

Used Fuel Reprocessing

Robert Jubin

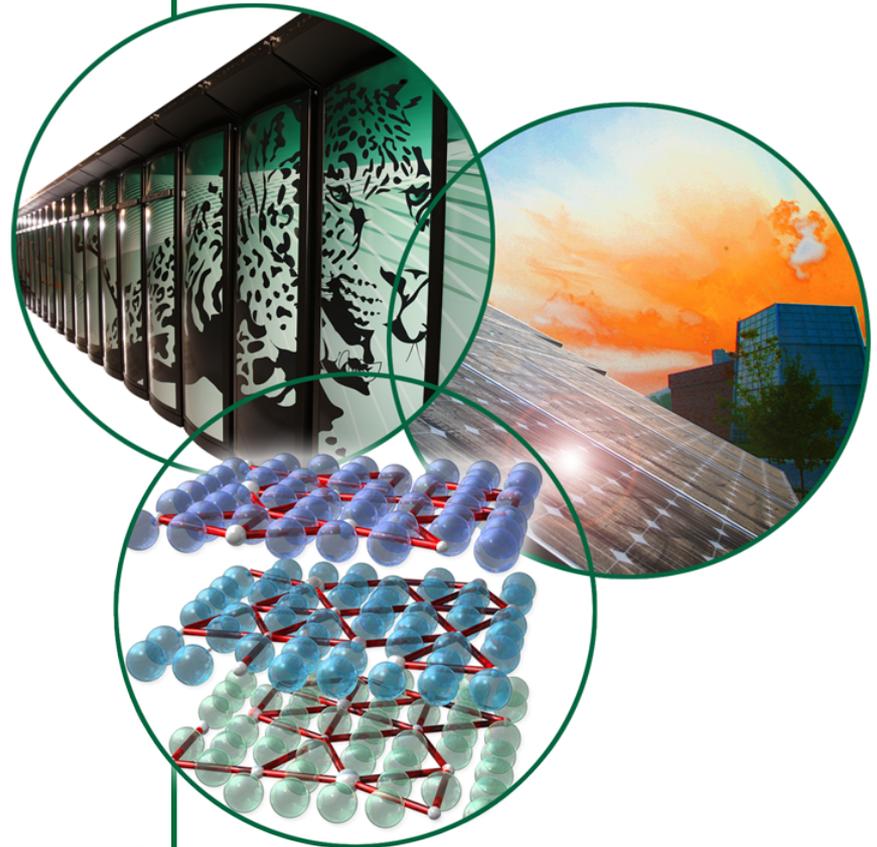
Fuel Cycle and Isotopes Division
Oak Ridge National Laboratory

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CRESP

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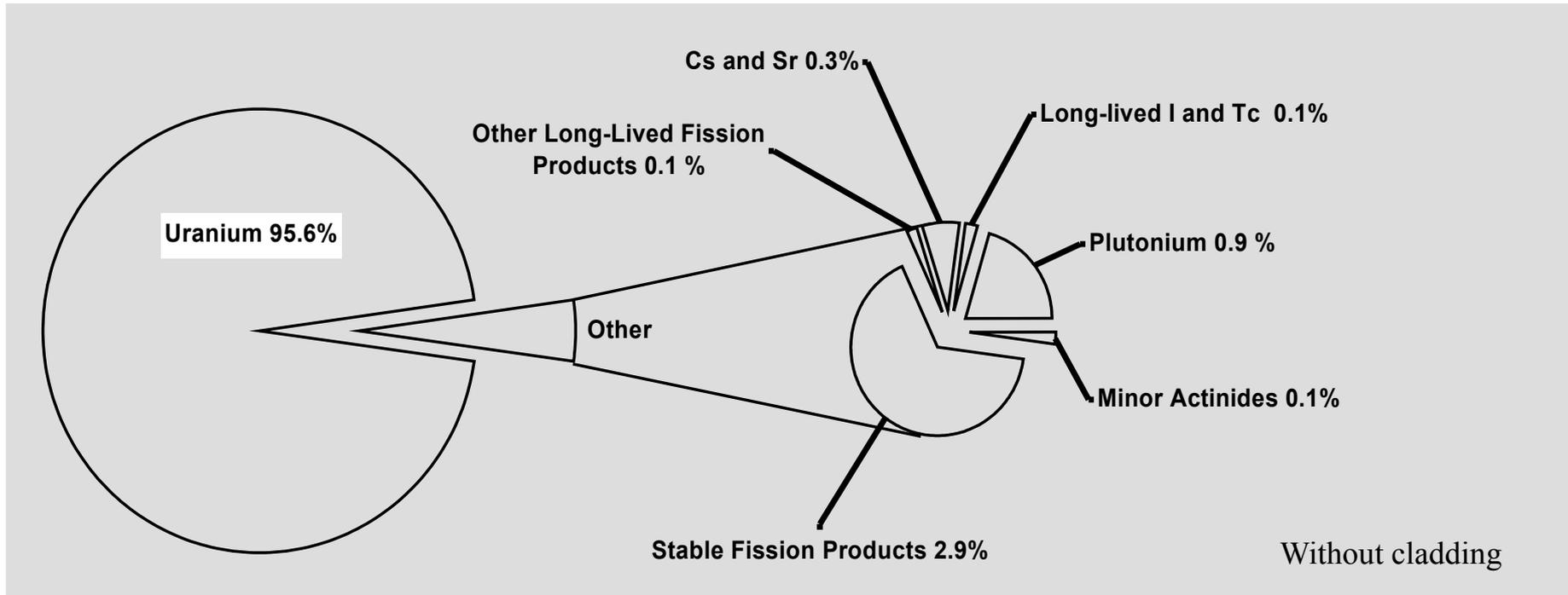
Overview

- **History of reprocessing**
- **Head-end**
- **Primary separations**
- **Product conversion**
- **Supporting separations**
- **Off-gas treatment**

Why Separate Components of Used Fuel?

- **Recover useful constituents of fuel for reuse**
 - Weapons (Pu)
 - Energy
 - Recycle
- **Waste management**
 - Condition fuel for optimized disposal
 - Recover long-lived radioactive elements for transmutation

Used (Spent) Nuclear Fuel – What Is It?



Most heat production is from Cs and Sr, which decay in ~300 yr

Most radiotoxicity is in long-lived fission products and the minor actinides, which can be transmuted and/or disposed in much smaller packages

Only about 5% of the energy value of the fuel is used in a once-through fuel cycle!

Aqueous Reprocessing - History

- **Began during Manhattan Project to recover Pu-239**
 - Seaborg first separated microgram quantities of Pu in 1942 using bismuth-phosphate precipitation process
 - Process scaled to kilogram quantity production at Hanford in 1944
 - **A scale-up factor of 10^9 !!!**
- **Solvent extraction processes followed to allow concurrent separation and recovery of both U and Pu and**
- **Reprocessing transitioned from defense to commercial use**
 - Focus on recycle of uranium and plutonium
 - Waste management

20 micrograms of plutonium hydroxide
1942



Hanford T-Plant 1944



Bismuth Phosphate Process

- **Advantages of Bismuth Phosphate Process**
 - Recovery of >95% of Pu
 - Decontamination factors from fission products of 10^7
- **Disadvantages of Bismuth Phosphate Process**
 - Batch operations
 - Inability to recovery uranium
 - Required numerous cycles and chemicals
 - Produced large volumes of high-level waste



Hanford T-Plant (1944)

Bismuth Phosphate Process

- Dissolution of irradiated fuel or targets in nitric acid
- Pu valence adjusted to Pu (IV) with sodium nitrite
- Add sodium phosphate and bismuth nitrate
 - Pu (IV) precipitates as $\text{Pu}_3(\text{PO}_4)_4$
- PPT re-dissolved in nitric acid, oxidized to Pu (VI), then re-ppt BiPO_4 to decontaminate Pu from fission products
- Recover Pu by reducing to Pu (IV) and re-ppt
- Repeat cycles w/ LaF to further decontaminate

REDOX Process

- **First solvent extraction process used in reprocessing**
 - Continuous process
 - Recovers both U and Pu with high yield and high decontamination factors from fission products
- **Developed at Argonne National Laboratory**
- **Tested in pilot plant at Oak Ridge National Lab 1948-49**
- **REDOX plant built in Hanford in 1951**
- **Used at Idaho for highly enriched uranium recovery**



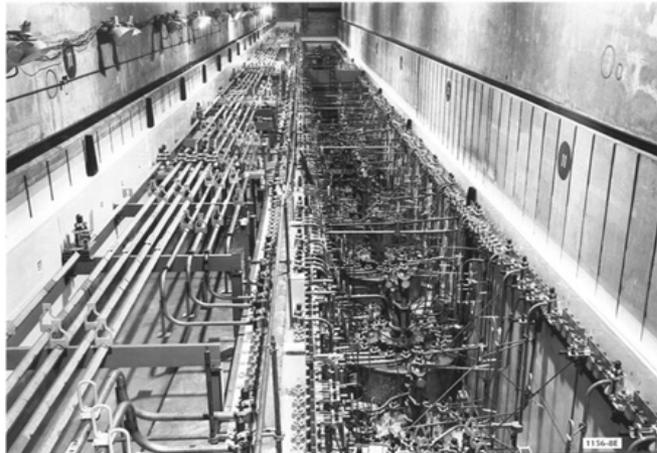
Hanford REDOX -Plant (1951)

BUTEX Process

- **Developed in late 1940's by British scientists at Chalk River Laboratory**
- **Utilized dibutyl carbitol as solvent**
 - Lower vapor pressure than hexone
 - Not stable when in extended contact with nitric acid
 - Possible pressurization as a result of degradation products
- **Nitric acid was used as salting agent**
 - Replaced need to use aluminum nitrate as in REDOX process
 - Lower waste volumes
- **Industrial operation at Windscale plant in UK until 1976**

PUREX Process

- **Tributyl phosphate used as the extractant in a hydrocarbon diluent (dodecane or kerosene)**
 - Suggested by Warf in 1949 for the recovery of Ce (IV) from rare earth nitrates
 - Developed by Knolls Atomic Power Lab. and tested at Oak Ridge in 1950-1952
 - Used for Pu production plant at Savannah River in 1954 (F-canyon) (H-canyon facility begin operation in 1955 and is still operational)
 - Replaced REDOX process at Hanford in 1956
 - Modified PUREX used in Idaho beginning in 1953 (first cycle)



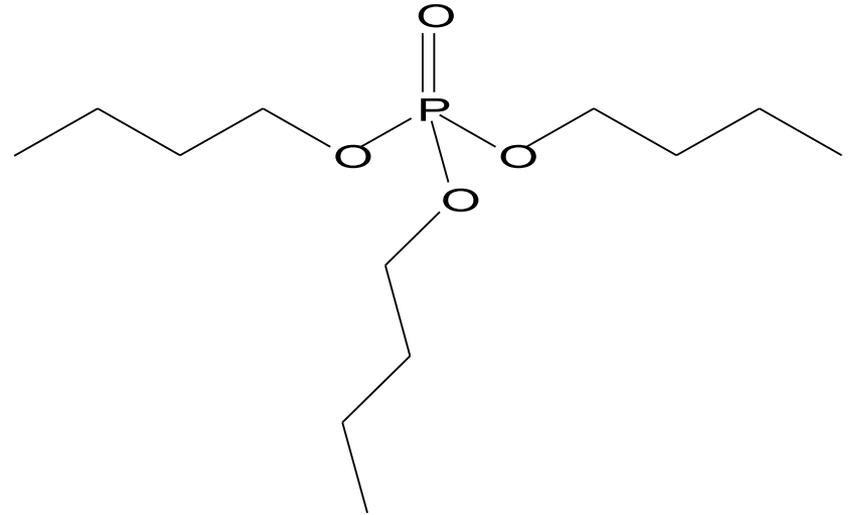
Savannah River Site -- interior of canyon



Courtesy Terry Todd
CRESP Seminar - August 9, 2009

PUREX Process

- Advantages of PUREX over REDOX process
 - Nitric acid is used as salting and scrubbing agent and can be evaporated – results in less HLW
 - TBP is less volatile and flammable than hexone
 - TBP is more chemically stable in a nitric acid environment
 - Operating costs are lower



PUREX Process – Commercial History in U.S.

- **West Valley, NY**
 - First plant in US to reprocess commercial SNF
 - Operated from 1966 until 1972
 - Capacity of 250-300 MTHM/yr
 - Shutdown due to high retrofit costs associated with changing safety and environmental regulations and construction of larger Barnwell facility
- **Morris, IL**
 - Construction halted in 1972, never operated
 - Close-coupled unit operations with fluoride volatility polishing step
- **Barnwell, SC**
 - 1500 MTHM capacity
 - Construction nearly completed- startup testing was in progress
 - 1977 change in US policy on reprocessing stopped construction
 - Plant never operated with spent nuclear fuel

Commercial-Scale Application of the PUREX Process Abroad

- **France**

- Magnox plant in Marcoule began operation in 1958 (~400 MT/yr)
- Magnox plant in La Hague began operation in 1967 (~400 MT/yr)
- LWR oxide plant (UP2) began in La Hague in 1976 (800 MT/yr)
- LWR oxide plant (UP3) began in La Hague in 1990 (800 MT/yr)

- **United Kingdom**

- Windscale plant for Magnox fuel began in 1964 (1200-1500 MT/yr)
- THORP LWR oxide plant began in 1994 (1000-1200 MT/yr)

- **Japan**

- Tokai-Mura plant began in 1975 (~200 MT/yr)
- Rokkasho plant currently undergoing hot commissioning (800 MT/yr)

- **Russia**

- Plant RT-1
- Began operation in 1976, 400 MT capacity
- Variety of headend processes for LWR, naval fuel, fast reactor fuel

PUREX Process – Current Commercial Operating Facilities

THORP, UK



La Hague, France



Rokkasho, Japan



Courtesy Terry Todd
CRESP Seminar - August 9, 2009

PUREX Process – Advantages and Disadvantages

- **Advantages**
 - Continuous operation/ High throughput
 - High purity and selectivity possible – can be tuned by flowsheet
 - Recycle solvent, minimizing waste
- **Disadvantages (not unique to PUREX SX process)**
 - Solvent degradation due to hydrolysis and radiolysis
 - Dilute process, requires substantial tankage and reagents
 - Historical handling of high-level waste
 - Stockpiles of plutonium oxide

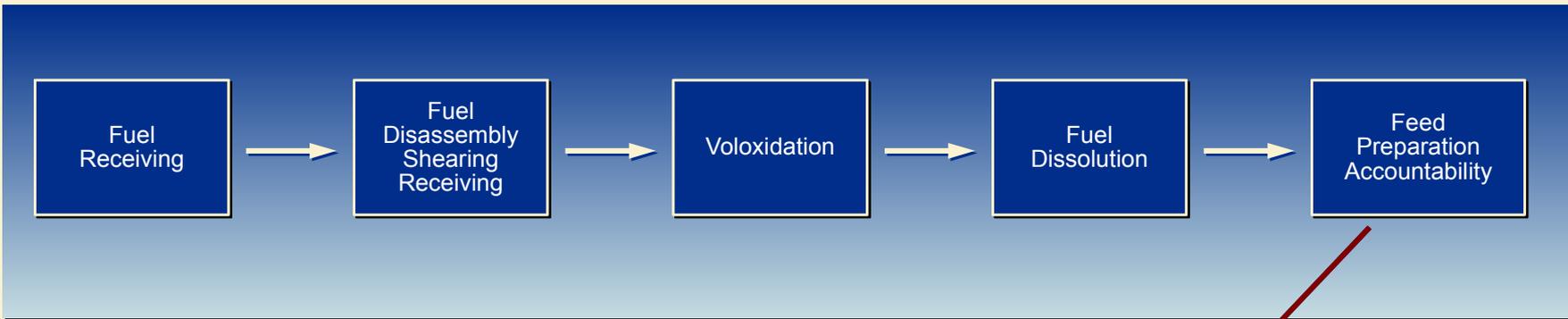


Electrochemical Processing Background

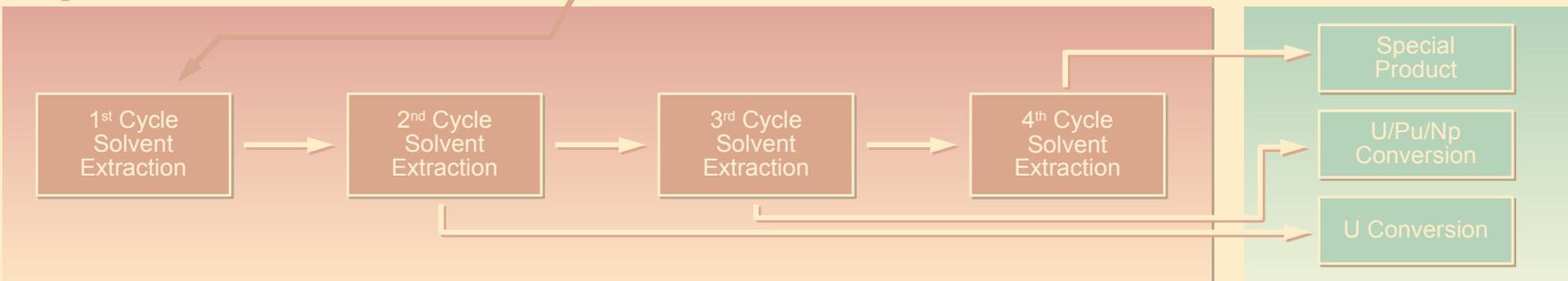


- Present generation of technology for recycling or treating spent fuel started in the 1980s
- Electrochemical processes were developed for the fast reactor fuel cycle
 - The fast reactor fuel does not require a high degree of decontamination
 - Potential compactness (co-location with reactor)
 - Resistance to radiation effects (short-cooled fuel can be processed)
 - Criticality control benefits
 - Compatibility with advanced (metal) fuel type

