Innovative Reprocessing Techniques

Global Climate & Energy Project

Stanford-MIT Fission Energy Workshop

Opportunities for Fundamental Research and Breakthrough in Fission

Cambridge, Massachusetts

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Outline

- **What spent fuel reprocessing is**
- **What is done today in commercial plants**
- **What modifications and additions are needed**

Physical Characteristics of LWR Fuel Assemblies (ORNL/TM-7431)

	BWR	PWR
Overall assembly length, m	4.470	4.059
Cross section, cm	13.9 x 13.9	21.4 x 21.4
Fuel element length, m	4.064	3.851
Active fuel height, m	3.759	3.658
Fuel element OD, cm	1.252	0.950
Fuel element array	8 x 8	17 x 17
Fuel elements/assembly	63	264
Assembly total weight, kg	275.7	657.9
Uranium/assembly, kg	183.3	461.4
UO_2/assembly, kg	208.0	523.4
Zircaloy/assembly, kg	99.5[a]	108.4[b]
Hardware/assembly, kg	12.4[c]	26.1[d]
Total metal/assembly, kg	111.9	134.5
Nominal volume/assembly, m[e]	0.0864[e]	0.186[e]

[a]Includes Zircaloy fuel-element spacers and fuel channel.

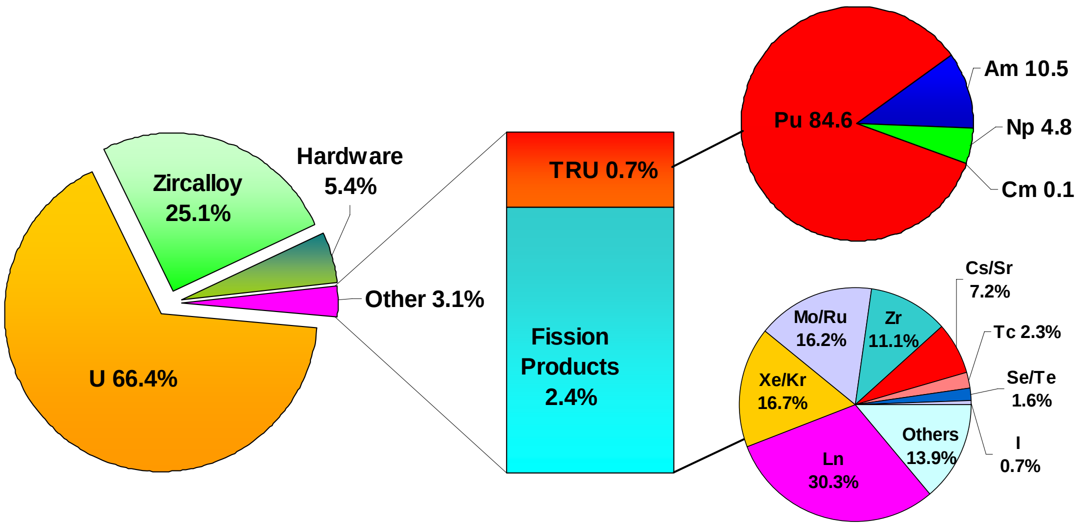
[b]Includes Zircaloy control-rod guide thimbles.

[c]Includes stainless steel tie-plates, Inconel springs, and plenum springs.

[d]Includes stainless steel nozzles and Inconel-718 grids.

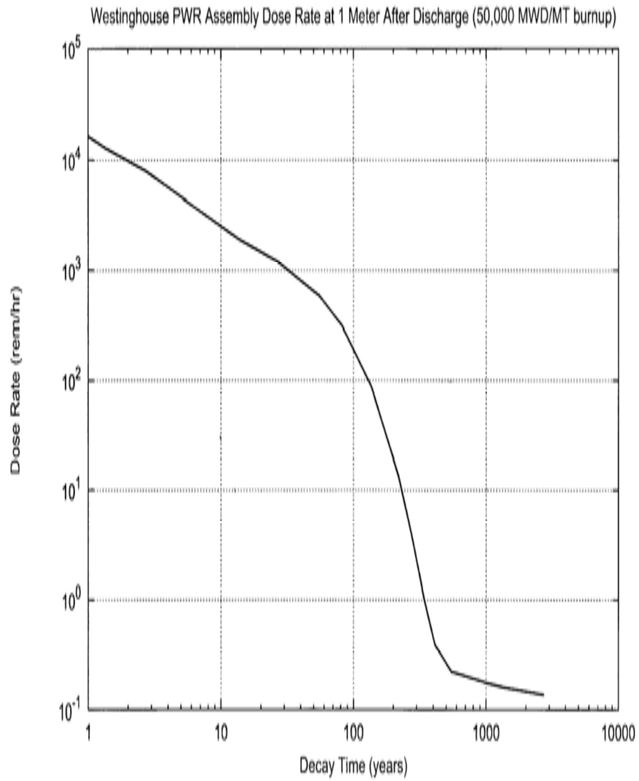
[e]Based on overall outside dimension.

