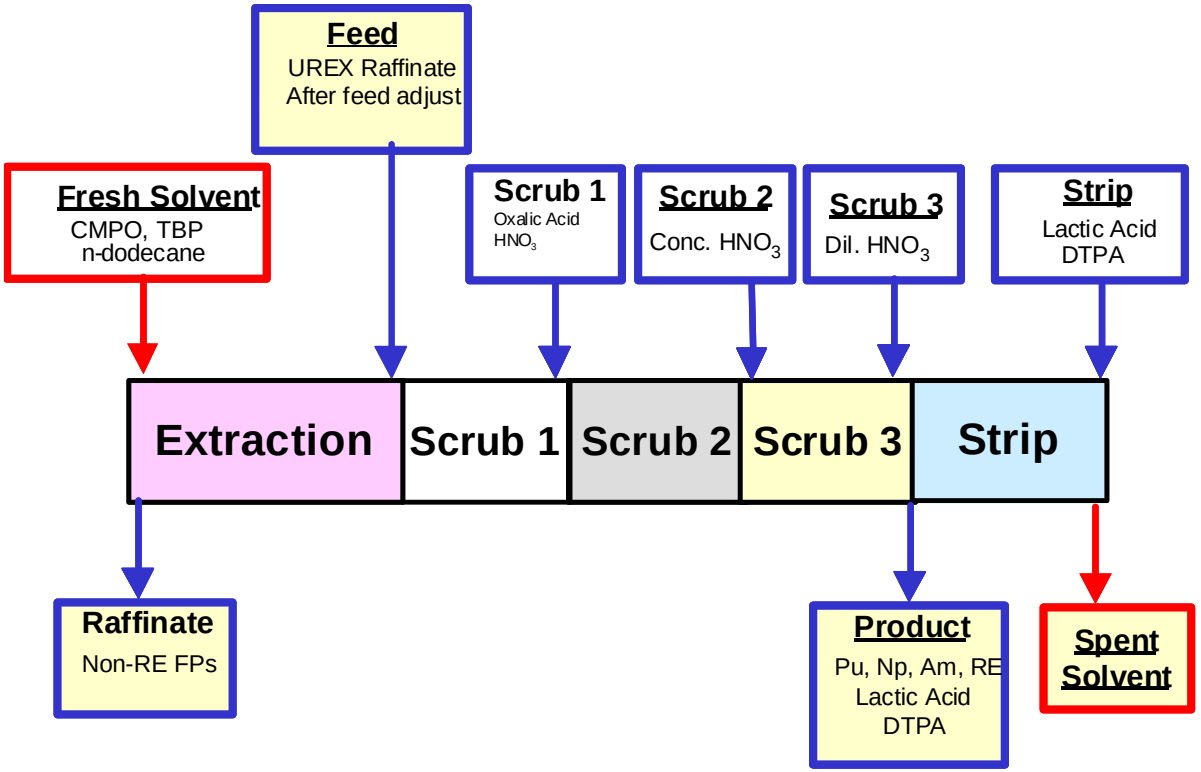
  - Expensive extractant but n-dodecane diluent
  - May require multiple scrubs to achieve purity requirements



CMPO

octyl(phenyl)-N,N –diisobytylcarboylmethyl phosphine oxide

TRUEX Process from 2005 UREX+1 Demonstration



Processing Options for An and Ln Separation

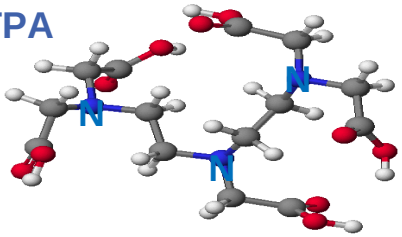
- **TALSPEAK**
  - HDEHP in n-dodecane
  - High separation factors and An recoveries have been demonstrated
  - Can be run for Am/Cm or Group TRU recovery (Pu/Np/Am/Cm)

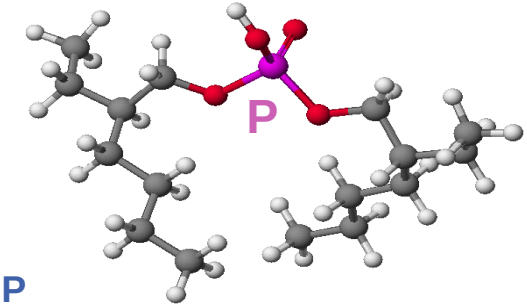
  - Feed requires good pH control
  - Slow Extraction Kinetics
  - TRU product in complex

- **Cyanex 301® Extractant**
  - Cyanex 301 in n-dodecane
  - High An recoveries

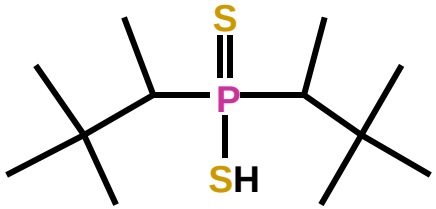
  - Feed requires good pH control
  - Only partial An-Ln separation was observed
  - Poor solvent stability > limited recycle
    - *No longer under consideration*