Head End

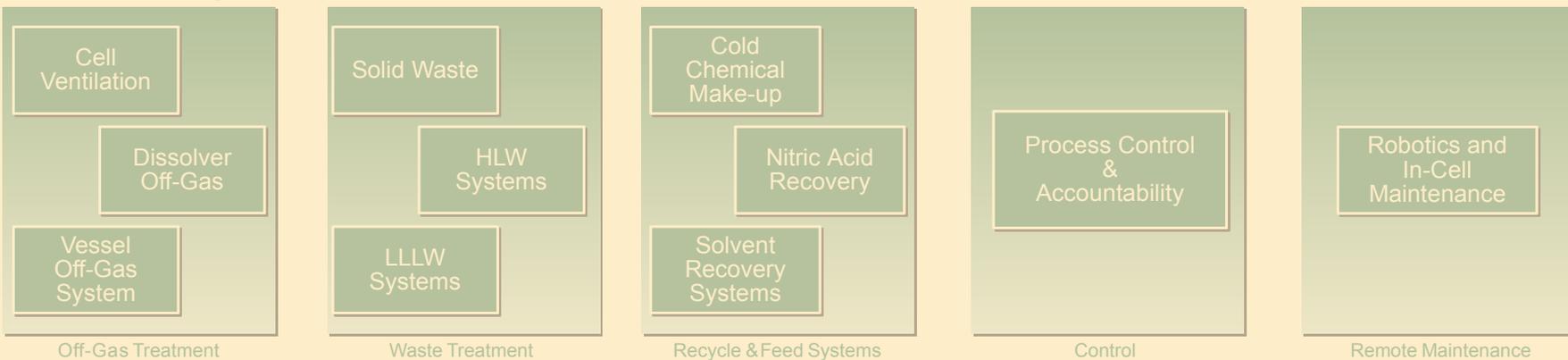


Separation Processes



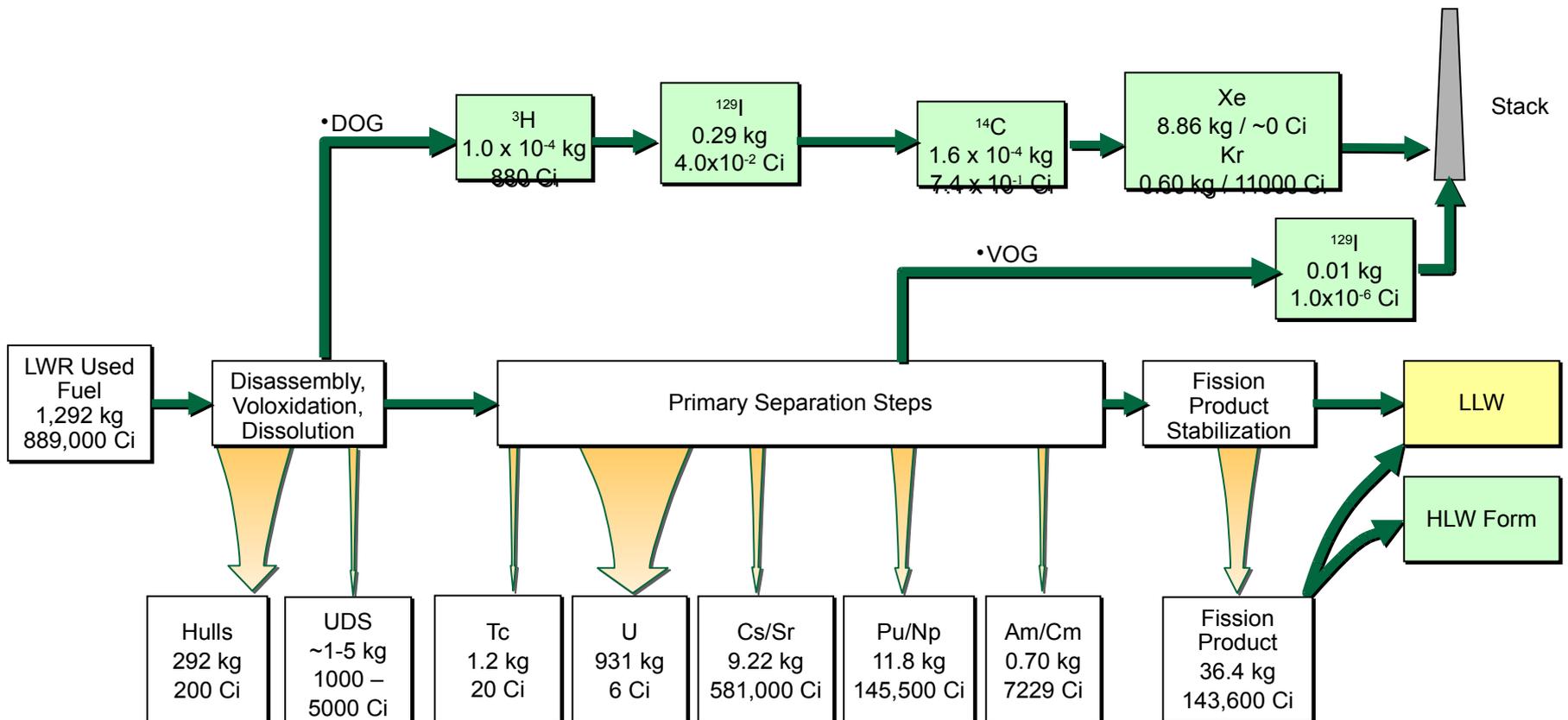
Conversion

Support Systems

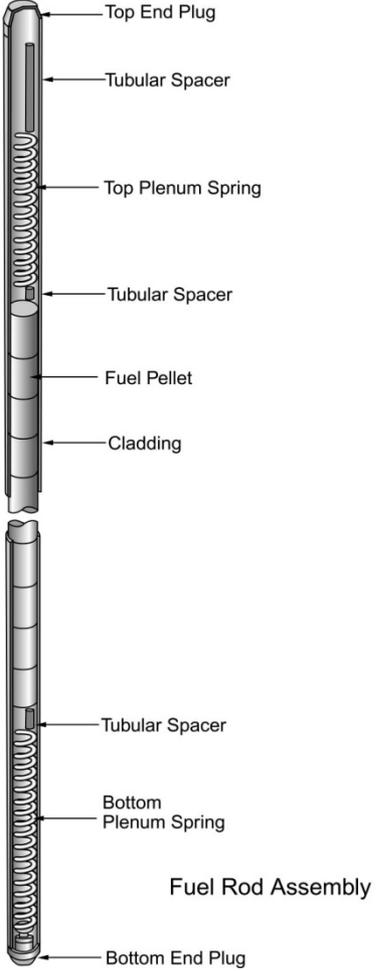
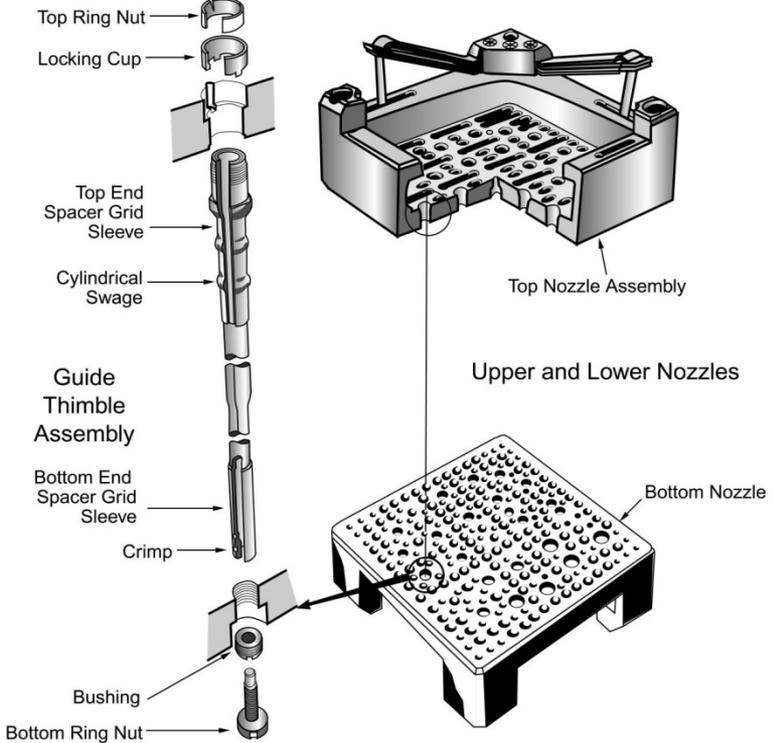
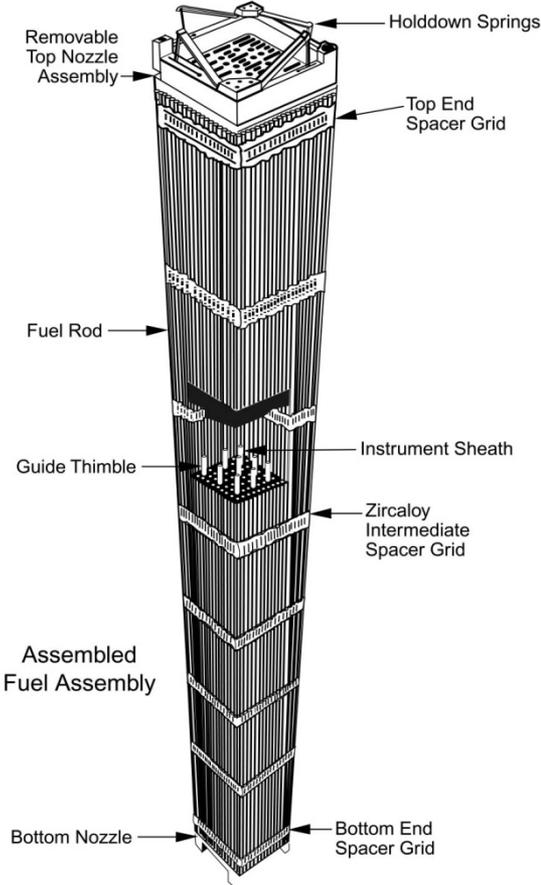


Simple Reprocessing Demonstration

(Mass Basis: 1 MT UNF; 55 GWd/MTIHM; 5 year Cooling)



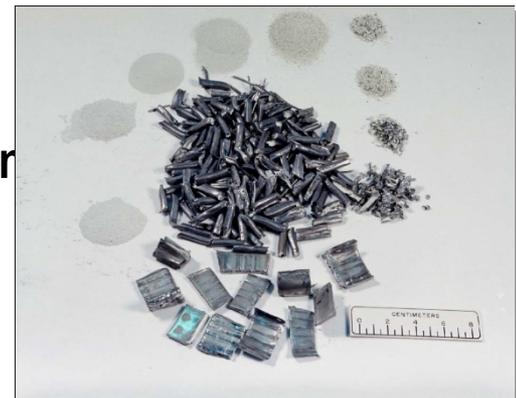
Major Components of PWR Fuel Assembly



(Croff, K/NSP-121/Part 23/R2)

Exposing Fuel/Target Material

- Preliminary step is to remove nonfuel-bearing hardware
- Process: State-of-the-art for most fuels (oxides) is to create short segments, exposing fuel/target material at the ends of the segments
 - Chemical decladding is uneconomical in most cases because of excessive waste production
 - Mechanical decladding is difficult and product losses can be high
 - Perforating the cladding does not sufficiently expose the contents
 - Metal fuels may be entirely dissolved
- Equipment: State-of-the-art is a mechanical shear
 - Saws were used in the past but were less reliable and generated excessive fines



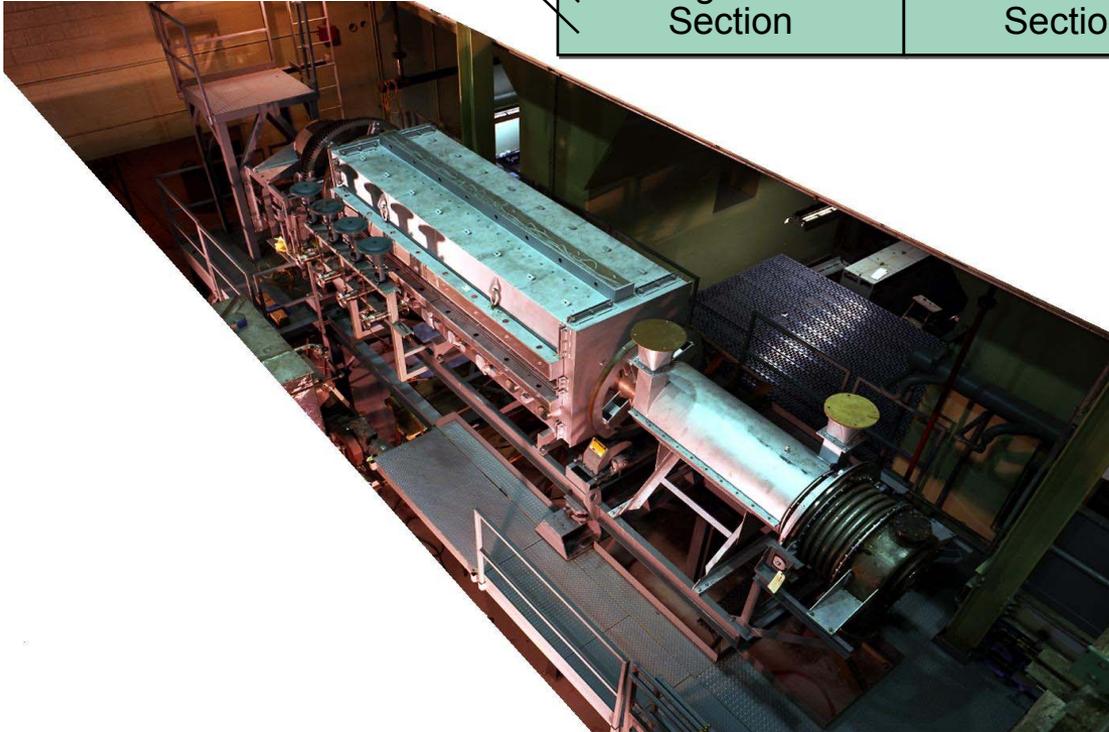
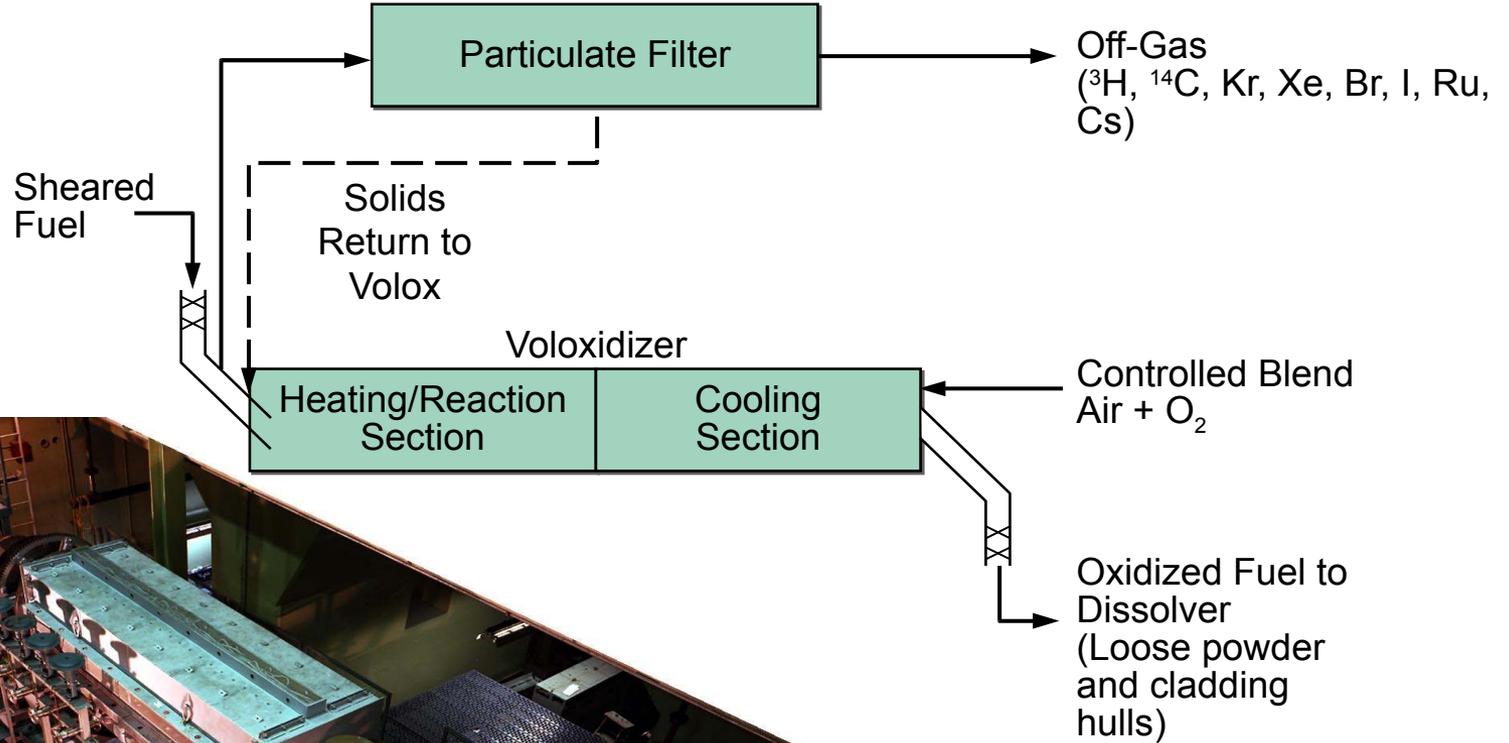
Sheared simulated fuel

(Croff, K/NSP-121/Part 23/R2)

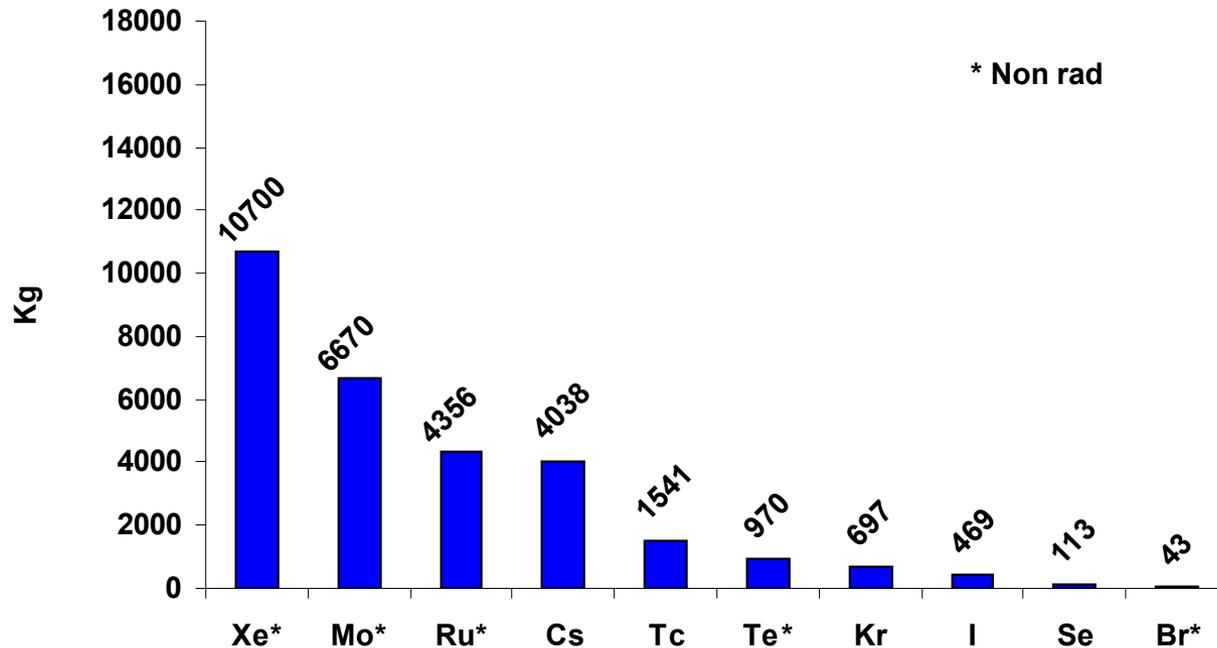
Voloxidation Basics

- **Dry head-end process to oxidize spent fuel oxide**
 - Release fuel from cladding
 - Release tritium from fuel prior to aqueous portion of processing plant
- **Process condition:**
 - Normal (Standard) is air at 450°C to 650°C
 - Resulting reaction: $3\text{UO}_2 + \text{O}_2 \rightarrow \text{U}_3\text{O}_8$
 - 99.9% of tritium released
 - 99% of fuel reduced to <44 μm particles
 - ~ 50% of C, 1% of I, and 5% Kr also released
- **Controls**
 - Temperature
 - Oxidizing environment, e.g., air, oxygen, ozone, etc.
 - Time