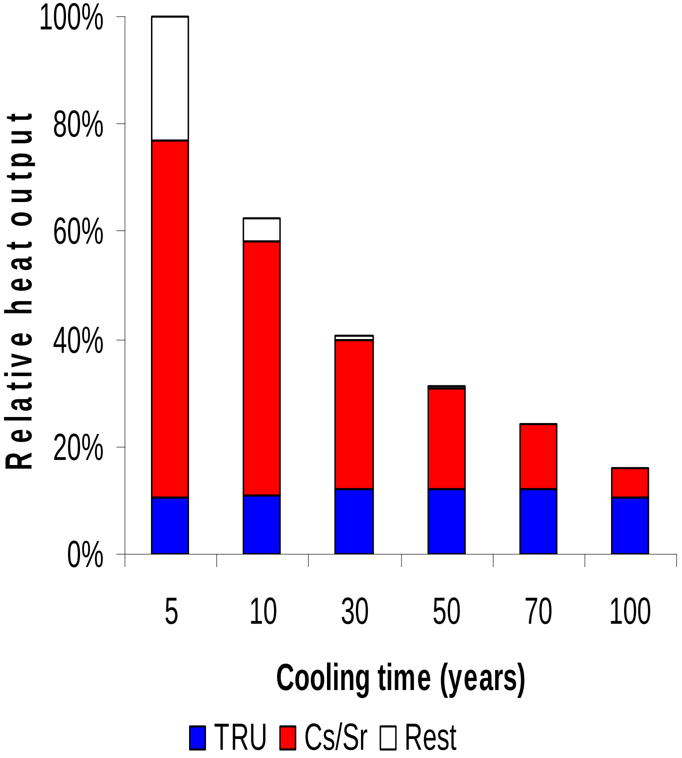
Mass Proportions of the Chemical Elements in Spent Fuel



- **Separation and recovery of the re-usable elements are the partitioning goals**
- **Each element can be chemically separated if desired**
- **Industrial deployment of separations processes depends on reliability, cost minimization, waste minimization, and provision of "sufficient" proliferation resistance features (engineered safeguards)**