DTPA



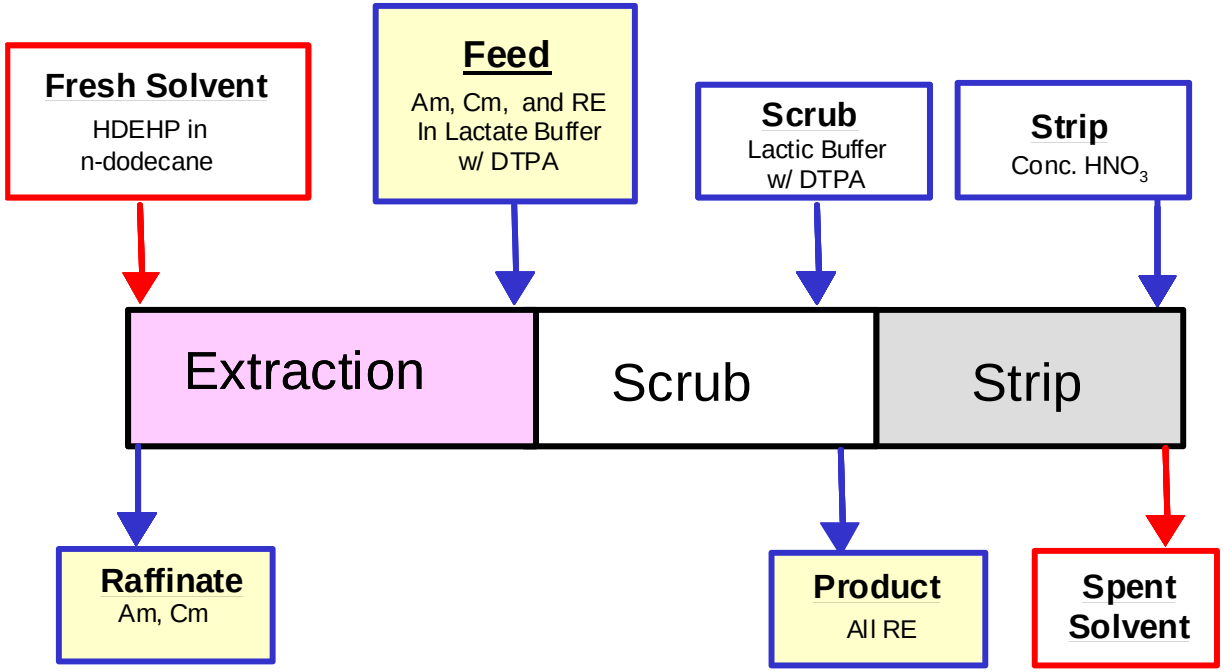


HDEHP
(di(2-ethylhexyl)phosphoric acid)

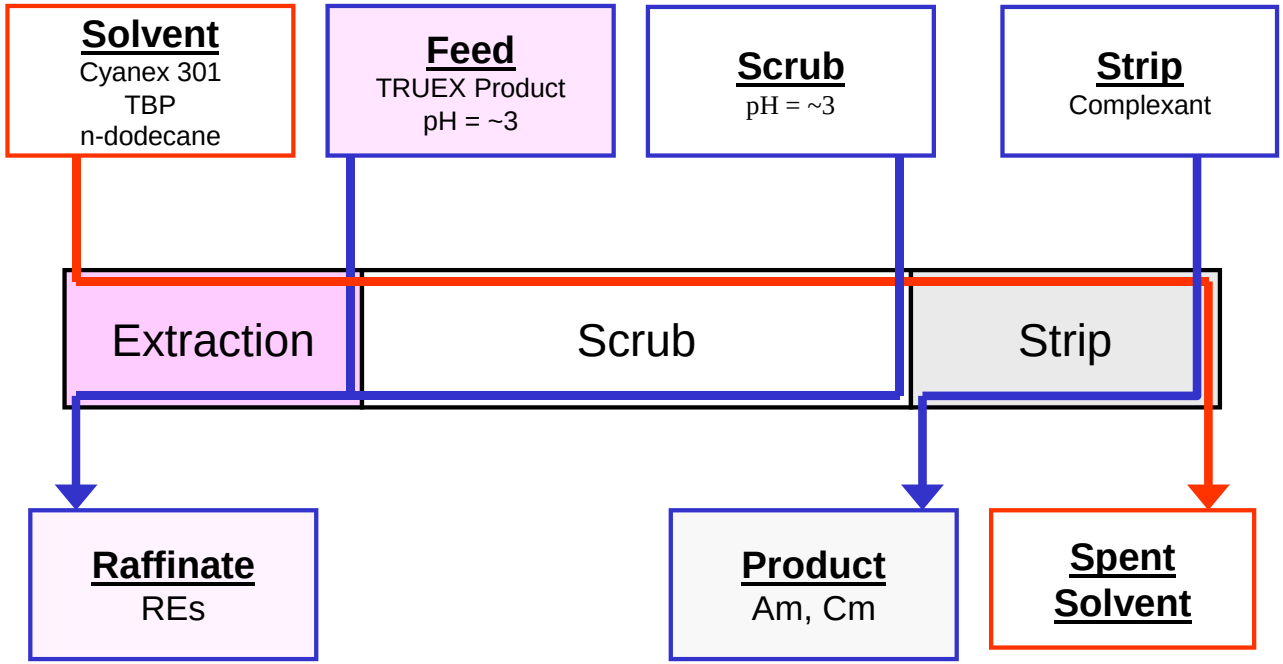


Cyanex 301
(bis(2,4,4-trimethylpentyl)dithiophosphinic acid)