Voloxidizer: Standard Operation



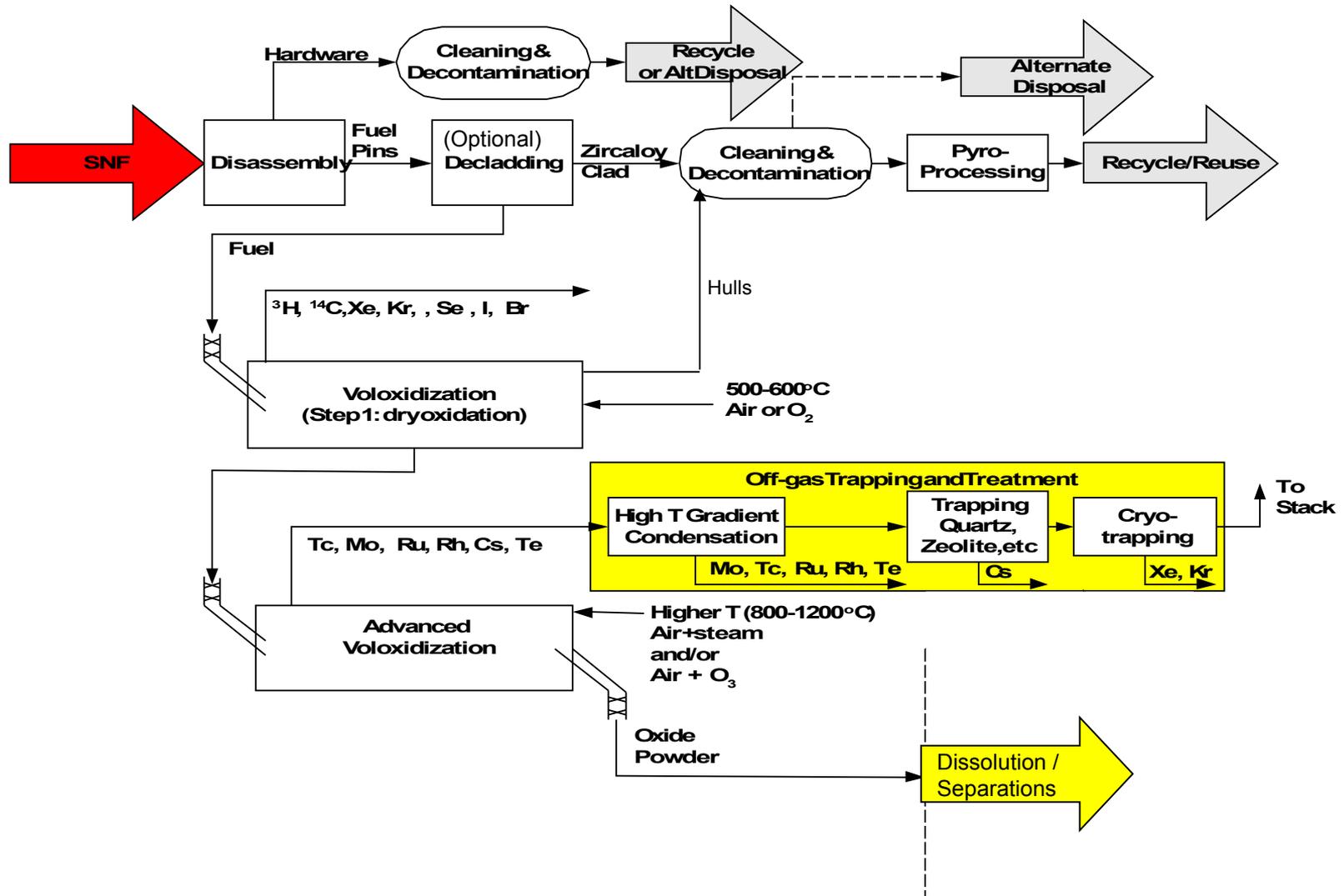
Species That Can Be Partially or Totally Removed During Head-end Treatment (Kg per 2000 MT of PWR-SF at 33GWd/MT)



Percent Removal

<u>^3H</u>	<u>^{14}C</u>	<u>^{85}Kr</u>	<u>^{129}I</u>	<u>Cs</u>	<u>Tc</u>	<u>Ru</u>	<u>Rh</u>	<u>Te</u>	<u>Mo</u>	
100	100	100	100	98	100	100	80	90	80	KAERI 1250°C in O ₂
				99	99	99	94	41	21	INL 1200°C #11 O ₂ /vacuum
				98	83	98	79	60	67	INL 1200°C #12 O ₂ /vacuum
					95	96			97	INL 1200°C #13 O ₂ /vacuum

Schematic of the Enhanced Voloxidation



Fuel Dissolution

- **Operations**
 - Exposed fuel or target material is placed in a perforated metal basket
 - Basket is immersed into hot nitric acid where essentially all of the fuel or target dissolves
 - Basket containing undissolved cladding is removed and cladding treated as waste
- **Equipment has proven to be challenging to design and operate**
 - Hot acid is corrosive
 - Significant toxic off-gas is evolved (radioactive and chemical)
 - Criticality must be avoided
- **State-of-the-art is now uses continuous dissolvers where the acid and fuel/target are fed in opposite ends of a nearly horizontal rotating cylinder (continuous rotary dissolver) or into the baskets on a "Ferris wheel" dissolver. Both designs immerses fuel segments in the acid for the required time.**

(Croff, K/NSP-121/Part 23/R2)

Dissolution Reactions

- For UO_2

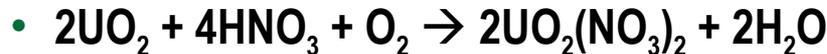
- At low acid:



- At high acid:



- “Fumeless”:

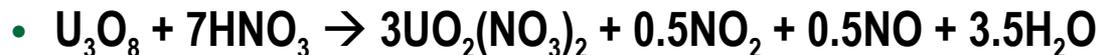


- For UO_3



- For U_3O_8

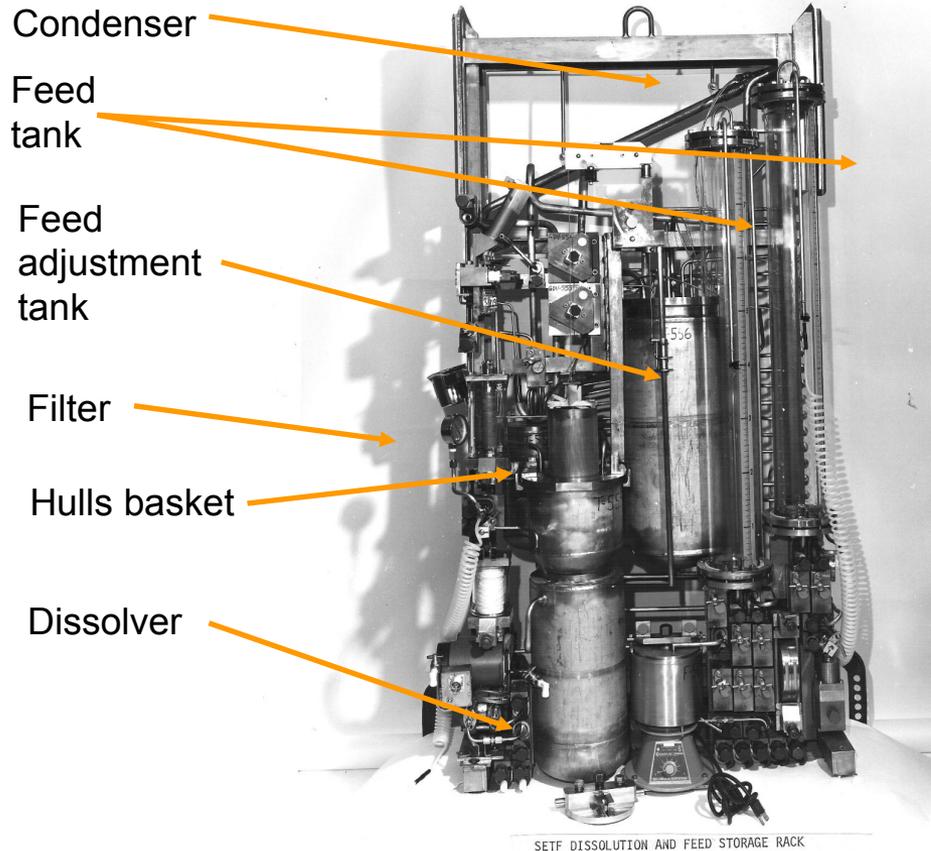
- Combining UO_2 and UO_3 reactions yields:



- By the approximate equation:



Development / Pilot Scale Dissolution Equipment



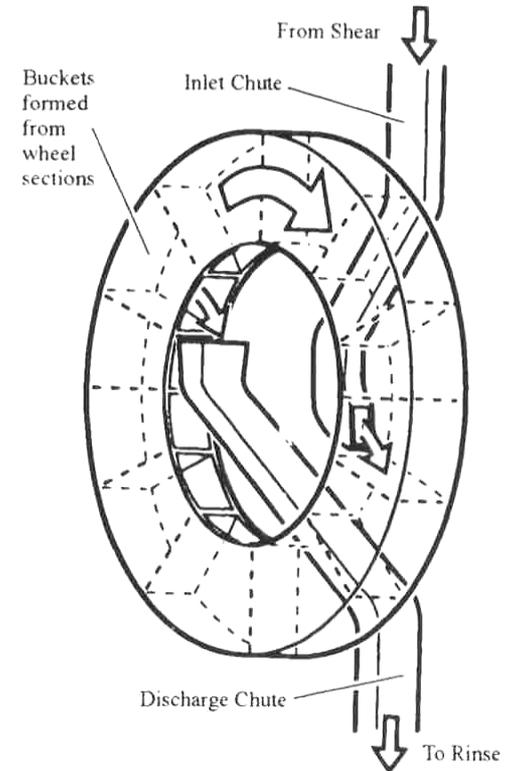
Radiochemical Engineering Development
Center Batch Dissolver Rack

- Utilize existing equipment from previous research with LWR fuel
 - ~14L stainless steel jacketed dissolution tank
 - Metal screen basket insert for sheared fuel pieces
 - ~25L stainless steel SX feed adjustment tank
 - Two 8L feed metering tanks
- Special powder feeder designed to handle voloxidized fuel will be installed on the dissolver tank

Dissolution Equipment

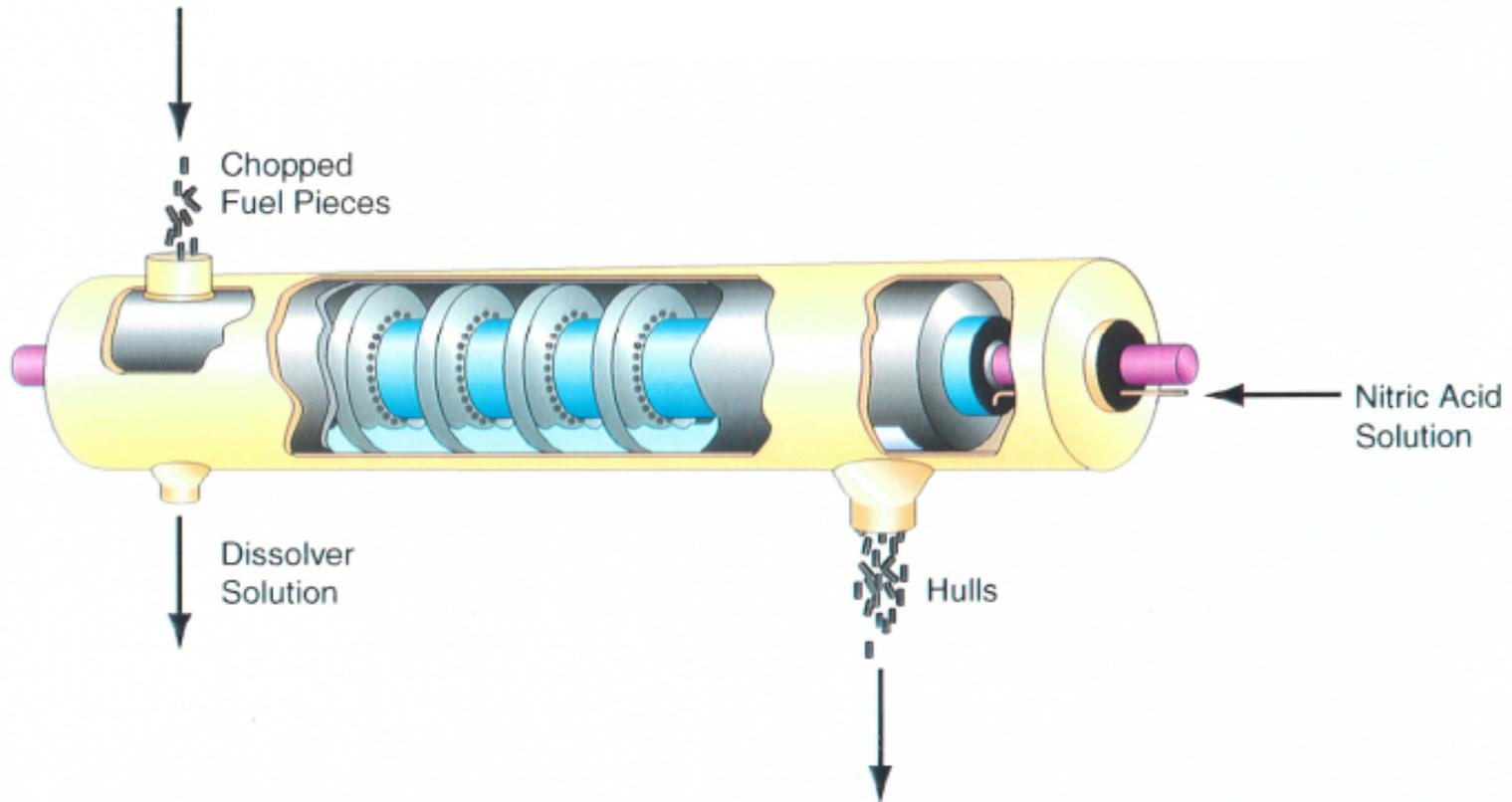
- **Ferris Wheel Dissolver**

- Nitric acid dissolves UO_2 pellet from cladding hull, forming $\text{UO}_2(\text{NO}_3)_2$ in solution
- Dissolver product contains approx. 300 g/l uranium
- Releases radioactive off-gas (iodine, krypton, xenon, carbon-14 small amounts of tritium)
- Undissolved solids are removed by centrifugation before transfer to extraction process
- Dissolution time controlled by rotation speed



Courtesy Terry Todd
Seminar to NRC - March 25, 2008

Continuous Rotary Dissolver



(Croff, K/NSP-121/Part 23/R2)

Feed Preparation

- Solution from the dissolver is
 - Clarified
 - Centrifugation
 - Filtration
 - Settling
 - Batched for accountability
 - Adjusted for concentration/composition
- Feed to Solvent Extraction System is an aqueous nitrate solution which can contain (depending on the fuel):

“Normal” State	“Special” State
$\text{UO}_2(\text{NO}_3)_2$	$\text{U}(\text{NO}_3)_4$
$\text{Pu}(\text{NO}_3)_4$	$\text{Pu}(\text{NO}_3)_3$
HNO_3	Reductants / Oxidants
Fission product nitrates	

- Important fission products:
 - Ruthenium
 - Zirconium
 - Rare earth lanthanides (La, Ce, Pr, Nd)
 - Iodine

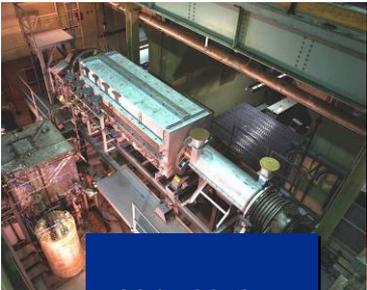
Fuel Reprocessing – Head End



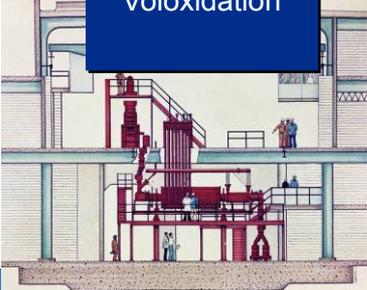
Fuel Receiving



Fuel Disassembly Shearing Receiving



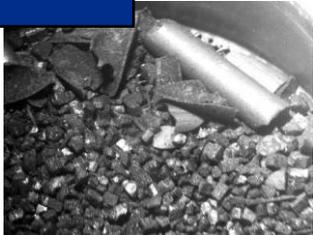
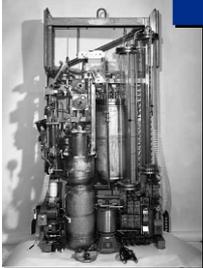
Voloxidation