The time factor is also extremely important – especially for repository benefits





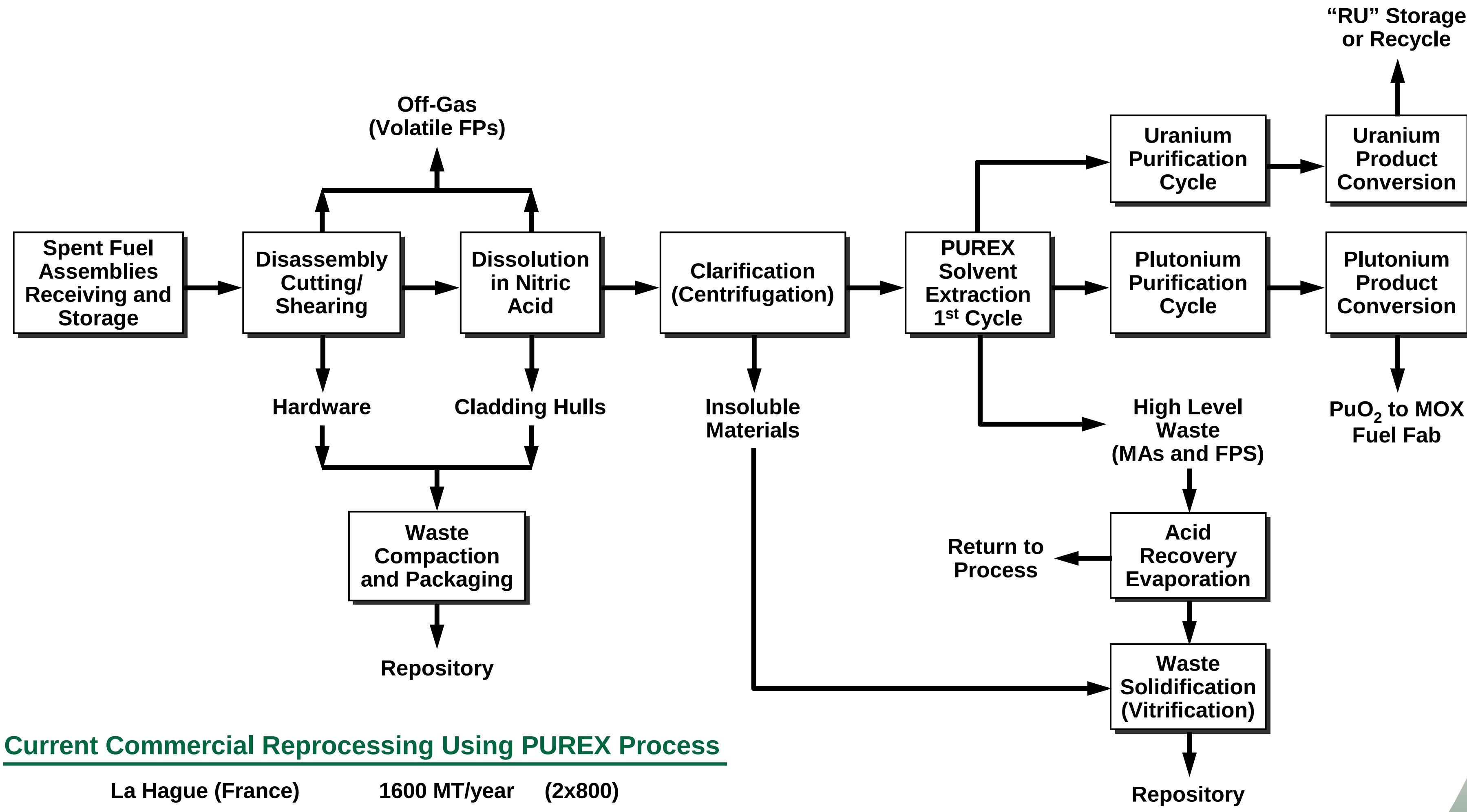
Significant Chemical Valences of the Spent Fuel Components

Iodine	$\mathbf{I^{-1}}$	
Technetium	$\mathbf{Tc^{+7}}$	
Uranium	U^{+4}, $\mathbf{U^{+6}}$	$UO_2(NO_3)_2 \cdot 6H_2O$ Uranyl nitrate hexahydrate (UNH)
Plutonium	Pu^{+3}, $\mathbf{Pu^{+4}}$, Pu^{+6}	
Neptunium	Np^{+4}, $\mathbf{Np^{+5}}$, Np^{+6}	
Americium	$\mathbf{Am^{+3}}$, Am^{+5}, Am^{+6}	
Curium	$\mathbf{Cm^{+3}}$, Cm^{+4}	
Lanthanide FP's	$\mathbf{Ln^{+3}}$	(Sm, Eu, Gd, Dy, etc.)
Zirconium	$\mathbf{Zr^{+4}}$, complexes	
Ruthenium	$\mathbf{Ru^{+3}}$, $\mathbf{Ru^{+4}}$, Ru^{+6}	
Molybdenum	$\mathbf{Mo^{+6}}$	
Strontium	$\mathbf{Sr^{+2}}$	
Cesium	$\mathbf{Cs^{+1}}$	

Separation Processes for Spent Fuel Components

- **Mechanical disassembly**
- **Dry pyrochemical treatment – removal of volatile components**
  - **Voloxidation**
  - **Fluoride volatility**
- **Aqueous-based processes**
  - **Dissolution in nitric acid**
  - **Clarification via centrifugation**
  - **Liquid-liquid solvent extraction**
  - **Liquid-solid ion exchange (including chromatographic ion exchange)**
  - **Liquid-solid extraction chromatography**
  - **Crystallization/filtration**
  - **Precipitation/filtration**
  - **Product conversion (denitration) calcination**
  - **Waste solidification – calcination – vitrification**
- **Pyro electrochemical processes**
  - **Dissolution in molten salt liquid**
  - **Electrolytic oxide reduction**
  - **Electro-refining (electroplating – metal/salt extraction)**
  - **Product recovery (mechanical removal from electrodes, metal casting, precipitation – centrifugation)**
  - **Waste solidification**