TALSPEAK Flowsheet from 2006 UREX+ Demonstration



Cyanex-301 Extractant Flowsheet from 2003 UREX+ Demonstration



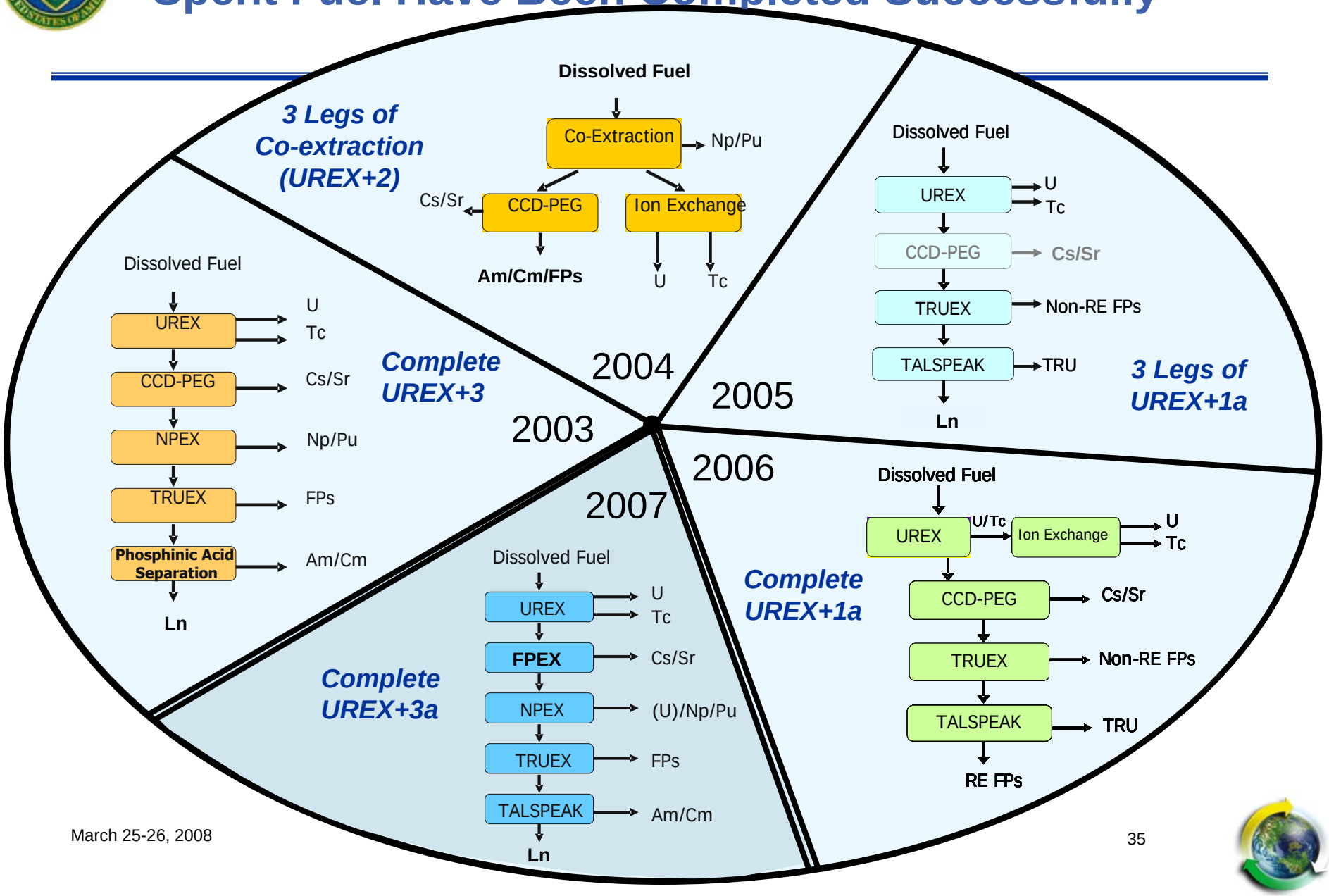
Potential Aqueous Processing Options That Have Been Demonstrated At Argonne

Process	Product #1	Product #2	Product #3	Product #4	Product #5	Product #6	Product #7
UREX+1	U	Tc	Cs/Sr	TRU/Ln	FP		
UREX+1a	**U**	**Tc**	**Cs/Sr**	**TRU**	**FP/Ln**		
UREX+1b	U	Tc	Cs/Sr	U/TRU	FP/Ln		
UREX+2	**U**	**Tc**	**Cs/Sr**	**Pu/Np**	**Am/Cm/Ln**	**FP**	
UREX+2a	U	Tc	Cs/Sr	U/Pu/Np	Am/Cm/Ln	FP	
UREX+3	U	Tc	Cs/Sr	Pu/Np	Am/Cm	FP/Ln	
UREX+3a	**U**	**Tc**	**Cs/Sr**	**U/Pu/Np**	**Am/Cm**	**FP/Ln**	
UREX+4	U	Tc	Cs/Sr	Pu/Np	Am	Cm	FP/Ln
UREX+4a	U	Tc	Cs/Sr	U/Pu/Np	Am	Cm	FP/Ln

Notes: (1) in all cases, iodine is removed as an off-gas from the dissolution process.
(2) processes are designed for the generation of no liquid high-level wastes

U: uranium (contributor to dose rate, and the mass and volume of high-level waste)
Tc: technetium (long-lived fission product, minor contributor to long-term dose)
Cs/Sr: cesium and strontium (primary short-term heat generators, affect waste form loading and repository drift loading)
TRU: transuranic elements: Pu - plutonium, Np - neptunium, Am - americium, Cm - curium (primary long-term dose rate contributors)
Ln: lanthanide (rare earth) fission products
FP: fission products other than cesium, strontium, technetium, iodine, and the lanthanides

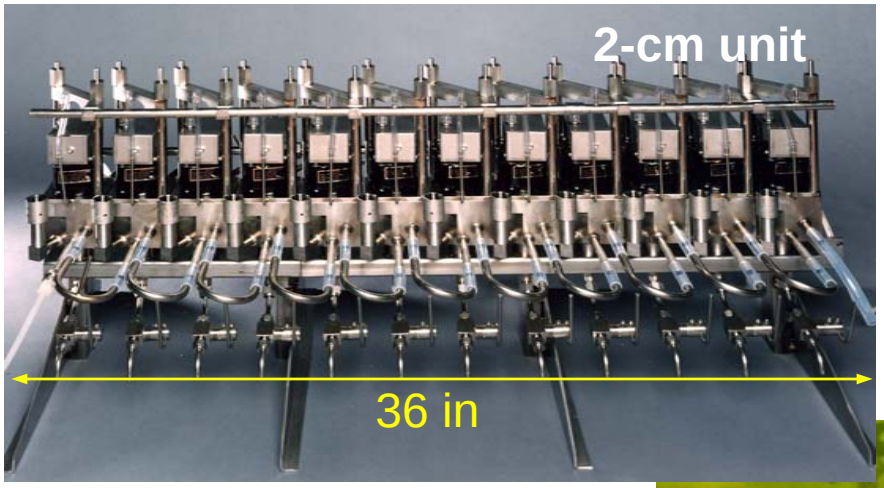
Five Demonstrations of UREX+ Processes With Spent Fuel Have Been Completed Successfully



The UREX+ Process Demonstrations

- **R&D for UREX+ process development includes:**
  - Process design and optimization using AMUSE
  - Equipment design
  - Process demonstration and post-test analysis
- **Objective of demonstration:**
  - Demonstrate that all desired spent-fuel constituents can be separated by aqueous processing
  - Show that product specifications for recycle or disposal are achievable
- **Flowsheets developed using AMUSE**
  - Test run with spent fuel in 2-cm contactor
  - All processes were run until steady state was achieved