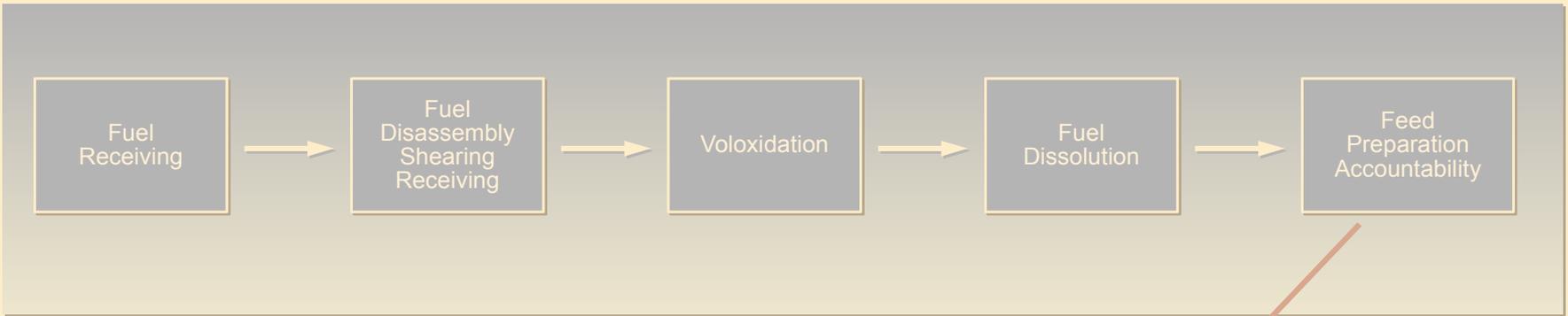
Feed Preparation Accountability



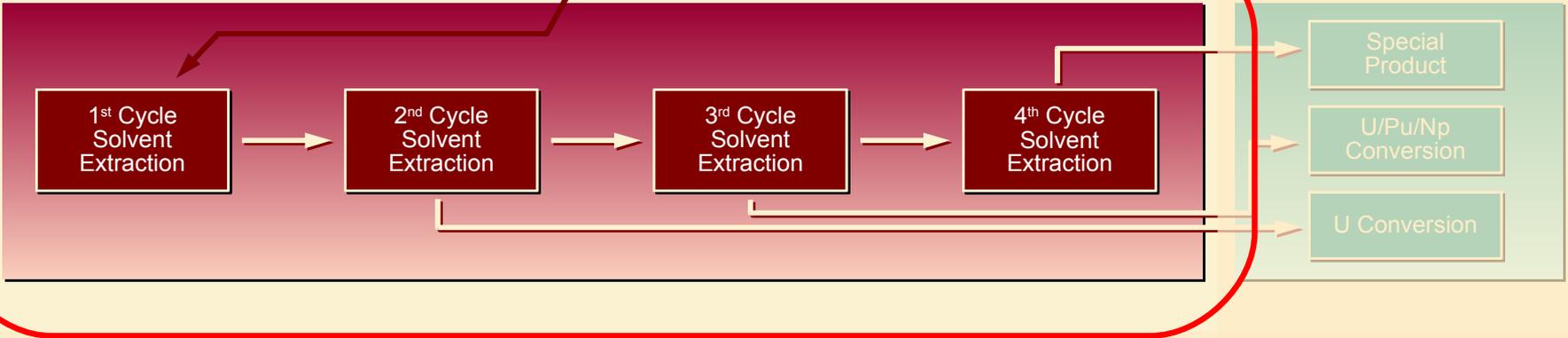
Fuel Dissolution



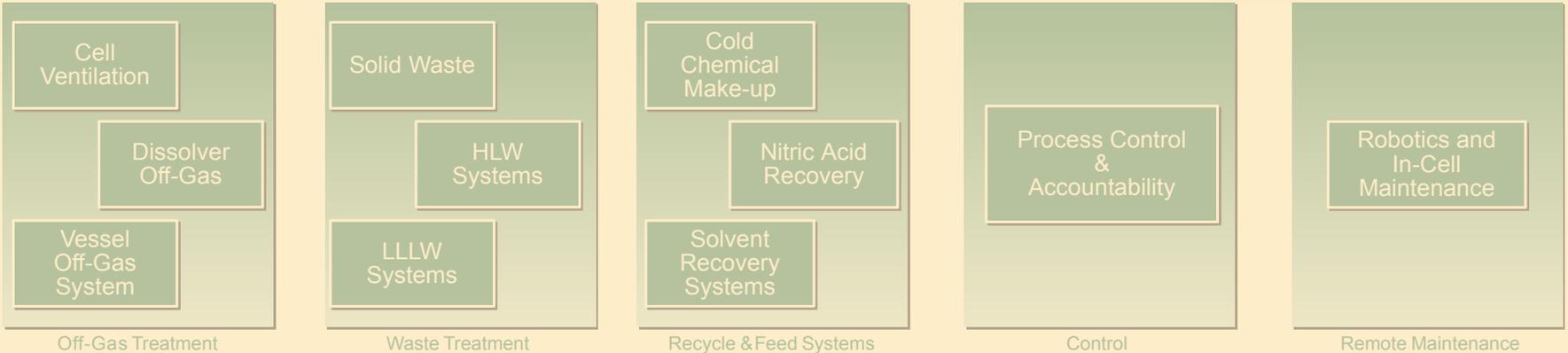
Head End



Separation Processes



Support Systems



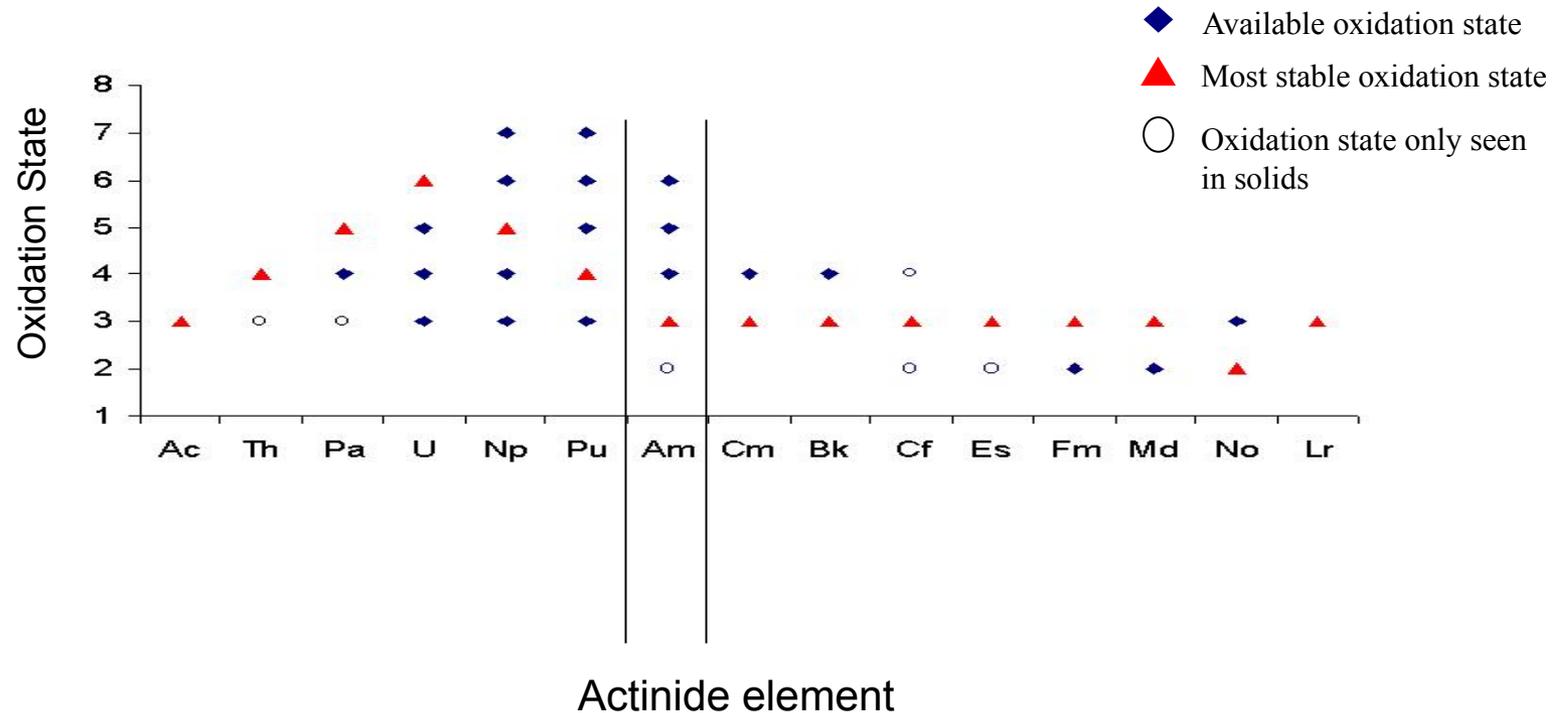
Solvent Extraction Basics

- **Solvent extraction: contact two immiscible liquids (aqueous and organic) such that a material of interest transfers from one liquid to the other**
 - Aqueous liquid: Nitric acid solution of spent fuel
 - Organic liquid: Tributyl phosphate (TBP) diluted in kerosene or n-dodecane
- **Controlling the separation**
 - Provide excess TBP
 - Vary acid concentration to recover uranium and plutonium
 - High Acid: $U + Pu \rightarrow TBP$
 - Low acid: $U + Pu \rightarrow \text{Aqueous}$
 - Add reducing agents to separate uranium and plutonium
 - Plutonium is reduced and returns to aqueous liquid
 - Uranium is not reduced and remains in TBP
 - Reductants: Ferrous sulfamate, hydrazine, U^{+4}

(Croff, K/NSP-121/Part 23/R2)

PUREX Process Chemistry

Early actinides have multiple oxidation states available in aqueous solution. The PUREX process makes use of this to separate U and Pu from fission products



PUREX Process Chemistry

- As a general rule only metal ions in the +4 and +6 oxidation states are extracted, this means that all other species present are rejected



- This leads to an effective separation of U and Pu away from nearly all other species in dissolved nuclear fuel

Single Solvent Extraction Stage

- Distribution Coefficient: $D_i = y_i / x_i$
where:
 y_i = concentration of i in the organic phase
 x_i = concentration of i in the aqueous phase

- Material Balance on Stage:

$$O(y_{n-1}) + A(x_{n+1}) = O(y_n) + A(x_n)$$

where:

O = organic volume

A = aqueous volume

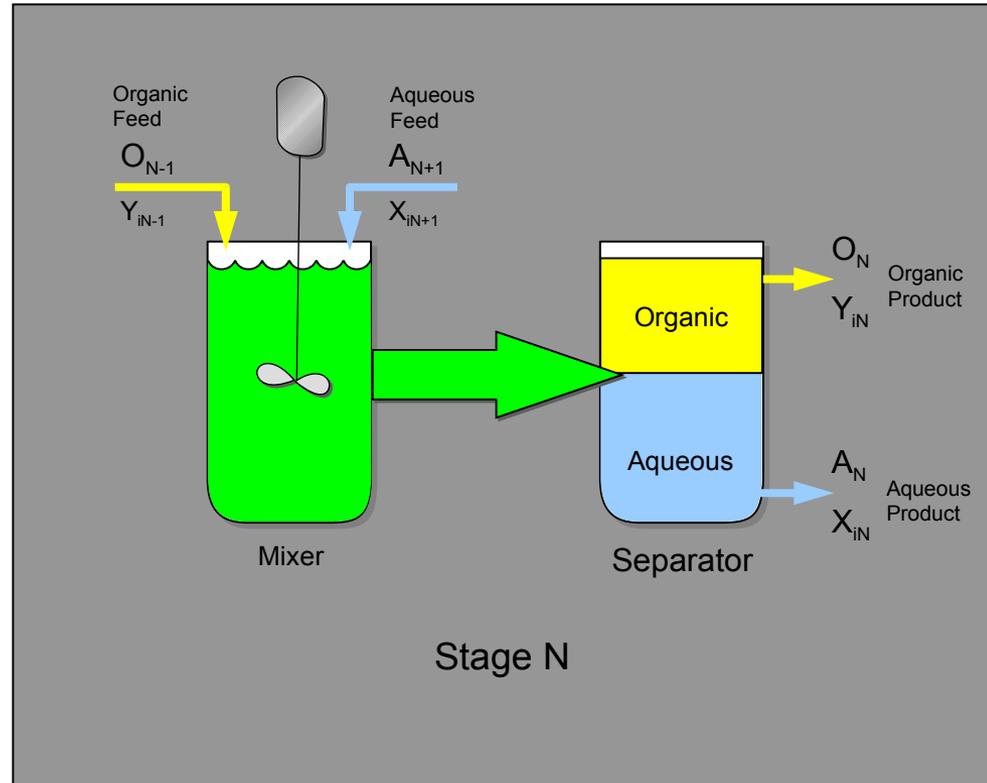
- What's extracted?

Assume: $y_{n-1} = 0$ and $D = y_n/x_n$ then:

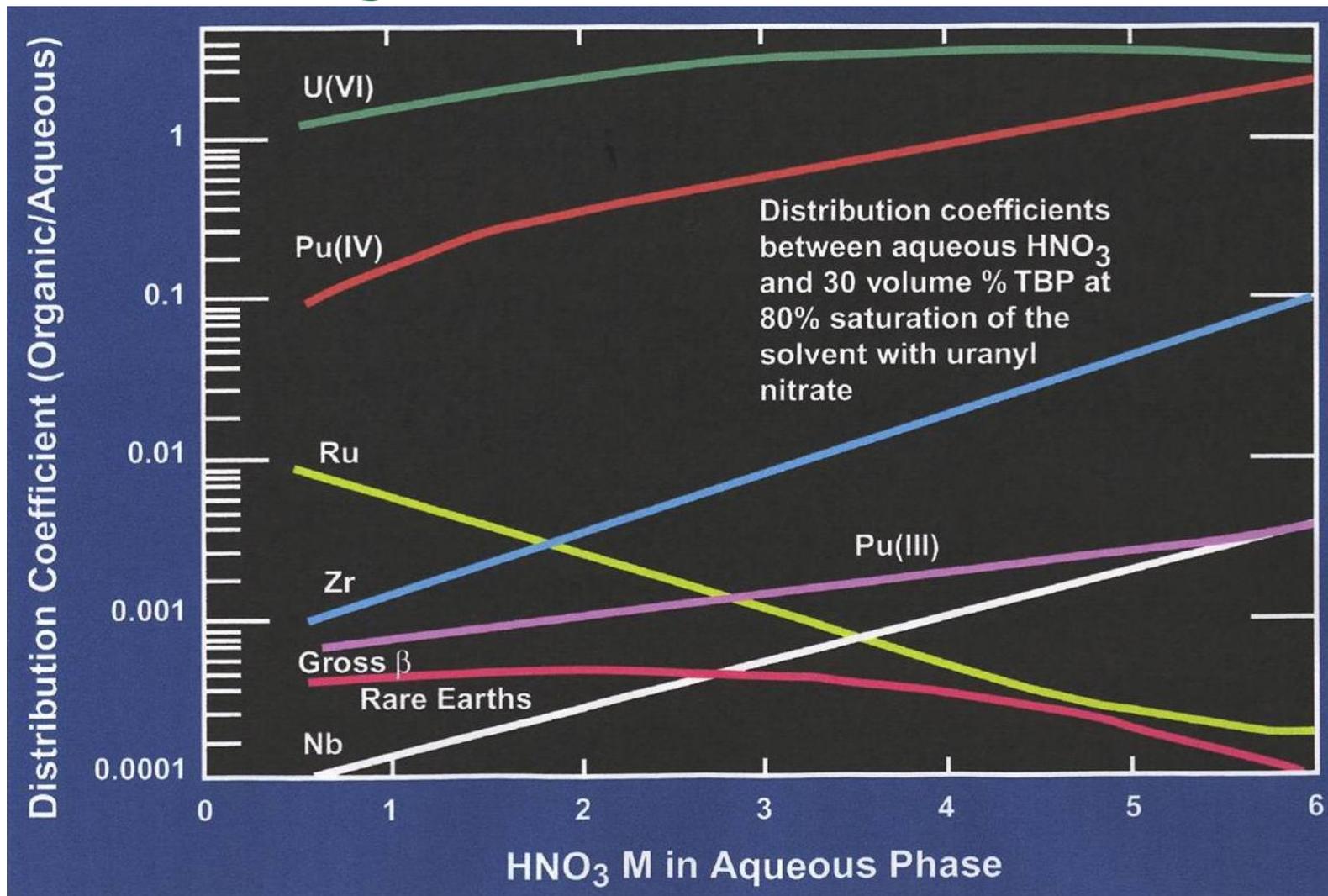
$$y_n = D(x_{n+1}) / (OD/A + 1)$$

The fraction extracted is:

$$O(y_n) / A(x_{n+1}) = (OD/A) / (1 + OD/A)$$



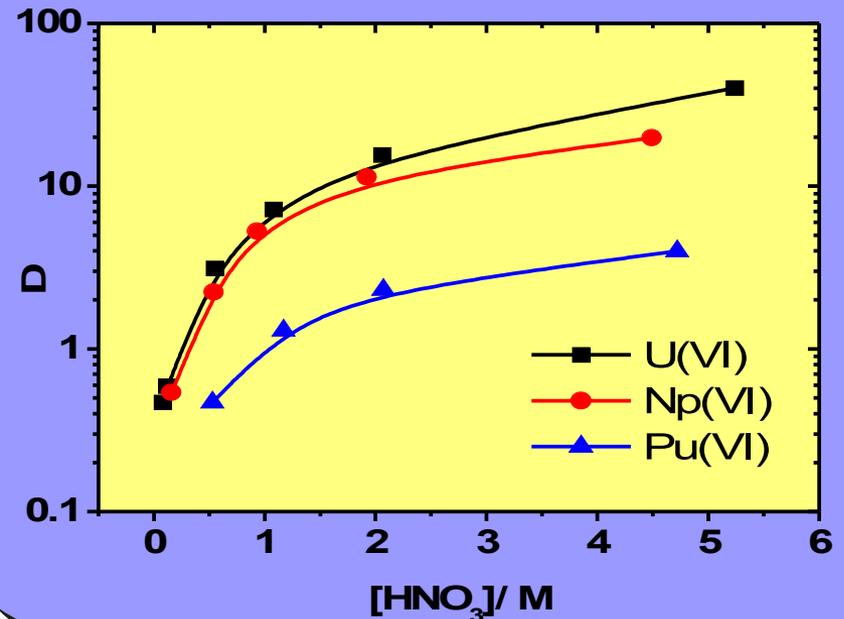
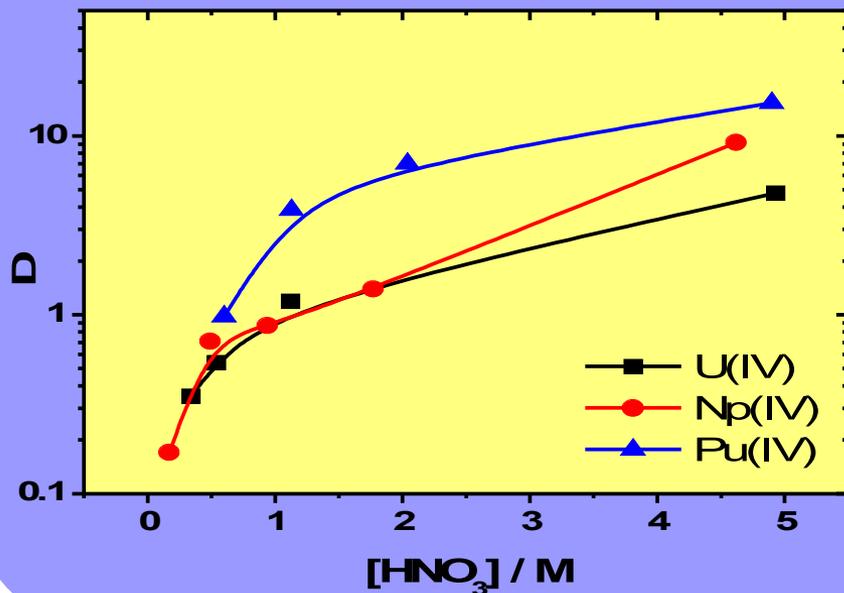
Effect of Nitric Acid Concentration on Extraction by TBP



(Croff, K/NSP-121/Part 23/R2)

PUREX Process – Basic Principles

- U, Np and Pu TBP extraction data plotted against each other, from this it can be seen that extractability (D) of the hexavalent actinides decreases across the series $\text{UO}_2^{2+} > \text{NpO}_2^{2+} > \text{PuO}_2^{2+}$. Conversely, the extractability (D) of the tetravalent actinides is seen to increase across the series $\text{U}^{4+} < \text{Np}^{4+} < \text{Pu}^{4+}$.