The Industrialized PUREX Process

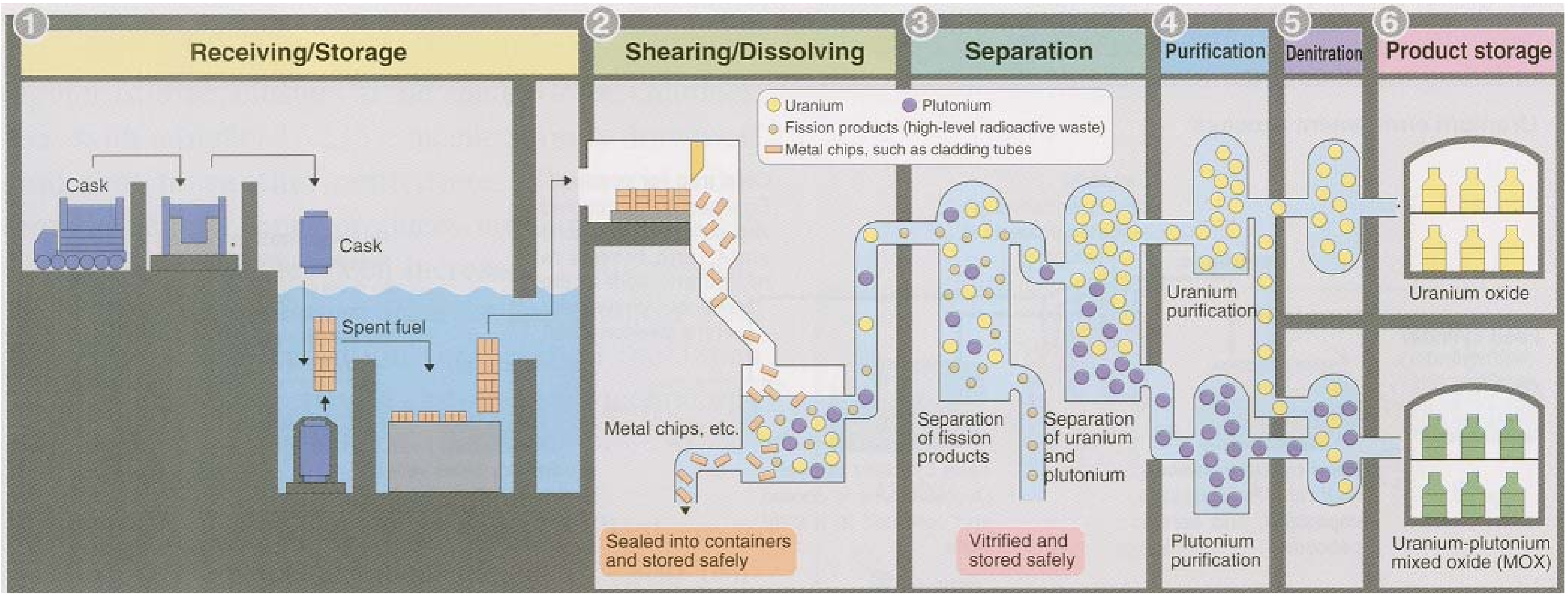


Current Commercial Reprocessing Using PUREX Process

La Hague (France)	1600 MT/year	(2x800)
THORP (U.K.)	1200 MT/year	
Rokkasho (Japan)	800 MT/year	
Mayak, Tomsk-7, K-26	500+ MT/year	

07-080

The Newest Plant – Rokkasho-mura Japan. Began hot operations in 2007.



Schematic separations plant operation.

Advanced Fuel Cycle Requirements

- **Development of process for Am-Cm separation from chemically similar lanthanide fission products**
- **Development/qualification/licensing of Am-Cm transmutation target form**
- **Development of process for recovery of plutonium in combination with other elements to meet safeguards policy criteria of "no separated plutonium." Combination with uranium and possibly neptunium appears to satisfy criteria**
- **Co-conversion of U-Pu or U-Pu-Np to mixed oxide**
- **Improved retention of volatile radionuclides – tritium, ^{14}C, ^{85}Kr, ^{129}I**
- **Development of recovery/recycle process for zirconium from cladding**
- **Implementation of recycle of uranium product**
- **Possible recovery-reuse of platinum group metals – Ru, Rh, Pd**
- **Improved waste forms**
- **Management of decay heat from ^{90}SrY and $^{137}CsBa$**