ANL Centrifugal Contactor Bank in Shielded Cell

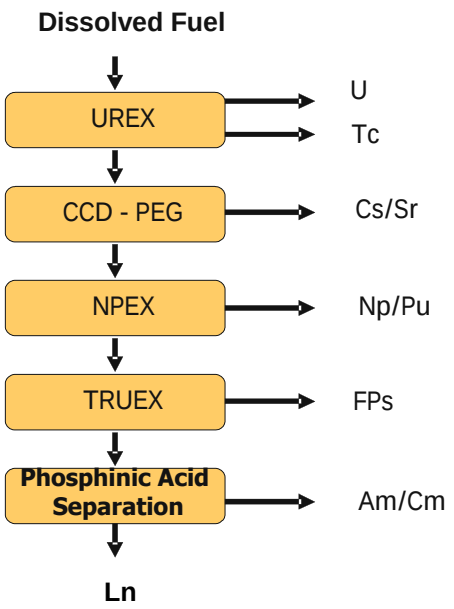


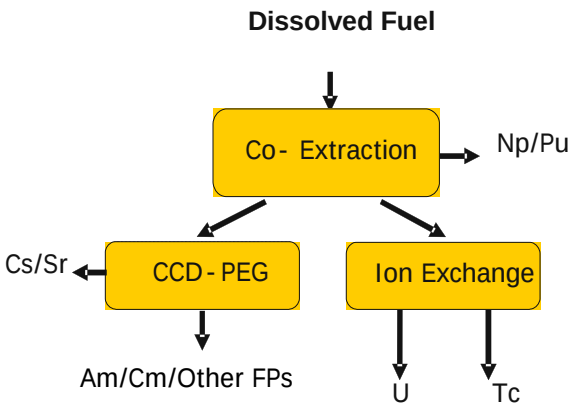
Spent Fuel Was Dissolved in Nitric Acid at Ambient Pressure and Under Moderately Higher Pressures

- **Tests were run with both clad and declad fuel**
- **0.5-1 kg fuel batches**
  - Sealed and ambient pressure vessels have been used
  - Undissolved solids were generally minimal
- **Solutions were stable**

UREX+2 and UREX+3 Were First Two UREX+ Process Demonstrations

- **UREX+3, as initially designed, differed significantly from more recent process flowsheets**
  - U-Tc separation was accomplished by selectively stripping
  - The Cyanex process was used for the Am/Cm separation
- **Co-extraction of U, Pu, Np, and Tc was used in first demonstration of UREX+2 process**
  - Pu/Np separated from U/Tc by selective stripping of solvent
  - U and Tc separated by ion





2003 UREX+3: Product Distributions

- **All primary components report to desired product streams**
  - Np and Tc fractions lower than targets
  - U and Tc separated by selective stripping rather than ion exchange
  - High rare earth content in Am/Cm product

Distribution in process effluent streams (%)

Component	Product	Raffinate
2003 UREX		
Tc	94.40	4.60
U	99.96	0.02
2003 NPEX		
Pu	99.6	0.4
Np	70.3	29.7
Cyanex 301		
RE	27.2	82.8
Am	99.98	0.02

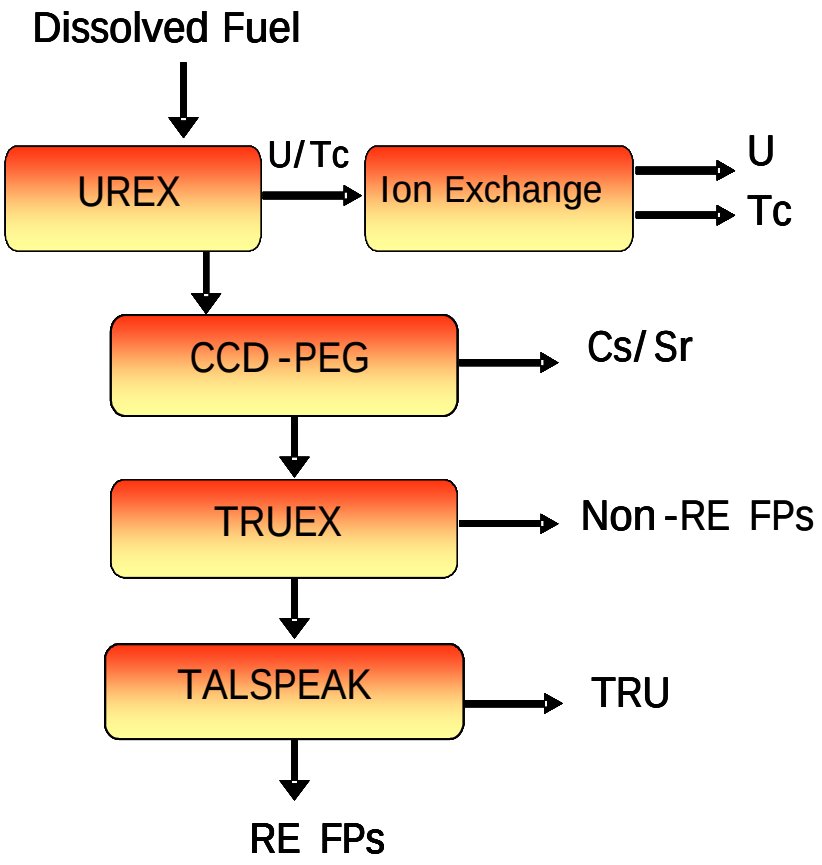
UREX+2 Co-Extraction Process: Product Distributions

- **All primary components report to desired product streams**
  - Tc, Np fractions lower than targets
  - Zr in Np/Pu product rather than raffinate due to other-phase carryover because of mis-match between contactor design and loaded-solvent density

Component	Product	Raffinate
	2004 Co-Extraction	
U	>99.9994	0.003
Tc	80.1	18.6
Pu	99.8	0.2
Np	87.2	12.8
	2004 CCD-PEG	
Cs	99.7	0.3
Sr	>98.6	<1.4

Urex+1a Spent Fuel Demonstration Consisted of Four Extraction Processes and an Ion Exchange Process

- **Produces a TRU product to serve as the feedstock for a fast reactor fuel**
- **Process was run in 2005 and 2006**
  - CCD-PEG was omitted in 2005
- **TALSPEAK process flowsheet was reworked in 2006 to account for slow process kinetics**



UREX+1a: UREX Process Results

- **Excellent hydraulic performance**
- **High recovery of all products**
- **Excellent TRU/Ln recovery obtained with TRUEX**
- **Refined TALSPEAK process for 2006 test met targets**