PUREX Process – Basic Principles

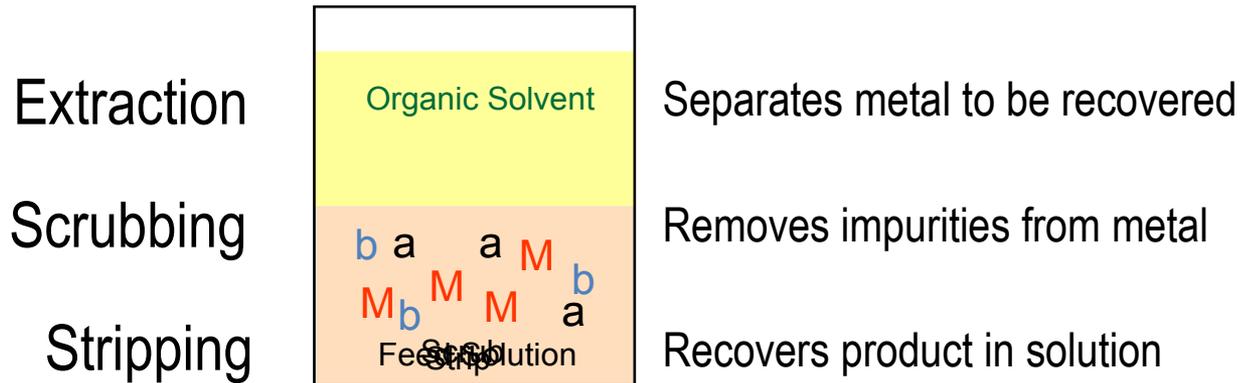
- To remove Pu from the organic phase Pu⁴⁺ is reduced to inextractable Pu³⁺ using a reducing agent, usually Fe²⁺ or U⁴⁺



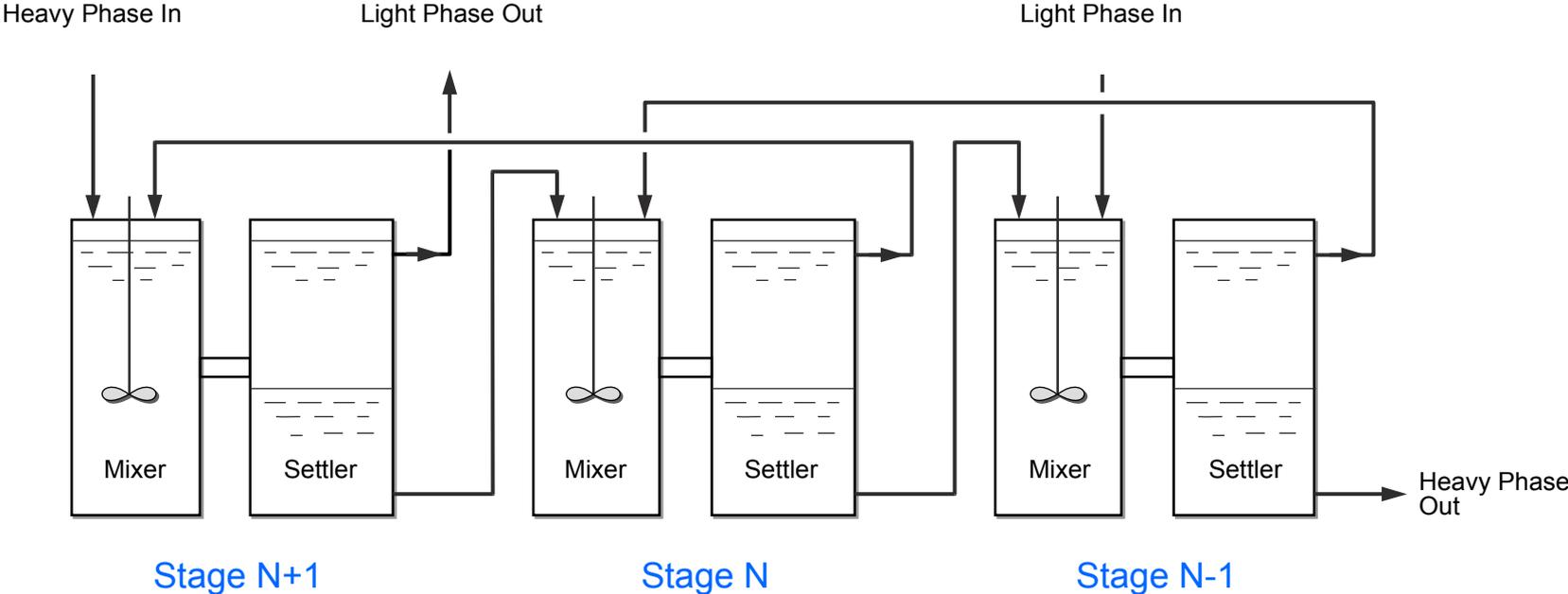
- This process leaves UO₂²⁺ unaffected and U⁴⁺ is also extractable
- Pu can be selectively back extracted.
- However, Pu³⁺ can be unstable in HNO₃ solutions because of the presence of nitrous acid, and thus hydrazine is added as a nitrous acid scavenger



PUREX Process – Basic Principles



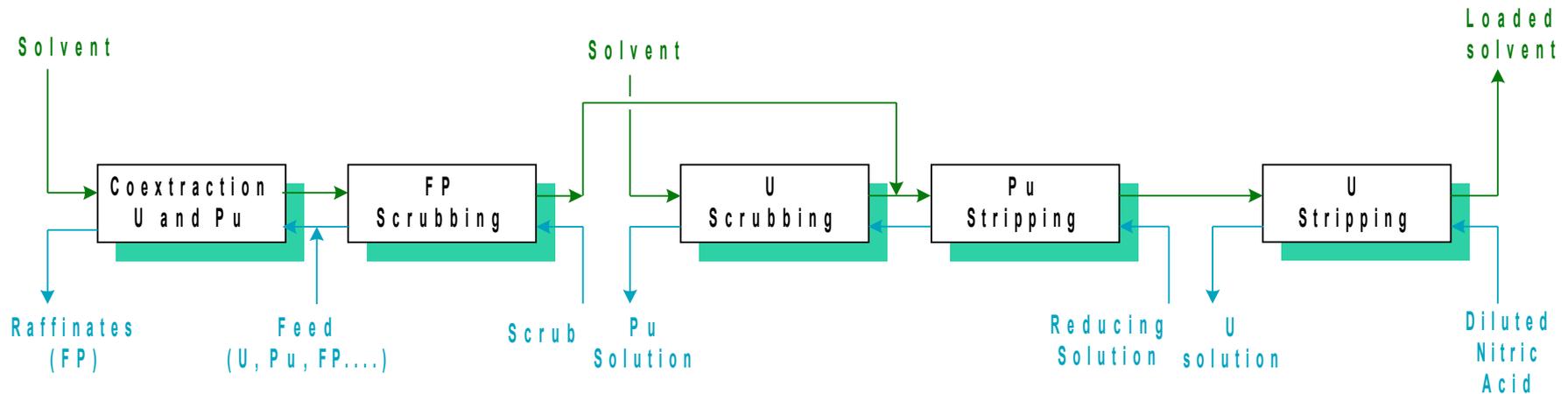
Multistage Operations



PUREX Process – Unit Operations

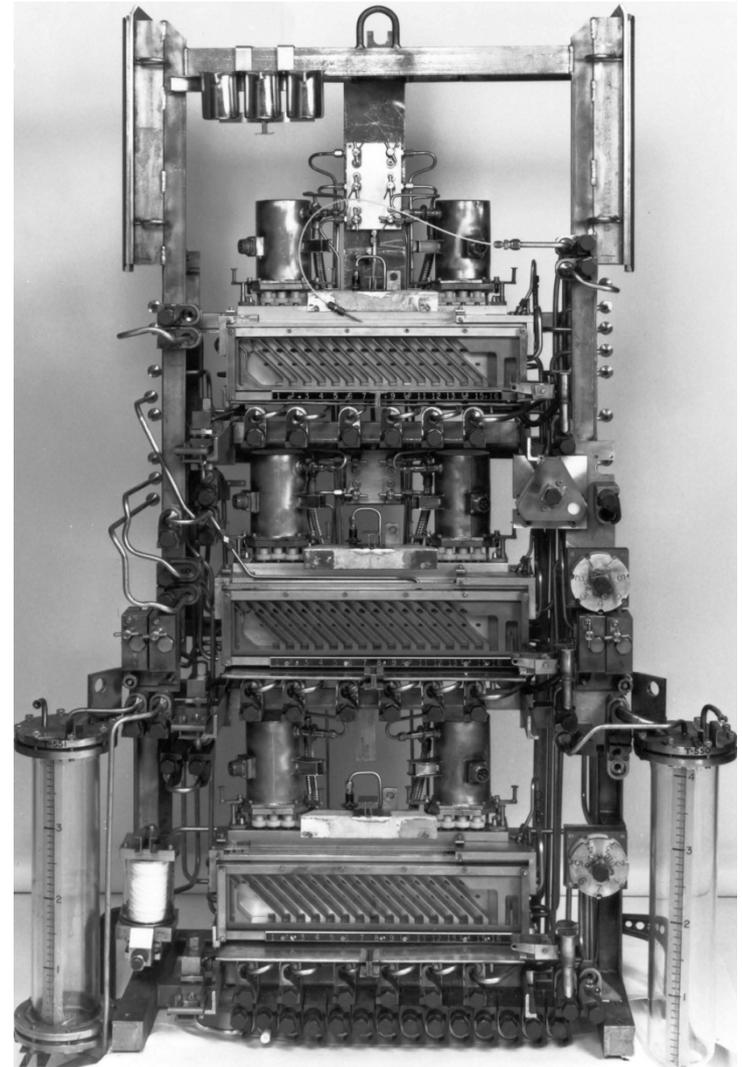
- Separations

- Countercurrent PUREX flowsheet (1st cycle or HA cycle)

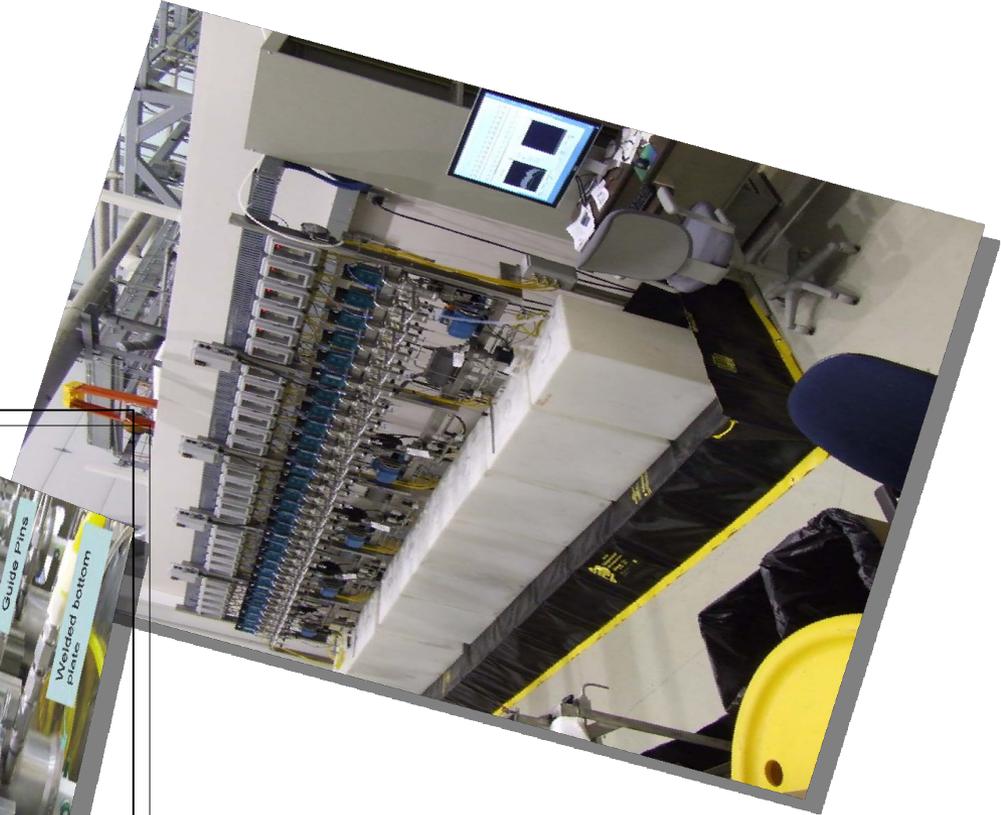
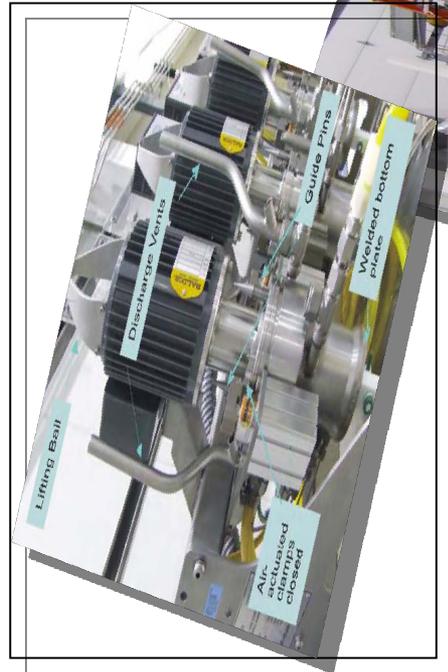
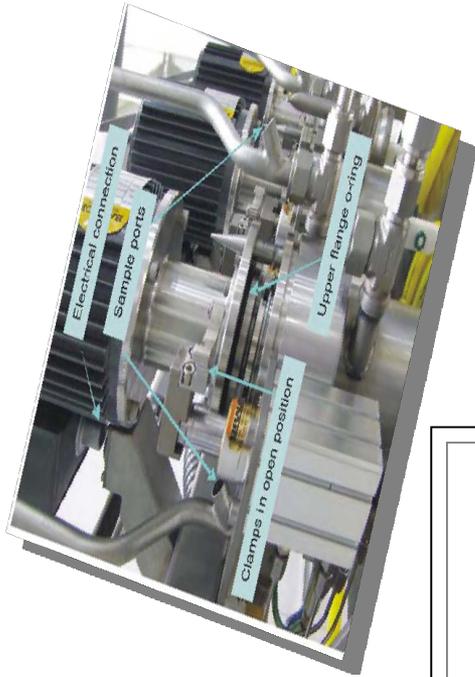


Solvent Extraction Equipment

- Originally designed and used for flow sheet testing using SNF
- Three banks of 16-stage mixer/settler contactors
 - *Extraction/scrub*
 - *Partition*
 - *Strip*
- Design offers flexibility in operations

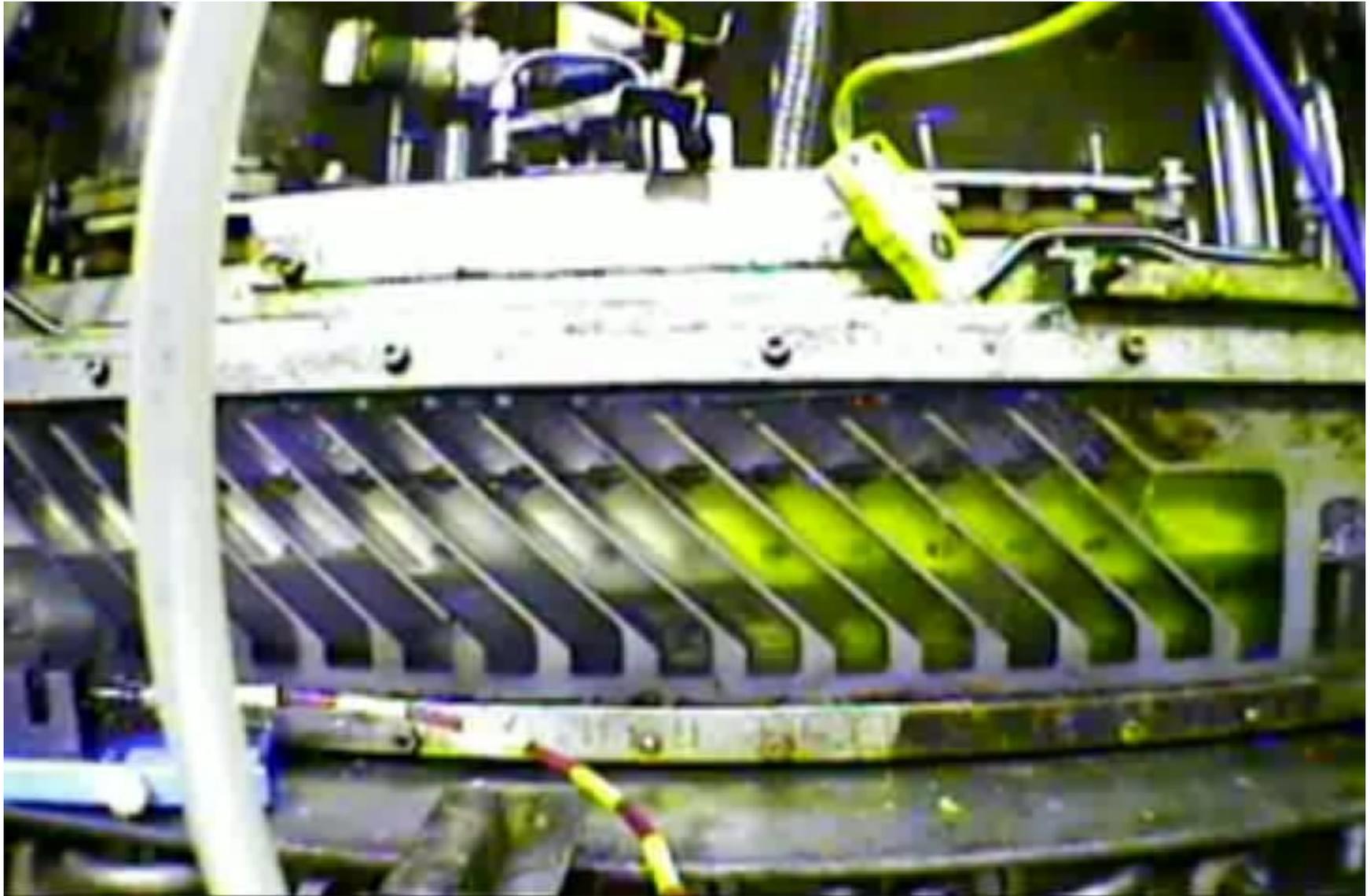


Experimental Scale Equipment

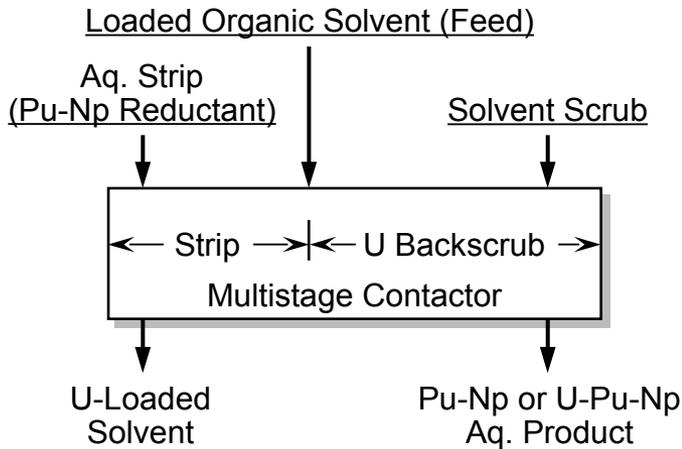
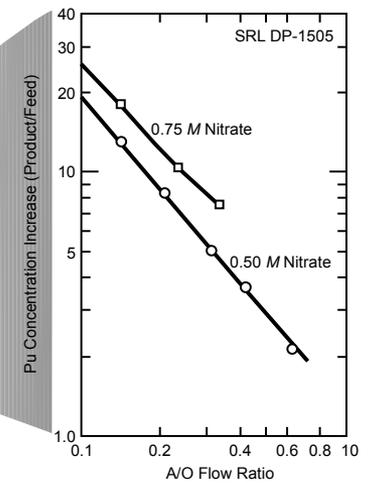