Am-Cm Recovery – UREX+3 Process

Feed = Raffinate Stream from TBP Extraction

Am-Cm-Ln Fission Products (FPs) – Other FPs

↓

TRUEX Solvent Extraction
Solvent: 1.4M TBP – 0.2M CMPO
In n-paraffin diluent

→ Other FPs

Am-Cm + Ln FPs

TALSPEAK Solvent Extraction
Solvent : 1 M HDEHP in n-paraffin diluent
Complexant: 0.05M DTPA in 1.5M Lactic Acid
pH~3

→ Ln FPs

↓

Am-Cm Product

New and Promising Extractants for An-Ln Separation

- **BTP synthesis not difficult – may be expensive**

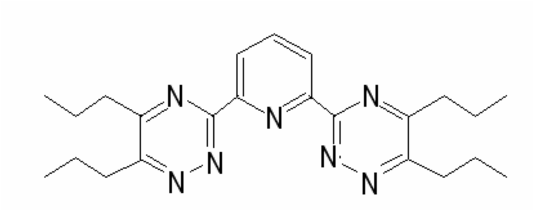
- **Good Am distribution to organic phase, limited Eu extraction, good separation factors for single stage contact at usefully high acidity**

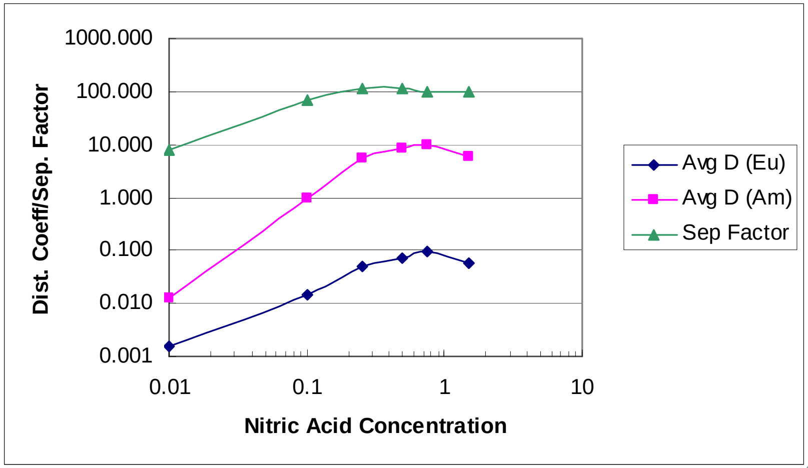
- **Good phase separation obtained and no precipitates**

- **Concerns about the stability of BTP (acidic hydrolysis and air oxidation)**

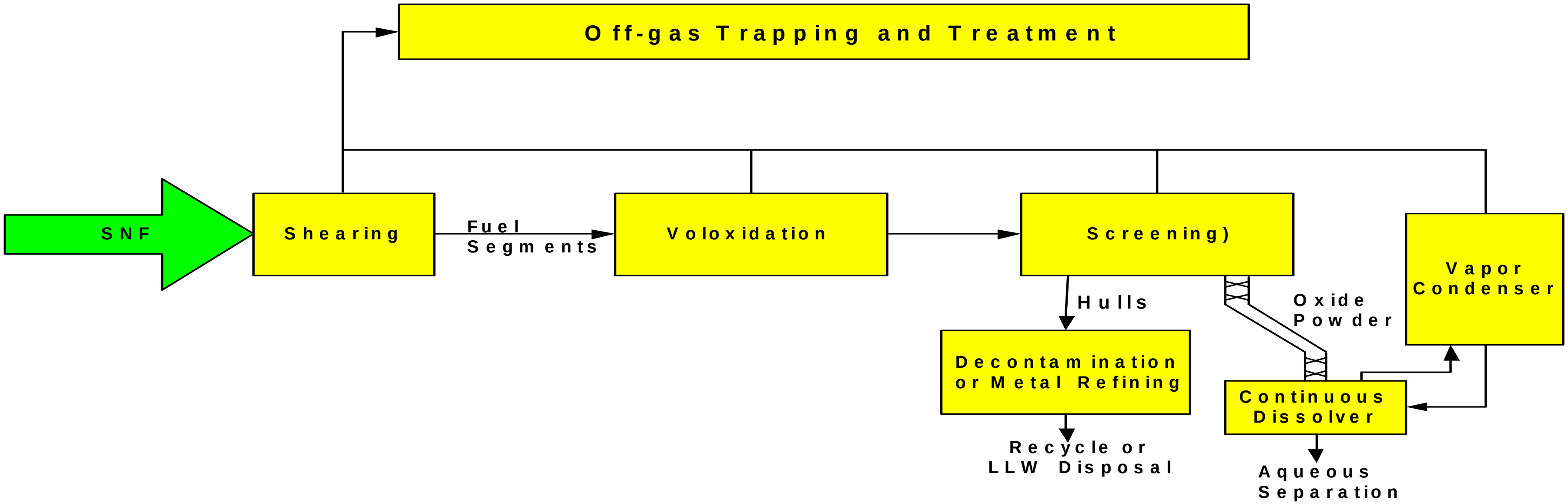
- **Impurities and other fission products may interfere with the actinide/lanthanide separations**