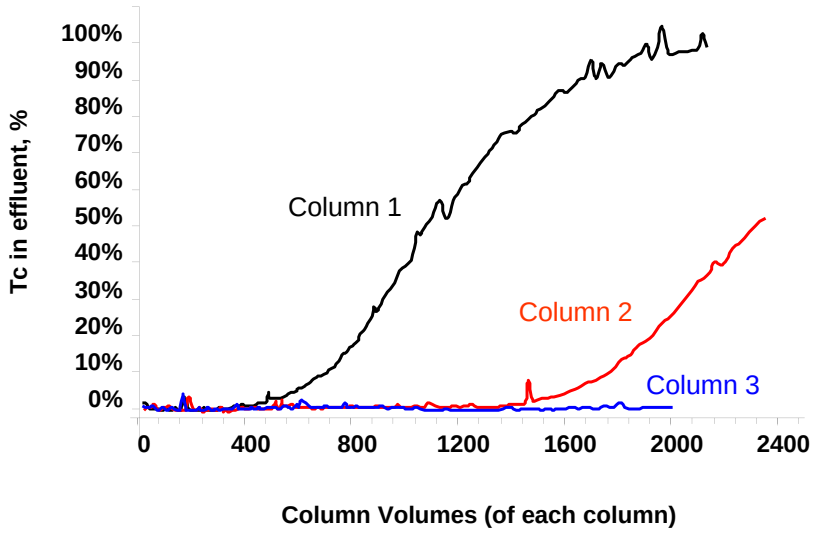
Distribution in process effluent streams (%)

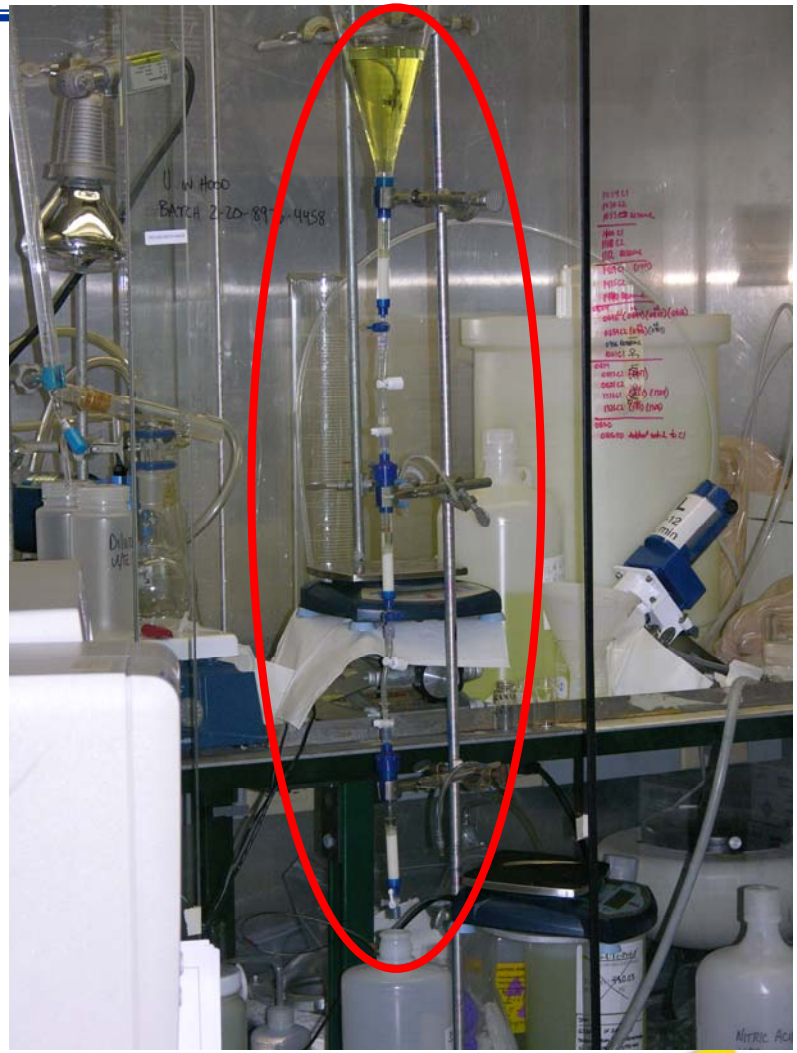
Year	2005		2006	
Component	Product	Raffinate	Product	Raffinate
		UREX		
U	>99.98	<0.02	99.997	0.003
Tc	97.1	2.9	95.5	4.5
		CCD-PEG		
Cs	NA*	NA	>99.85%	<0.15%
Sr	NA	NA	99.9%	0.1%
		TALSPEAK		
Pu	99.8	0.2	<0.005	>99.995
Am	0.001	99.999	<0.03	>99.97
Ln	88	12	>99.97	<0.03

NA: CCD-PEG not run as part of 2005 demonstration

U/Tc Separation by Ion Exchange Chromatography

- **Determine breakthrough capacity of IX resin**
- **Experimental conditions**
  - Three column test
  - Room temperature