INL Centrifugal Contactor
Engineer Scale System

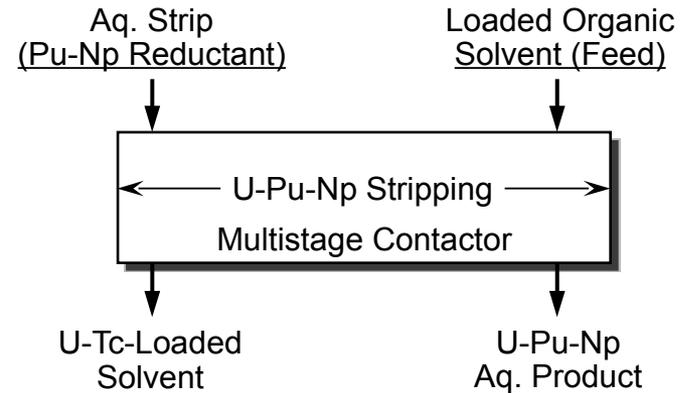
Solvent Extraction Equipment in Operation



Partial Partitioning of Uranium



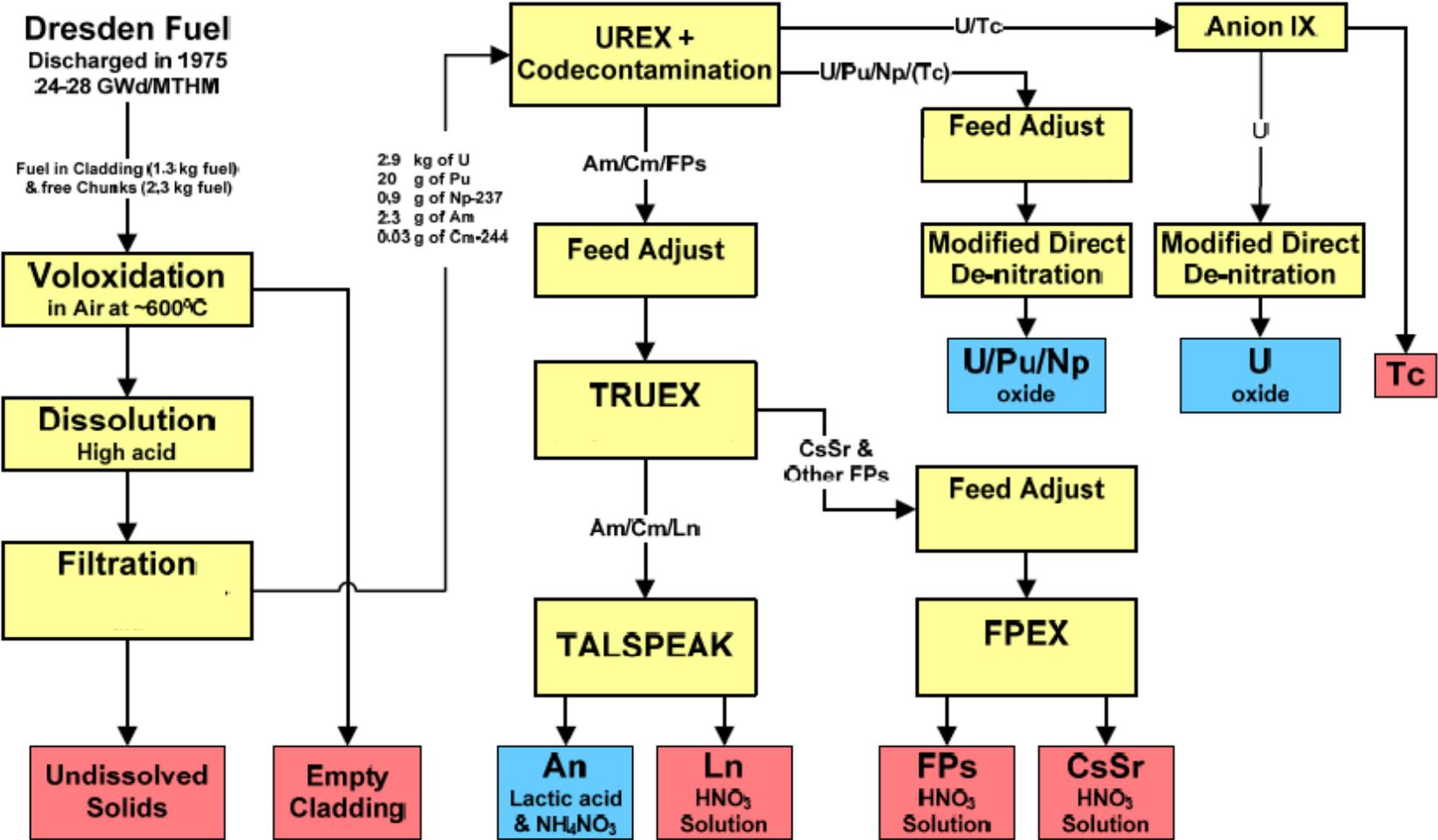
PUREX-Type
Partitioning Contactor Bank
(Complete or partial partitioning is possible)



UREX+ Codecon Flowsheet
Partial Partitioning Contactor Bank

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

Recent Demonstration Flowsheet

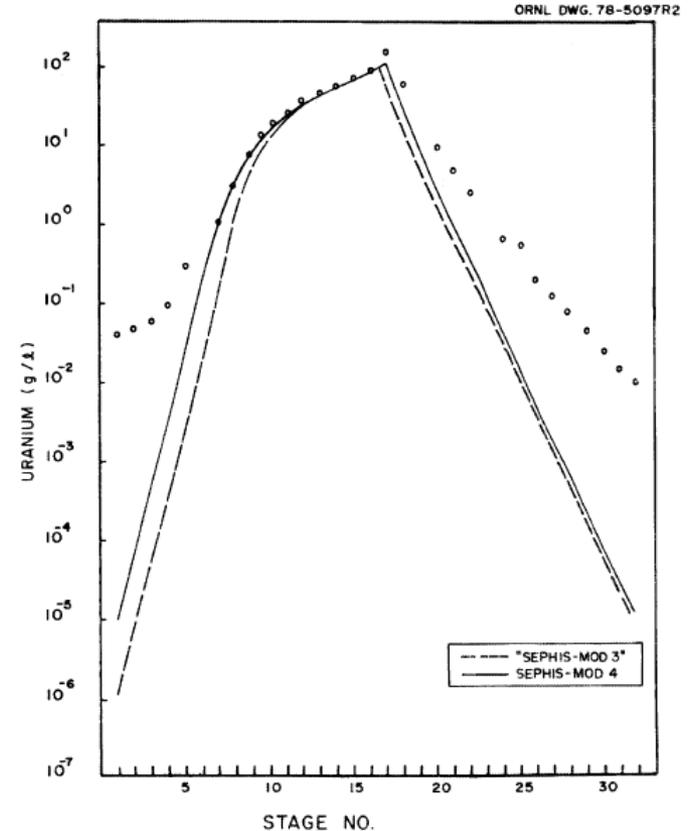


Co-extraction / Partial Partitioning Products

Material	Feed Content	Total volume collected and normalized distribution based on stream samples taken during the run			
		Raffinate	U-Pu-Np Product	U-Tc Product	Waste Organic
Total Volume	11.34 L	37.2 L	7.6 L	55.7 L	56.2 L
Acidity	2.7	2.5 NH^+	0.6 NH^+	~0.04 NH^+	
U	2950 g	0.012%	6.24%	93.49%	0.26%
Pu	20.45 g	0.011%	99.88%	0.105%	0.005%
Np-237	0.890 g	<0.7%	>98.8%	<0.2%	<0.2%
Am	2.27 g	99.98%	0.0037%	0.012%	0.0006%
Cm-244	0.031 g	99.61%	<0.02%	0.30%	0.073%
Total TRU	2972 g				
Y	1.02 g	>99.95%	<0.02%	<0.02%	
Zr	7.45 g	99.77%	<0.007%	0.22%	
Mo	6.68 g	99.94%	0.043%	0.02%	
Tc	1.12 g	2.01%	31.63%	66.36%	
Ru	0.49 g	99.65%	<0.05%	0.29%	
Pd	0.009 g	>98.1%	<1.0%	<0.8%	
Total	6.79 g				

Product Purity

- Barnwell Nuclear Fuel Plant (BNFP)
 - Pu product (Benedict, et al, 1981)
 - < 100 ppm U,
 - < 40 μ Ci/g Pu total gamma
 - < 5 μ Ci/g Pu zirconium-niobium activity
- One PUREX cycle upper limit on fission product DF for U or Pu of about 1000 (Wymer and Vondra, 1981)
- Multiple cycles can be used to improve product purity



Product Purity Standards

- **ASTM C753 Uranium dioxide powder**
 - $\leq 1500 \mu\text{g/g U}$ total impurities
 - $\leq 250 \mu\text{g/g U}$ for iron and molybdenum
 - $\leq 200 \mu\text{g/g U}$ for Nitrogen
 - Thorium impurities are limited to $\leq 10 \mu\text{g/g U}$
- **ASTM C773 Uranium dioxide pellets**
 - $\leq 1500 \mu\text{g/g U}$ total impurities
 - $\leq 500 \mu\text{g/g U}$ for iron and molybdenum
 - $\leq 75 \mu\text{g/g U}$ for Nitrogen
 - Thorium impurities are limited to $\leq 10 \mu\text{g/g U}$
- **ASTM C1008 Fast reactor MOX**
 - $\leq 5000 \mu\text{g/g U+Pu}$ total impurities (excluding Am and Th)

Ion Exchange Basics

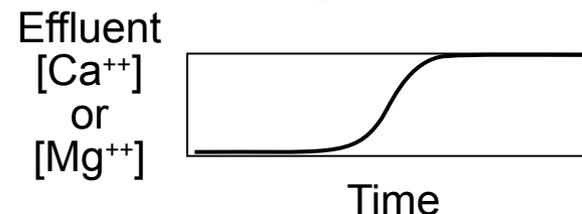
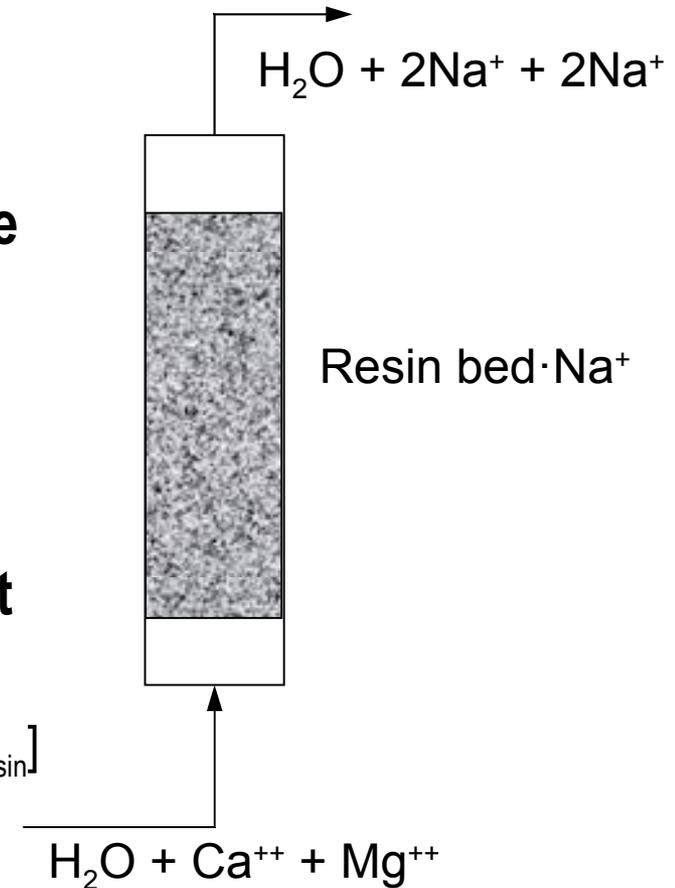
- **Ion exchange:** Passing an aqueous solution over a solid substance that will preferentially remove certain constituents (ions) from the solution by exchanging them with ions attached to the ion exchanger. The removed constituents are recovered by separating the solution from the ion exchanger or by washing the ion exchange column contents with another liquid.
 - **Aqueous solution:** typically a high or low nitric acid solution of U + Pu or dissolved spent fuel
 - **Ion exchange material:** Typically an organic polymer in sizes ranging from small beads to larger random shapes. May be inorganic.
 - **Wash solution:** Typically a low- or high-concentration nitric acid solution
- **Controlling the separation**
 - **Desired constituent** retained by (loaded on) ion exchange material and recovered (eluted) by “opposite” type of solution
 - **Undesired constituent** retained by (loaded on) ion exchange material and recovered (eluted) by “opposite” type of solution

(Croff, K/NSP-121/Part 23/R2)

Common Example of Ion Exchange

- Removal of minerals from “hard” water
 - $\text{Ca}^{++} + 2\text{Na}^+ \cdot \text{resin}^- \rightarrow \text{Ca}^{++} \cdot (\text{resin})_2^- + 2\text{Na}^+$, and
 - $\text{Mg}^{++} + 2\text{Na}^+ \cdot \text{resin}^- \rightarrow \text{Mg}^{++} \cdot (\text{resin})_2^- + 2\text{Na}^+$
- Other constituents in the solution for which the ion exchange resin is not selective will remain in the aqueous solution and pass through the ion exchange bed.
- The capacity of ion exchange material is finite and can be defined by the equilibrium constant (K) (King, 1971):

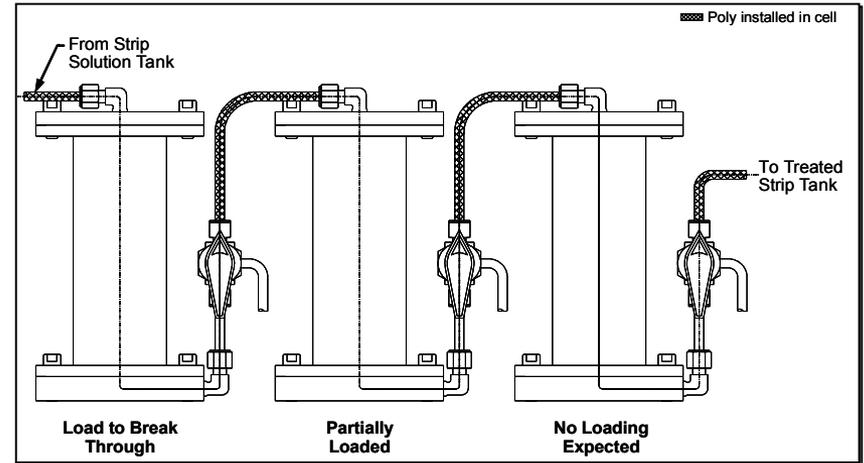
$$K_{\text{Ca}^{++}\text{-Na}^+} = \frac{[(\text{Ca}^{++})_{\text{resin}} (\text{Na}^+)_{\text{aqueous}}^2]}{[(\text{Ca}^{++})_{\text{aqueous}} (\text{Na}^+)_{\text{resin}}^2]}$$



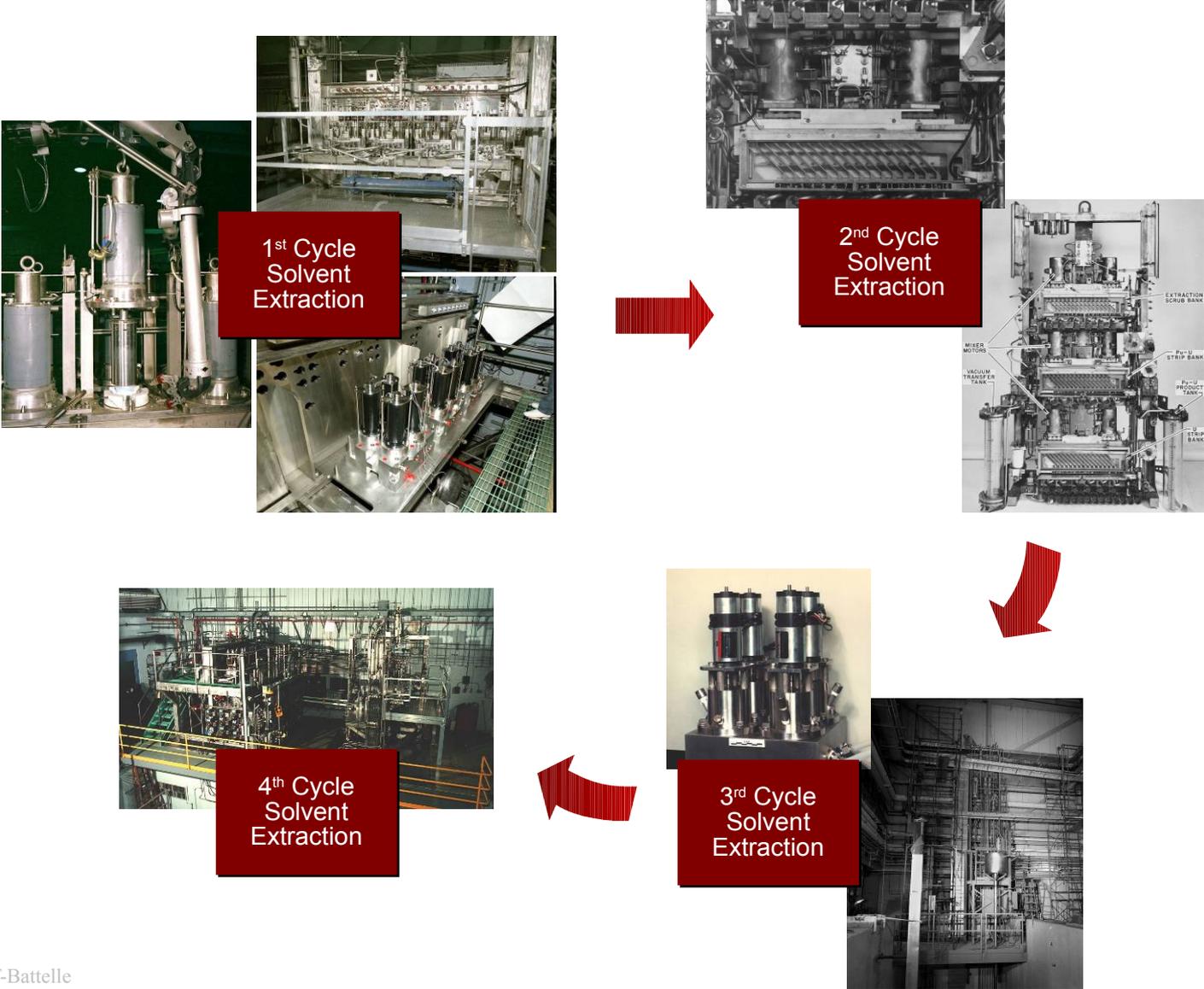
King, C. Judson, Separation Processes, McGraw-Hill Book Company, New York, NY, 1971.