2,6-bis(5,6-*n*-propyl-1,2,4-triazin-3-yl)-pyridine (BTP)





Background -- Head End Schematic



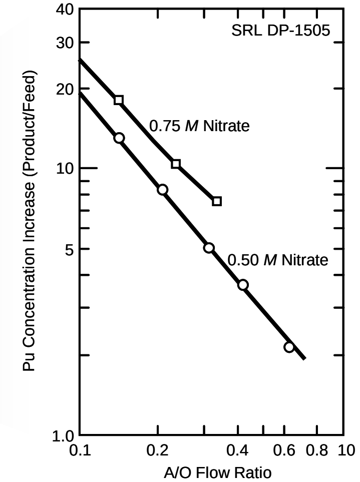
Removal efficiency of target fission products depends on the voloxidation temperature and atmosphere. Based on Korean process development data, at 1250°C in oxygen atmosphere, volatile and semi-volatile fission product removals are:

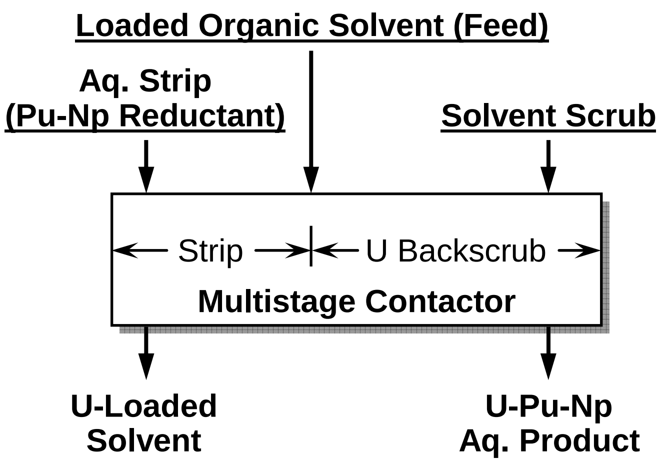
Percent Removal

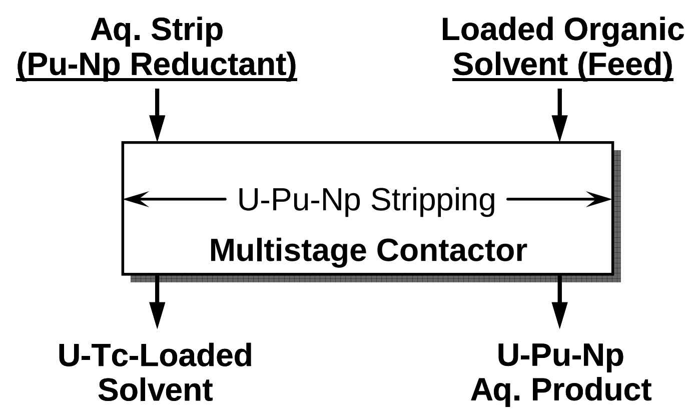
3H	14C	85Kr	129I	Cs	Tc	Ru	Rh	Te	Mo
100	100	100	100	98	100	100	80	90	80

E. H. Kim
KAERI Flowsheet Study
March 2007

Recovery of "Unseparated Plutonium"