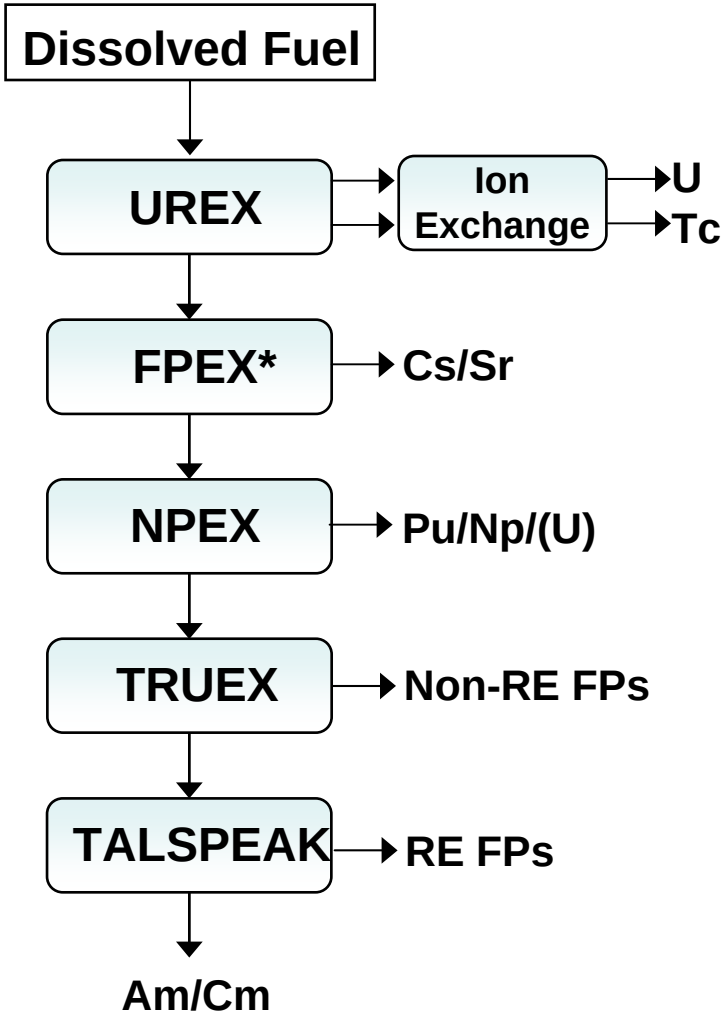


ANL UREX+ Spent Fuel Demonstrations

- **UREX achieved process targets**
- **Excellent TRU/RE recovery obtained with TRUEX**
- **Refined TALSPEAK process for 2006 test met targets**
  - Fuel requirements – DF > 2000
  - Repository requirement – TRU loss < 0.01%
- **Excellent hydraulic performance in all processes**

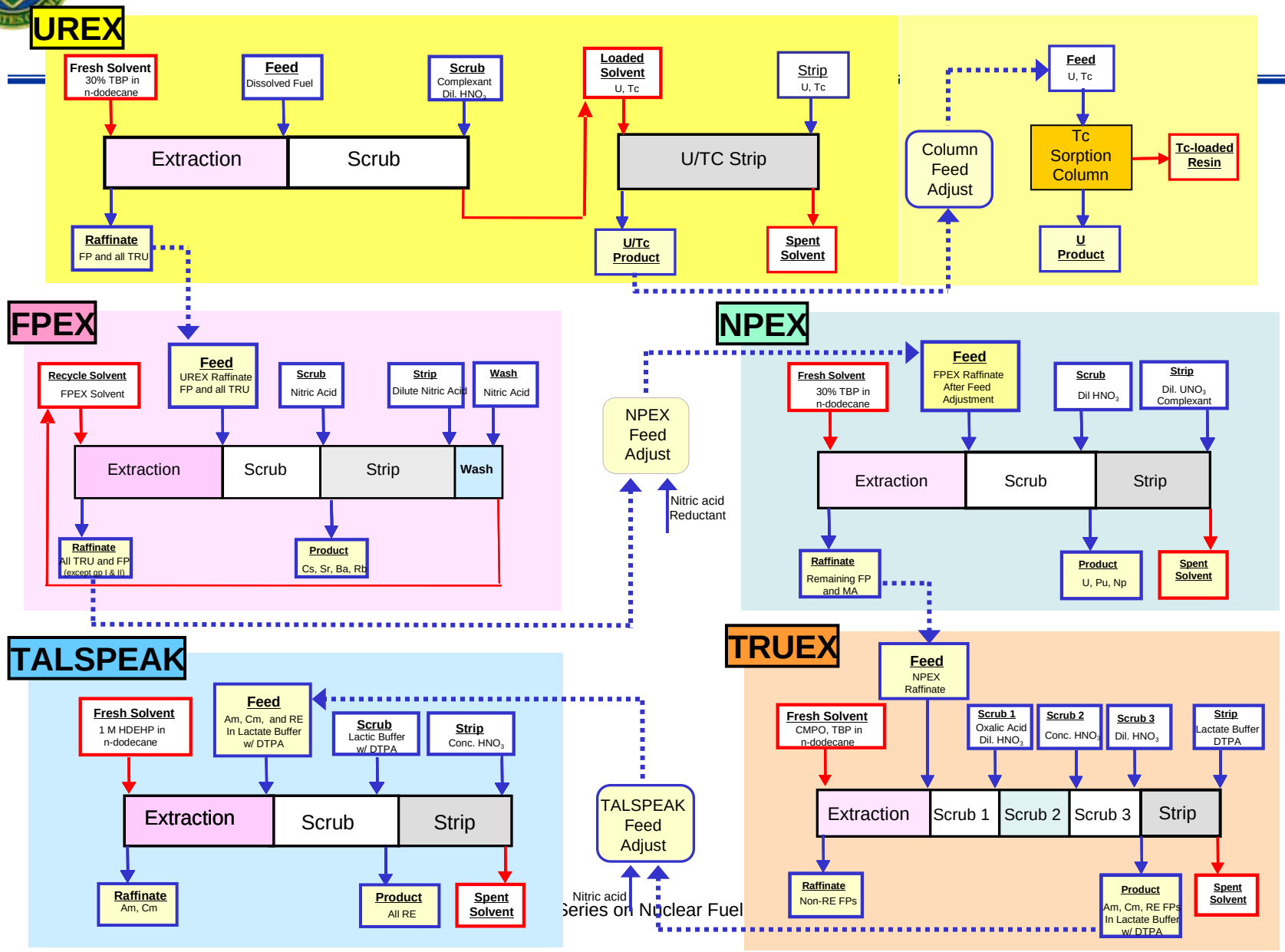
In FY-2007 UREX+3a Was Demonstrated

- **UREX+3a is being developed to produce a U/Pu/Np product**
  - Am/Cm product for targets
- **FPEX was run in place of CCD-PEG for Cs/Sr recovery**
- **In NPEX, U was added to yield a U/Np/Pu product**
- **Chemical analysis is to be completed in FY-2008**



*CCD-PEG may be run as an alternate for FPEX

FY07 UREX+3a Flowsheet



UREX+3a: Preliminary Results

- Elements report to desired product streams in all processes
- FPEX demonstrated high Cs and Sr recoveries
- Refined TRUEX process showed excellent recovery of An and Ln
- Analysis is incomplete, additional results are pending

Distribution in process effluent streams (%)

Element	Raffinate	Product
2007 UREX		
U	0.001%	99.999%
FPEX		
Cs	BD*	(100%)
Sr	<0.1%	>99.9%
2007 NPEX		
Pu	0.07%	99.93%
Np	Bkgd*	(100%)
2007 TRUEX		
Am	BD	(100%)