Technetium Recovery by Ion Exchange

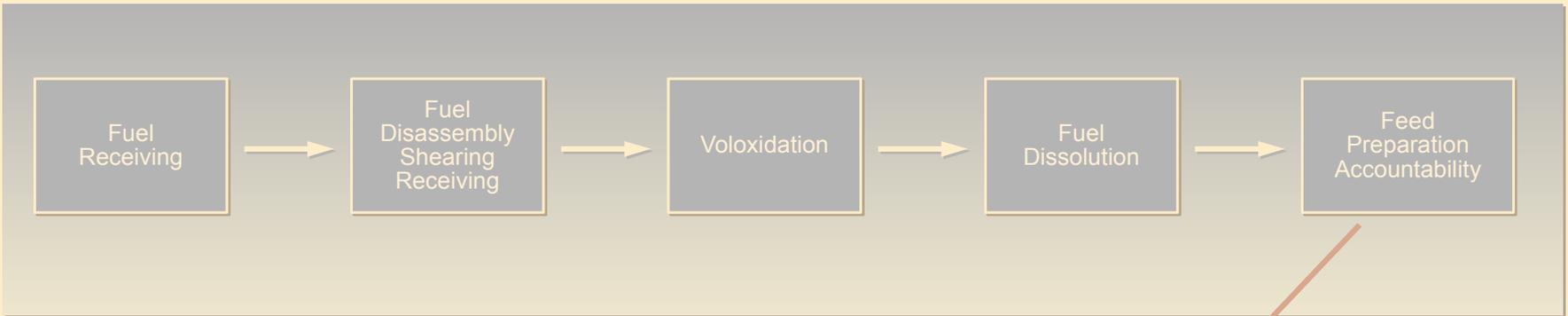
- Worked with LANL to design Tc recovery and solidification system
 - Ion exchange columns fabricated for in-cell loading
 - LANL supplied pretreated Reillex HP resin (80°C HNO₃)
 - Columns installed in REDC Hot Cells
 - Tc recovery operations from CETE Run 1 (Dresden)
 - Uranium retained for conversion to oxide
 - Tc recovered and converted to shippable form (NH₄TcO₄)
 - Evaporation @ ~62°C and reduced pressure



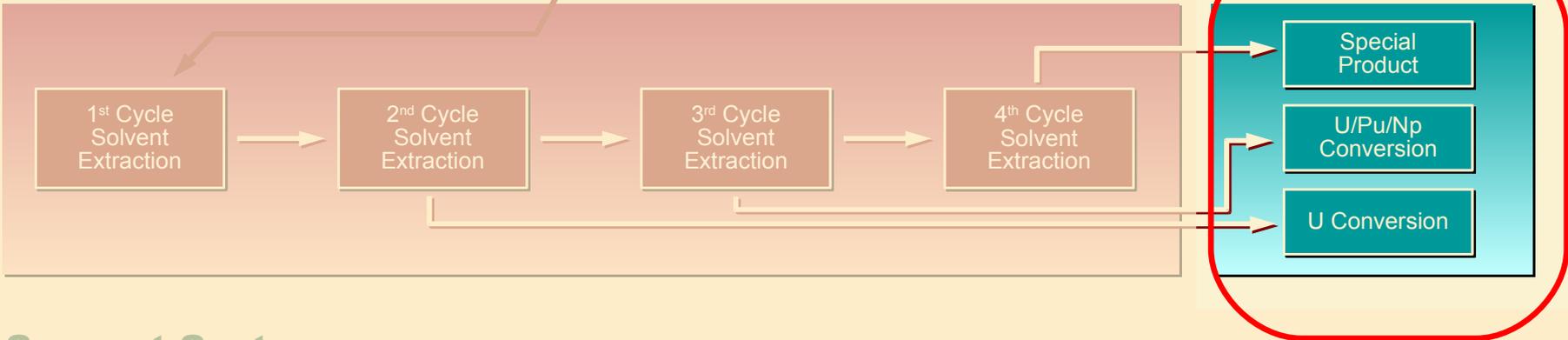
Fuel Reprocessing: Primary Separations Processes



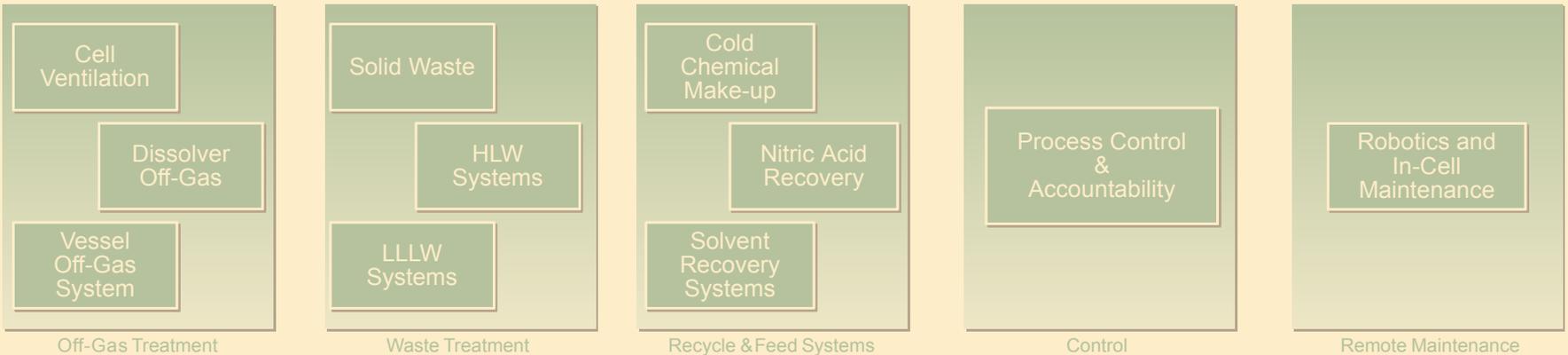
Head End



Separation Processes



Support Systems



Product Conversion

- **Concentrate aqueous plutonium solution and purify: Evaporation, ion exchange, solvent extraction**
- **Precipitate plutonium: Trifluoride, oxalate, peroxide**
- **Conversion: Tetrafluoride or oxide-fluoride mix**
- **Reduction to metal: With calcium metal and iodine catalyst in a closed vessel**
- **Alternative: Calcine (strongly heat) oxalate precipitate to form oxide, then reduce with a mix of calcium metal and calcium chloride**

(Croff, K/NSP-121/Part 23/R2)

Product Denitration

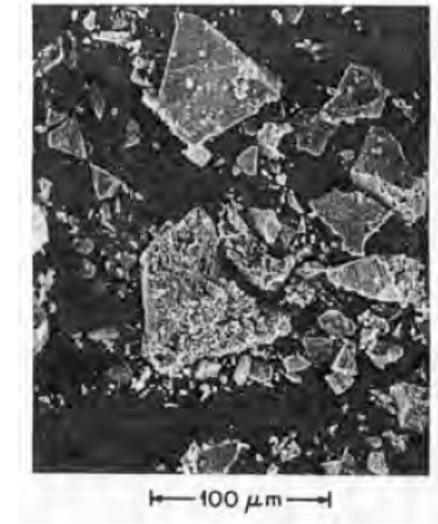
- **Direct Denitration**

- Thermally decomposes metal nitrates to oxide
- In the case of uranium (uranyl nitrate hexahydrate):
 - Intermediary compounds formed
 - Trihydrate (m.p. 113C); dihydrate (m.p. 184C)
 - Nitrate salt decomposes above 184C

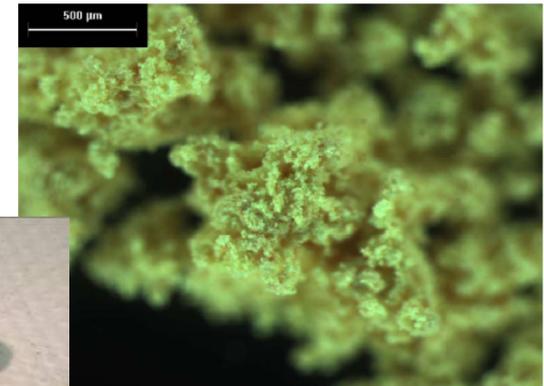
- **Modified Direct Denitration**

- Addition of inorganic nitrate salt to metal nitrate
- Uses rotary kiln to thermally decompose double salt to metal oxides
- Avoids the formation of sticky mastic phase
- Resulting products have higher surface area
- Produces a powder with good ceramic properties for pellet fabrication
- Further R&D required
 - Process development
 - Scaleup
 - Qualifying the ceramic product

Traditional Direct Denitration
(Picture from P. Haas report)



Modified Direct Denitration
(Picture of MDD-produced DU)

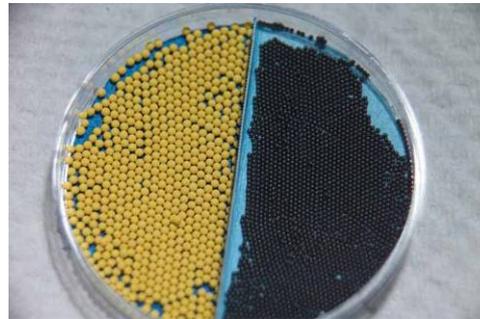


Fuel Reprocessing: Product Conversion

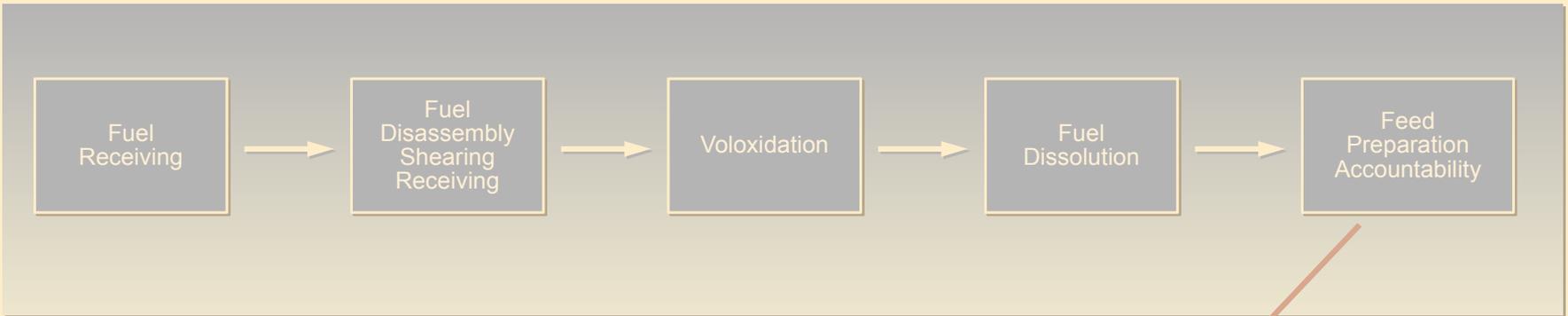
Special Product

Pu/Np
Conversion

U Conversion



Head End

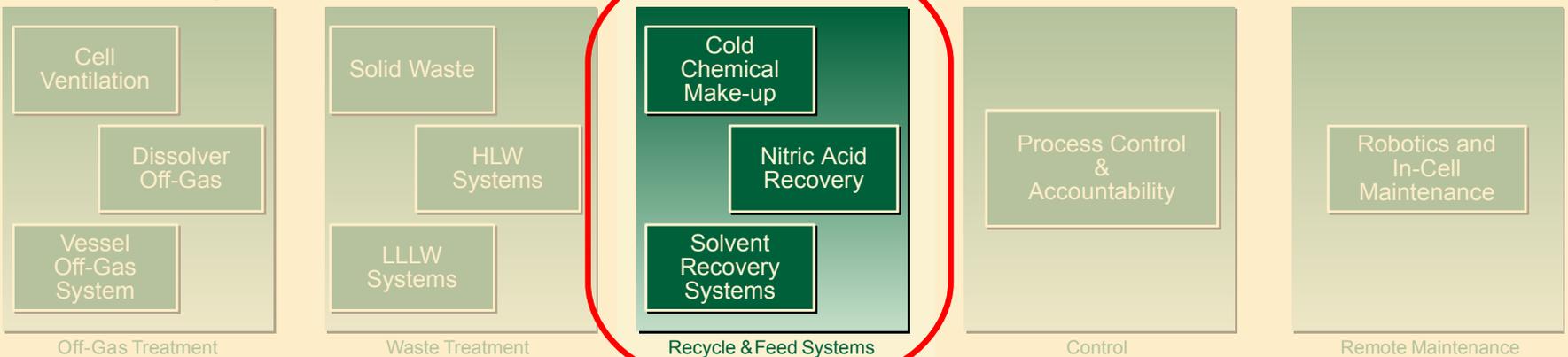


Separation Processes



Conversion

Support Systems



Recycle / Recovery Systems

- **Aqueous based fuel recycle facilities require significant quantities of chemicals to carry out separations**
 - Nitric Acid
 - Solvent
 - Chemical for process adjustments
- **Minimal liquid waste storage**
- **Fuel enters as a solid and wastes leave as solids**
- **Recovery and reuse of process chemicals is critical**
 - Recover nitric acid from off-gas (dissolver, evaporators, product conversion, waste solidification, etc.)
 - Dilute stream – concentrated by distillation
 - Extraction solvents are recycled
 - Requires purification – “solvent washing”

Distillation Basics

- **Distillation is the separations process most people think of**
 - Widely used in the petrochemical industry
 - A more secondary role in fuel recycle operations
- **Distillation: Separating one or more constituents from a liquid mixture by utilizing the variations in boiling points or vapor pressure. The liquid to be separated is boiled and then the vapor condensed. The condensed vapor, typically the purified product, is referred to as the distillate or overheads and the residual liquids are called the bottoms.**
 - The vapor contains more of the components with lower boiling points and the bottoms is depleted in these components.
- **Controlling the separations**
 - Reflux ratio – the quantity of condensate returned to the top of the distillation column relative to the quantity removed as a product
 - Boil-up rate
 - Number of stages

Applications of Distillation / Evaporation

- **Acid recycle**
 - Nitric acid recovery from off-gas and waste processing
 - Dissolution in 800MT/yr plant requires $\sim 10^6$ liters concentrated acid per yr
 - Accumulation of corrosion products
- **Product concentration**
 - Evaporation commonly used
 - Between SX cycles
 - Prior to conversion
 - Basically the same as distillation with only one stage
- **Waste concentration**

Red Oil Issues

- **Created by decomposition of TBP by nitric acid, under elevated temperature**
 - Influenced by presences of heavy metal (U or Pu), which causes higher organic solubility in aqueous solution and increases the density of the organic solution (possibly > aqueous phase)
 - Decomposition of TBP is a function of HNO_3 concentration and temp.
- **Primary concern is in evaporators that concentrate heavy metals in product**
- **Red oil reactions can be very energetic, and have resulted in large explosions at reprocessing facilities**
- **Typical safety measures include diluent washes or steam stripping of aqueous product streams to remove trace amounts of TBP before evaporation or denitration**
- **Diluent nitration may also play a role in the formation**
- **Major accidents detailed in Defense Nuclear Facilities Safety Board (DNFSB) report “Tech 33” Nov. 2003**

Controls to Avoid Red Oil Accidents

- **Temperature control**
 - Maintain solutions at less than 130 °C at all times
- **Pressure control**
 - Adequate ventilation to avoid buildup of explosive gases
- **Mass control**
 - Minimize or eliminate organics (TBP) from aqueous streams
 - Decanters, diluent washes, etc.
- **Concentration control**
 - < 10 M HNO₃
 - With solutions of uranyl nitrate, boiling temperature and density must be monitored
- **Multiple methods need to be employed so that no single parameter failure can lead to red oil formation**

Steam Stripping

- **Used to remove trace organics from aqueous streams**
- **Steam is used to transfer the organics from the heated aqueous to the vapor phase**
 - **Conducted close to boiling point of aqueous phase**
 - **Concentrated organic is recovered**
- **May be used to recover the dissolved and entrained organic in aqueous product streams prior to concentration to avoid red-oil formation**
- **May also be used to recover diluent from organic phase**
 - **Diluent then used in “Diluent wash” of aqueous product streams to recover organics**

Diluent Wash

- **The use of an organic diluent to recover dissolved and entrained TBP from aqueous streams**
- **Mixer Settler or Centrifugal contactor running at high A/O ratio**
- **1 or more stages may be used to obtain desired recovery**

Solvent Treatment / Washing

- **Solvents are degraded by radiolysis and chemical hydrolysis**
 - If allowed to accumulate, the organic phase will have increased retention of U, Pu, Zr, Nb, Ru.
 - At high levels changes in physical properties will occur
- **Solvent treatment**
 - Sodium carbonate scrub is used to remove primary degradation products (H₂MBP and HDBP)
 - Resin beds can remove the alkylphosphoric acids
 - Distillation can purify both the diluent and the TBP to a quality comparable to unirradiated

Wymer, R. G, and Vondra, B. L, Light Water Reactor Nuclear Fuel Cycle, CRC Press, Inc., Boca Raton, FL, 1981.