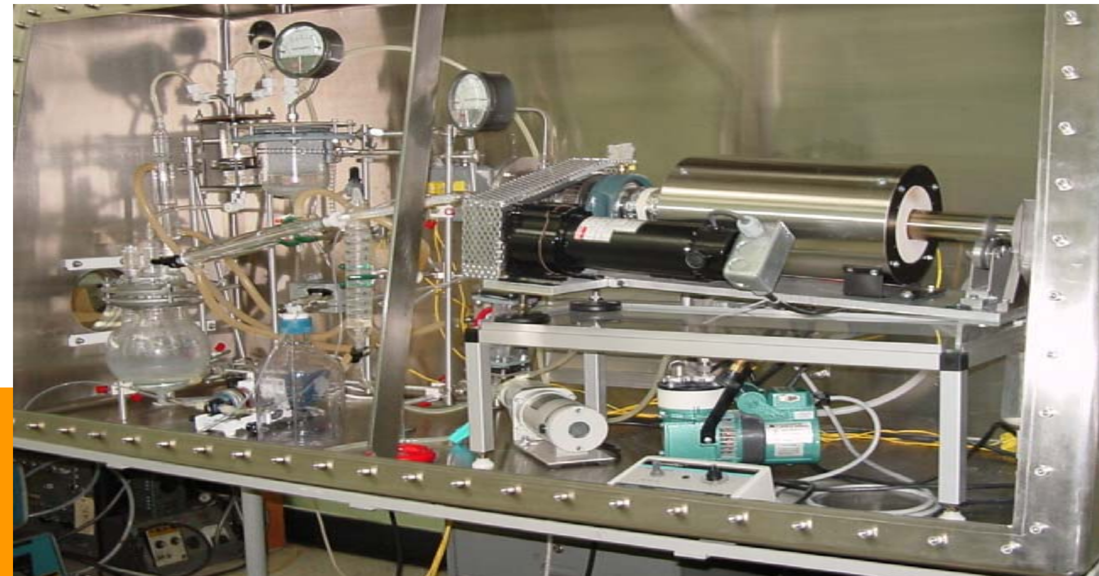
PUREX-Type
Partitioning Contactor Bank
(Complete or partial partitioning is possible)

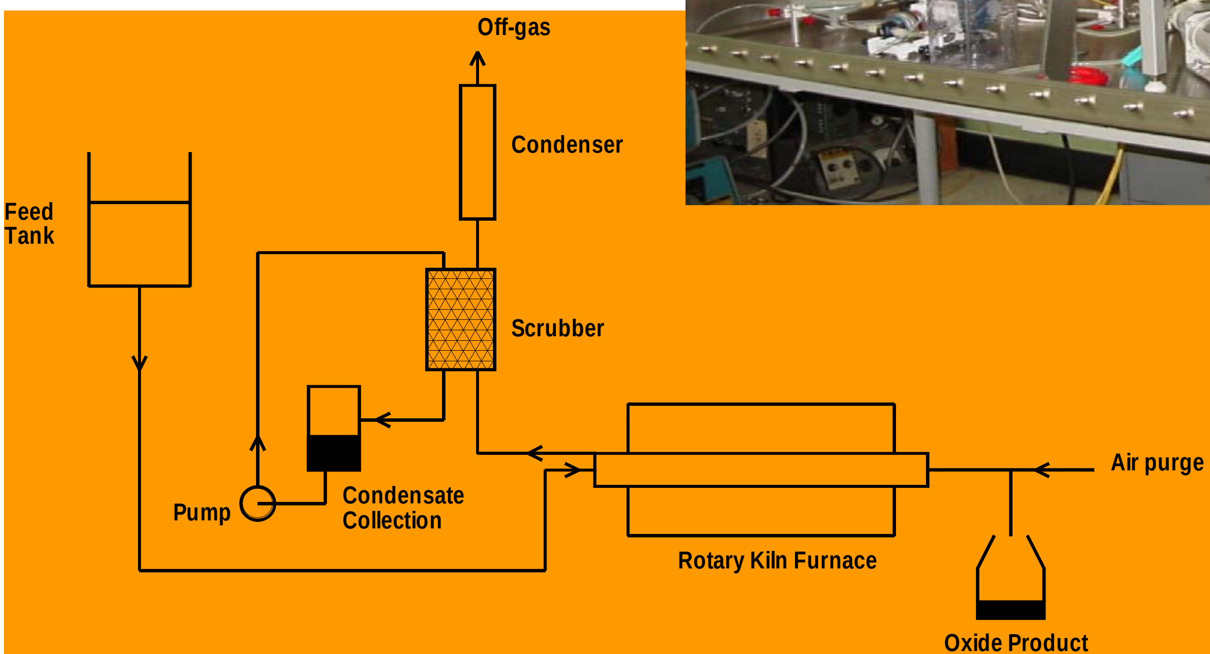
UREX+ Codecon Flowsheet
Partial Partitioning Contactor Bank