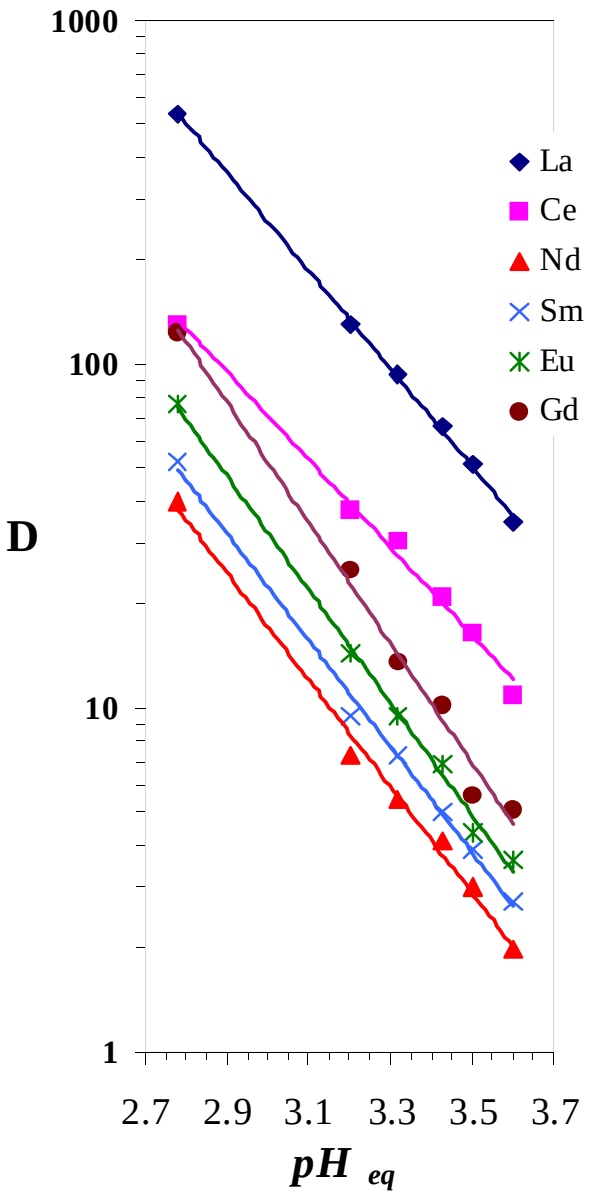
*BD = below detection limits; bkgd = at background levels

Effects of pH on Ln Distribution

- **D-value Dependence on pH**
  - Light lanthanide (La) has lowest power dependency
  - Heavier lanthanide (Gd) has higher dependency
- **D value dependency on pH for HDEHP-extraction alone is + 3 order**

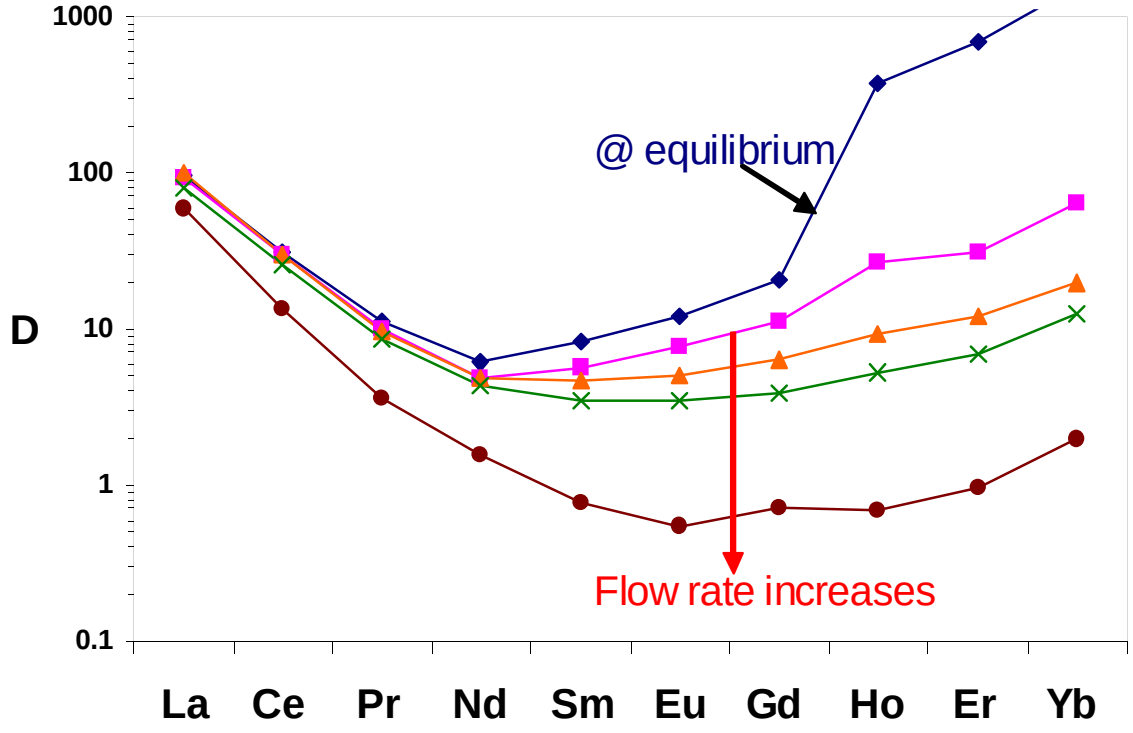
$$Me^{3+} + 3(HL)_2 \Leftrightarrow Me(L{\cdot}HL)_3 + 3H^+$$

- **D value dependency based on DTPA-complexation can be up to -5 order**
  - Depending on H_5DTPA acid equilibria at each pH



TALSPEAK-Process Development—Kinetics

- Performed a series of one-stage tests in a 2-cm centrifugal contactor
- As flow rate increases, the minimum is shifted from Nd to Sm-Eu
- Based on contactor tests, it appears that mixing is less intense in the contactor than in our batch vessel



2007 TALSPEAK Demonstrations--Effluents

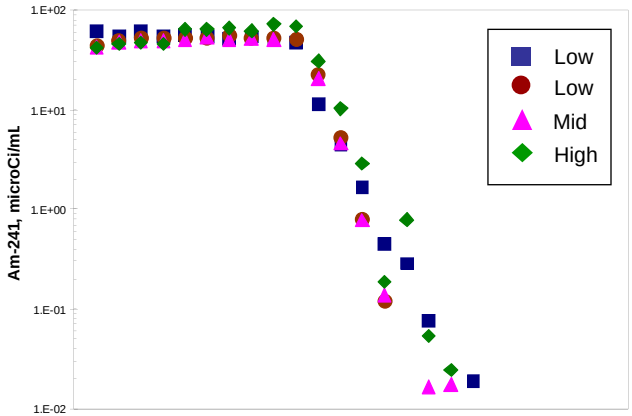
- **Distribution of lanthanides and TRU easily met process goals**
  - < 1% mass of actinide product was lanthanides
  - ≤ 0.01% of TRU in Ln product
- **Effects of higher throughputs (shorter contacting time) were seen**
  - Effect of flow rate not as strong as suspected
  - Actinide behavior was more consistent than that of lanthanides