- **Hydroxylamine nitrate (HAN) is used as combination Pu-Np reductant – aqueous salting agent**
- **Excess HAN is U-Pu-Np product readily decomposed by NO_x to gases and water**
- **No holding reductant (hydrazine) is required**

Co-conversion of U-Pu-(Np)

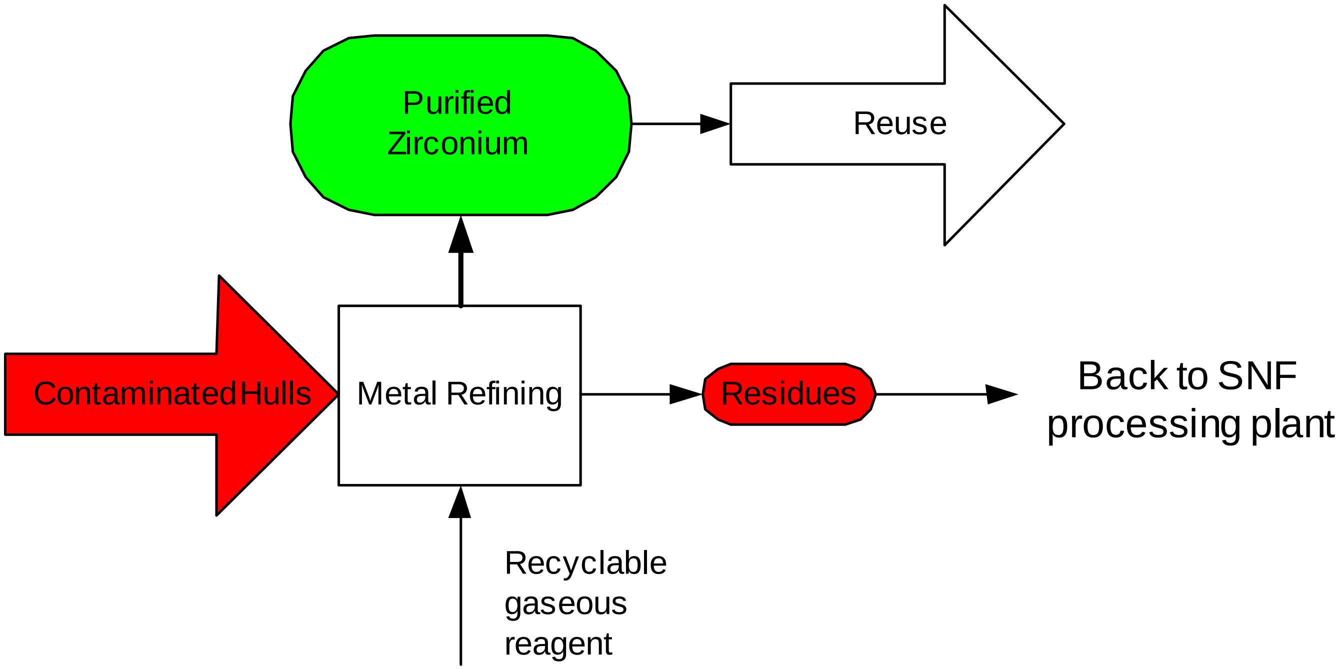
Uranium/TRU actinides in liquid nitrate solutions are co-converted to oxide powder for use in fuel fabrication. The Modified Direct Denitration (MDD) process is used.





- **Process developed at ORNL in 1980s**
- **Can be used for uranium product and mixed oxide products**
- **Produces powder that can be directly fabricated into fuel pellets**

Zirconium Recovery from Cladding



- **Purified zirconium will remain radioactive**
  - **^{93}Zr is not a significant radiological problem**
    - **Half-life is 1.53M years**
    - **Beta emission at only 90 keV (max.)**

Summary and Conclusions

- **Reprocessing is a crucial step in the recycle of spent fuel components**
- **All chemical element components of spent fuel, including plutonium, can be separated**
- **The time factor is extremely important because of the radioactive decay process**
- **All current industrial reprocessing plants use the PUREX process**
- **Additional component recovery, recycle, and re-use processes are necessary for future successful, industrial-scale closure of the nuclear fuel cycle**