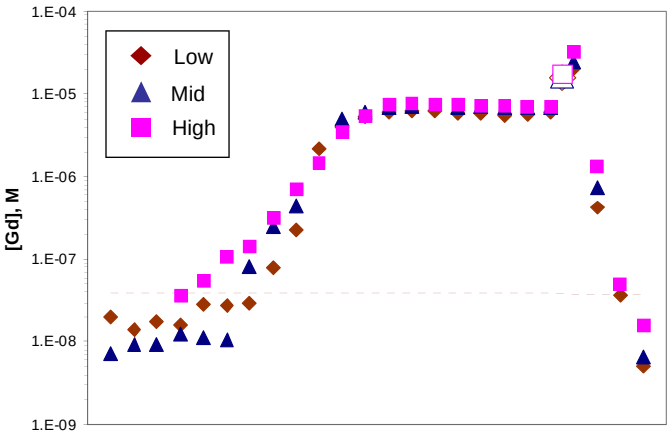
Distribution in process effluent streams (%)

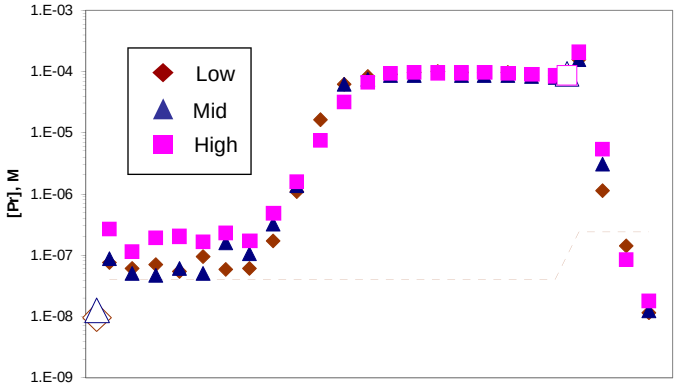
Feed Flow Rate	Rare Earth Product		TRU Product	
	RE, %	TRU, %	RE, %	TRU, %
Low	99.9998	BD	0.002	(100)
Mid	99.7	BD	0.03	(100)
High	99.997	0.002	0.003	99.998

BD = Below Detection Limits

Lanthanide Behavior—Aqueous-Phase Stage Profiles

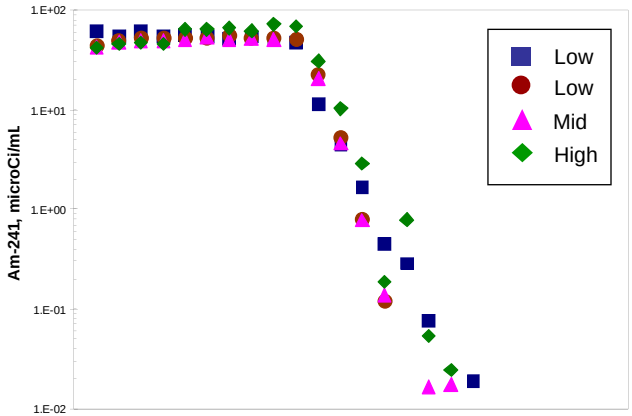


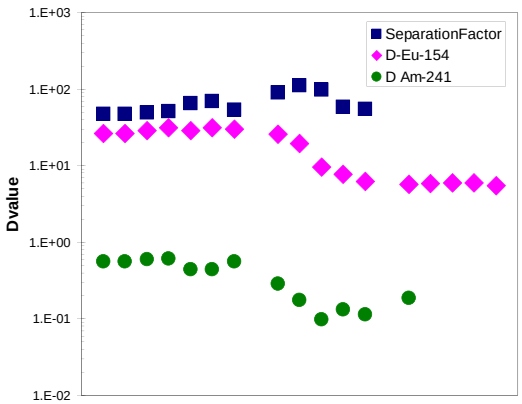


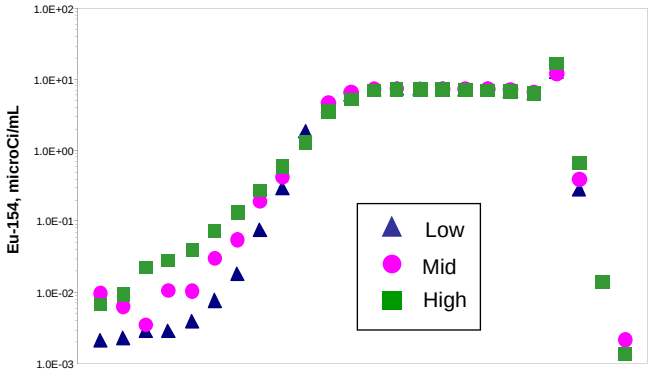


- **Light lanthanides (La and Pr) do not show a kinetic effect**
- **The heavier lanthanide (Gd) does**
  - As did Eu

Am vs. Eu Behavior--Stage Profile







- **Effects at higher flow rates (less contact time) are seen for Eu aqueous-phase stage profile**
  - Better extraction at lower flow rates
- **However, even at highest flow rate, separation factors for Eu over Am are ~50 in extraction section.**
  - ~100 in scrub section

Summary of UREX+ Process Demonstrations with Spent Nuclear Fuel

- **All demonstrations have proven the feasibility of the UREX+ processes to achieve program goals**
  - UREX has been repeatedly demonstrated to be viable for the selective extraction of U and Tc
  - Co-extraction of U, Pu, Np, and Tc with subsequent selective stripping of Pu/Np and U/Tc proved viable
  - Cs/Sr recovery was achieved using both CCD-PEG and FPEX
  - NPEX process recovers Pu and Np; produces U/Pu/Np product
  - TRUEX has been demonstrated in four tests for An/Ln recovery
  - TALSPEAK successfully separated actinides from lanthanides at high purities as required for fuel fabrication
    - *Tests at different flow rates proved the robustness of the process for scale-up*