Fuel Reprocessing: Recycle and Feed Systems



Nitric Acid
Recovery

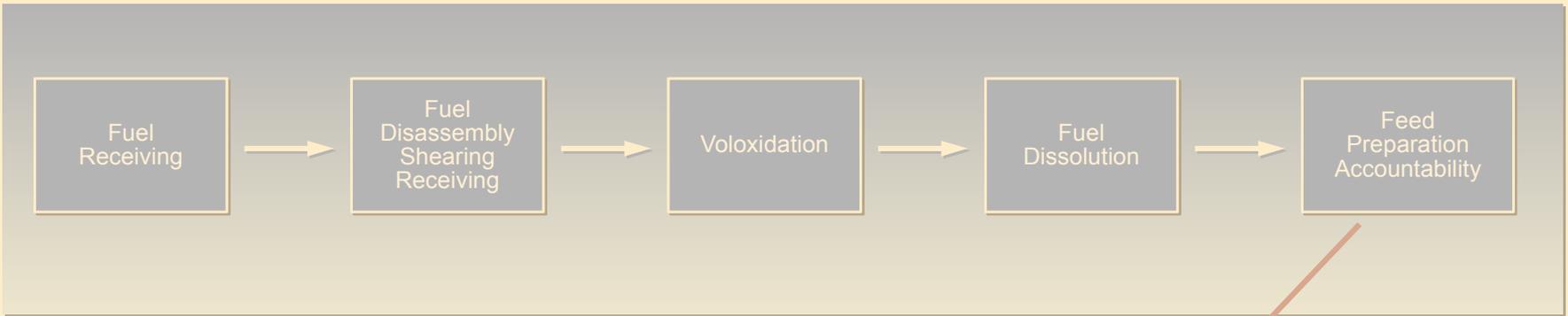


Cold Chemical
Make-up

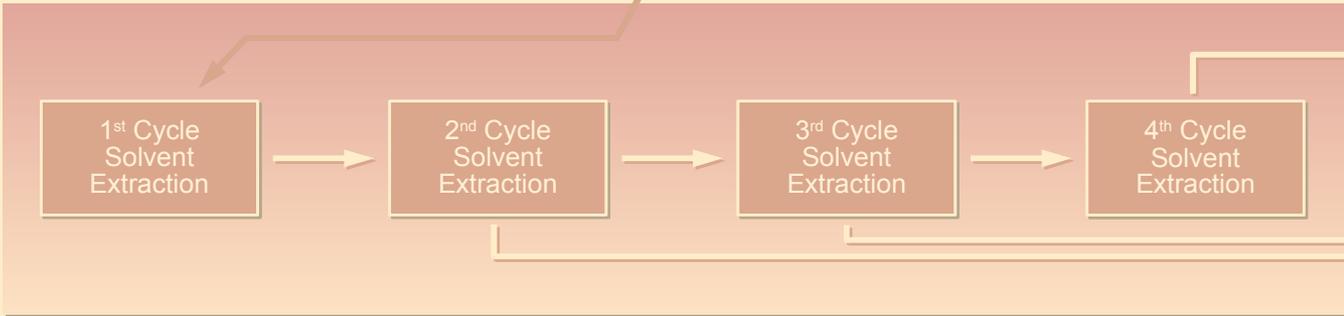


Solvent
Recovery
Systems

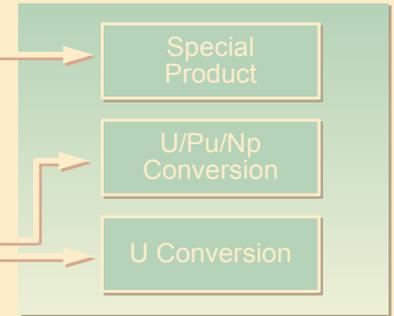
Head End



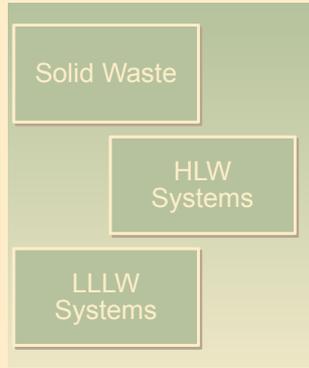
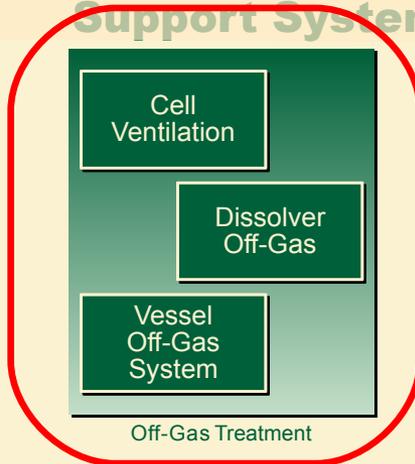
Separation Processes



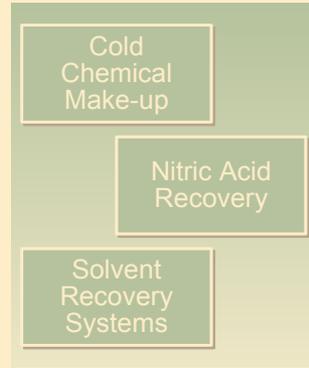
Conversion



Support Systems



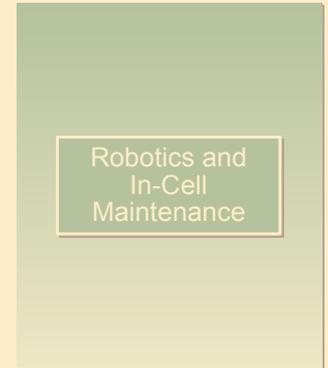
Waste Treatment



Recycle & Feed Systems



Control



Remote Maintenance

Off-gas Treatment

- Volatile components considered have wide range of half-lives and disposal requirements:
 - ^3H 12.31 yr
 - ^{14}C 5715 yr
 - Xe Stable and very short half-life < 30 days
 - ^{85}Kr 10.76 yr
 - ^{129}I 1.57×10^7 yr
- Assumes regulatory drivers unlikely to be relaxed

Regulatory Drivers: 40 CFR 190

- (a) The annual dose equivalent does not exceed 25 millirems to the whole body, 75 millirems to the thyroid, and 25 millirems to any other organ of any member of the public as the result of exposures to planned discharges of radioactive materials, radon and its daughters excepted, to the general environment from uranium fuel cycle operations and to radiation from these operations
- (b) The total quantity of radioactive materials entering the general environment from the entire uranium fuel cycle, **per gigawatt-year of electrical energy produced by the fuel cycle, contains less than 50,000 curies of krypton-85, 5 millicuries of iodine-129, and 0.5 millicuries combined of plutonium-239 and other alpha-emitting transuranic radionuclides with half-lives greater than one year**

isotope	Ci/MTIHM	Ci/GW(e)-yr	Min Required DF
¹²⁹ I	0.02648	0.89	178
³⁵ Kr (5 year cooled)	7121	239,000	4.77
³⁵ Kr (10 year cooled)	5154	173,000	3.45
³⁵ Kr (30 year cooled)	1414	47,000	0.95

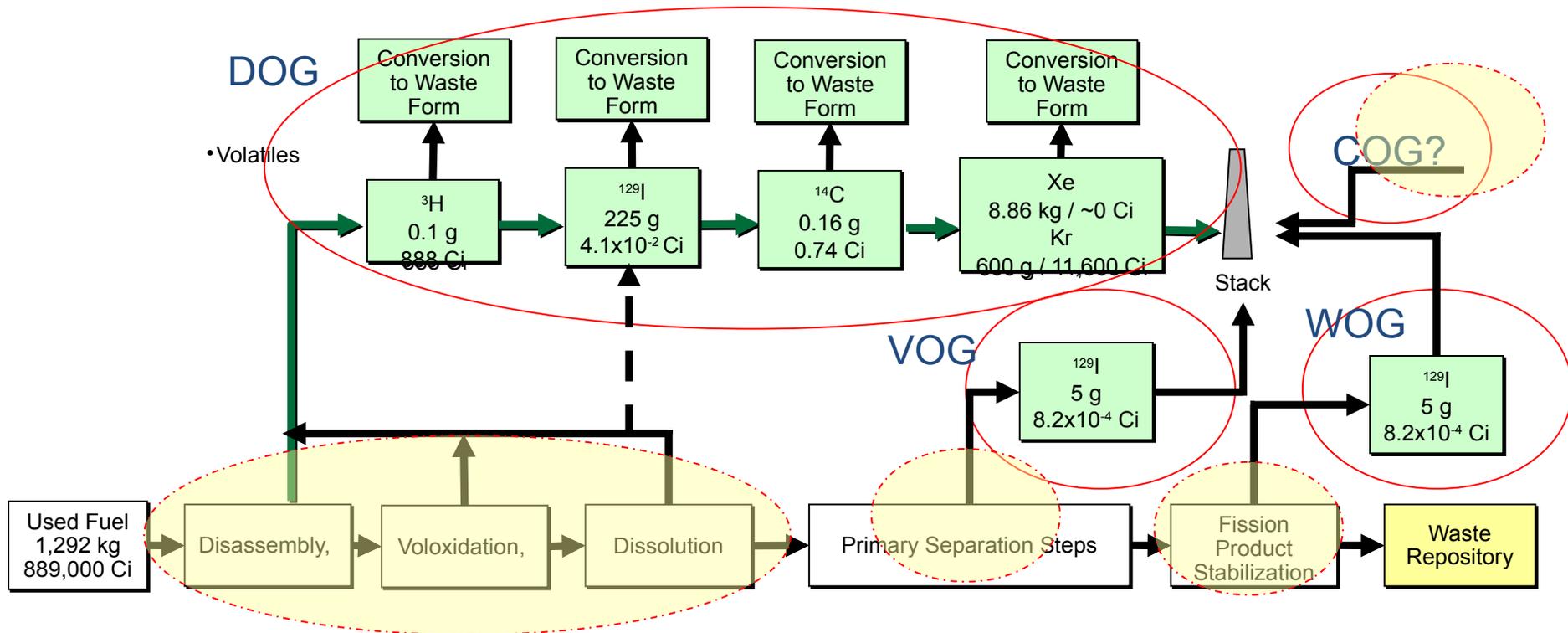
Note: Burn-up: 33 GWd/MTIHM

Regulatory Drivers: 10 CFR 20, 40 CFR 61

10 CFR 20	Air (Ci/m³) at site boundary	Water (Ci/m³)
Tritium	1.0 x 10⁻⁷	1.0 x 10⁻³
Carbon-14 (as CO₂)	3.0 x 10⁻⁵	---
Krypton-85	7.0 x 10⁻⁷	N/A
Iodine-129	4.0 x 10⁻¹¹	2.0 x 10⁻⁷

40 CFR 61.92: 10 mrem/yr dose equivalent to any member of the public

Bounding the Off-Gas problem



(Mass Basis: 1 MT initial heavy metal UNF;
55 GWd/MTIHM; 5 year Cooling)

Estimates of Volatile Fission and Activation Products¹

	Fuel Source	
	Reference Case	
Burnup (Gigawatt days per Metric tonne [GWd/MT])	55	
Initial Enrichment (%)	5	
Cooling Time (years)	20	
Isotopes	Grams/MTIHM	Ci/MTIHM
Krypton		
Kr-82	2	
Kr-83	60.83	
Kr-84	178.5	
Kr-85	11.23	4407
Kr-86	325.8	
Kr Total	578.36	4407
Xenon		
Xe-128	6.15	
Xe-129	0.05	
Xe-130	21.56	
Xe-131	600.9	
Xe-132	1906	
Xe-134	2521	
Xe-136	3793	
Xe Total	8848.65	

	Fuel Source	
	Reference Case	
Burnup (Gigawatt days per Metric tonne [GWd/MT])	55	
Initial Enrichment (%)	5	
Cooling Time (years)	20	
Isotopes	Grams/MTIHM	Ci/MTIHM
Carbon		
C-12	88.32	
C-13	11.45	
C-14	0.17	0.74
C Total	99.94	0.74
Iodine		
I-127	73.31	
I-129	234.9	4.15E-02
I Total	308.21	4.15E-02
Tritium		
H-1	1.35E-02	
H-2	1.32E-05	
H-3	3.89E-02	375.46
H Total	5.24E-02	375.46

¹ORIGEN2 v2.2

Source Terms

	Total released to off-gas streams (g/MTIHM)	VoxOG (g/MTIHM)	DOG (g/MTIHM)	VOG (g/MTIHM)	VoxOG (ppmv)	DOG (ppmv)	VOG (ppmv)
Water (UNF)	0.502	0.502	--	--	0.37	-- Removed in VoxOG	
H ₂ O (process)		7.24 – 10,000	75 205		12 – 16,000	3.25 x 10 ⁴	
CO ₂ UNF	364	182	182		Combined with DOG	50.5	
CO ₂ process		---	1700		Combined with DOG	4.4 x 10 ²	
	310	---	300	9.25	Combined with DOG	7.1	0.14
Cl (from HNO ₃)	126		126		Combined with DOG	11.0	
Kr	578.4	289.2	289.2	--	Combined with DOG	42	
Ar _{air}	60900				Combined with DOG	9300	
Kr _{air}	15.6				Combined with DOG	1.1	
Xe	8848	4424	4424	--	Combined with DOG	413	

Basis: 55GWd/MTIHM, 20 year cooled
 VoxOG rate 540 L/MTIHM
 DOG rate 2000 L/MTIHM
 VOG rate is 4000 L/MTIHM
 Air cell at 15°C dew point

Gas to Voloxidizer has -60°C dew point
 DOG cooled to 25°C after leaving dissolver
 50% Kr/Xe release in Voloxidizer
 50% CO₂ release in Voloxidizer
 97% I₂ released in Dissolver, balance to VOG

Tritium Recovery

- **Tritium recovery is primarily a drying operation**
 - Tritium oxidized to HTO
 - Molecular sieves with temperature swing regeneration using dry nitrogen
- **Recovery of tritium requires relatively clean separation of the iodine and HTO during the regeneration operations. This is a major, but not limiting, assumption.**
 - Assumes desire to separate the long half-life iodine from the relatively short half-life tritium for disposal
 - Iodine could be captured on a secondary recovery bed (AgZ) during recovery or alter sequence of processing steps
 - HTO stream could be recovered in cold trap
- **HTO also has permit limits for a LLW site**

Iodine Recovery

- The distribution of ^{129}I in gas and liquid process streams has been measured at the Karlsruhe reprocessing plant (WAK) (Herrmann, et al., 1993) and predicted for the BNFP (Hebel and Cottone, 1982)
 - About 94% to 99% of the ^{129}I reports to the Dissolver Off-Gas (DOG)
 - Remaining is distributed among the aqueous high, medium and low-level waste
 - DF of 1000 requires 99.9% recovery of iodine for entire plant
- The primary recovery technology is applied to the DOG
- The Vessel Off-Gas (VOG) may/must also be treated in an attempt to recover ^{129}I which escapes from the process vessels by out-gassing (required if facility DF is greater than 100)
- The small quantities of iodine remaining in the waste solutions may also be released over an extended period from the waste tanks

¹⁴C Recovery

- The bulk of the ¹⁴C found in the irradiated nuclear fuel is assumed to be evolved as CO₂ into the DOG during fuel dissolution
- Diluted 1000-5000 X by CO₂ in dissolver air sparge
 - ~ 150 Ci/yr released by 200 MTIHM plant
 - ~ 110 g of ¹⁴CO₂ diluted with ~ 760 kg nonradioactive CO₂,
 - To reduce the impact of nonradioactive CO₂, the process could be designed to remove the CO₂ from air prior to sparging the dissolver, minimizing sparge gas flow or using nitrogen in place of air
- If standard voloxidation is used then approximately 50% of the ¹⁴C will be released in the voloxidizer
- Caustic scrub followed by immobilization as grout may meet LLW standards, but similar to tritium may be limited by disposal facility permit

Krypton Recovery

- Most ^{85}Kr (>99%) remains in SNF until it is sheared and dissolved
- ^{85}Kr would be released in the shear and dissolver off-gasses
- ^{85}Kr is released in the DOG in the range of hundreds of parts per million
- $\sim 2 \times 10^6$ Ci/yr of ^{85}Kr released in the shear and dissolver off-gasses of a 200 t/yr FRP (5 yr cooling)
- Recovery processes are based on physical separation from the off-gas since krypton is chemically inert
- $\sim 95\%$ of Kr is stable
- Xenon, a chemically stable fission product is also recovered by these processes
 - Xenon is present at about 10 times the krypton mass concentration in the gas stream
 - Complicates Kr recovery and immobilization
 - May possibly have commercial value if clean enough

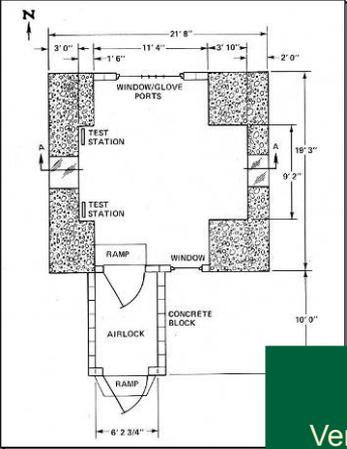
A Word on Complexity – What Looks Simple on a Block Diagram Isn't!



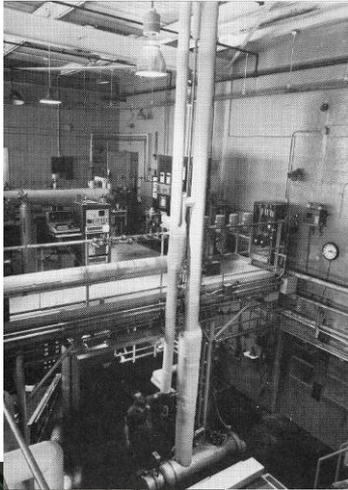
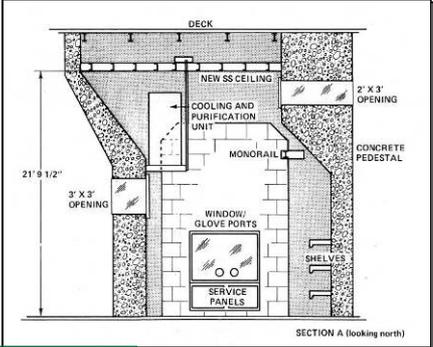
Other Considerations--

- **What has not been addressed?**
 - **VOG systems**
 - Typically higher flow
 - Much lower concentrations
 - Organics
 - **Waste system off-gas treatment systems**
 - **Cell Off gas systems**
 - Air / Inert / Purity (NO_x and other contaminants)
 - **Particulate filters**
 - **Chemical treatment technologies**
 - **Chemical impurities that add to waste volume**
 - Br / Cl in make-up acid
- **Other factors**
 - **Reuse options, e.g. Xe sales – purity requirements**

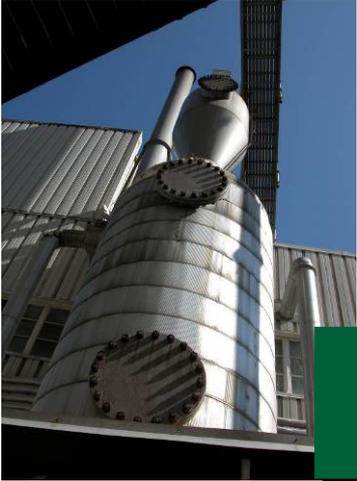
Fuel Reprocessing: Off Gas Treatment



Cell Ventilation



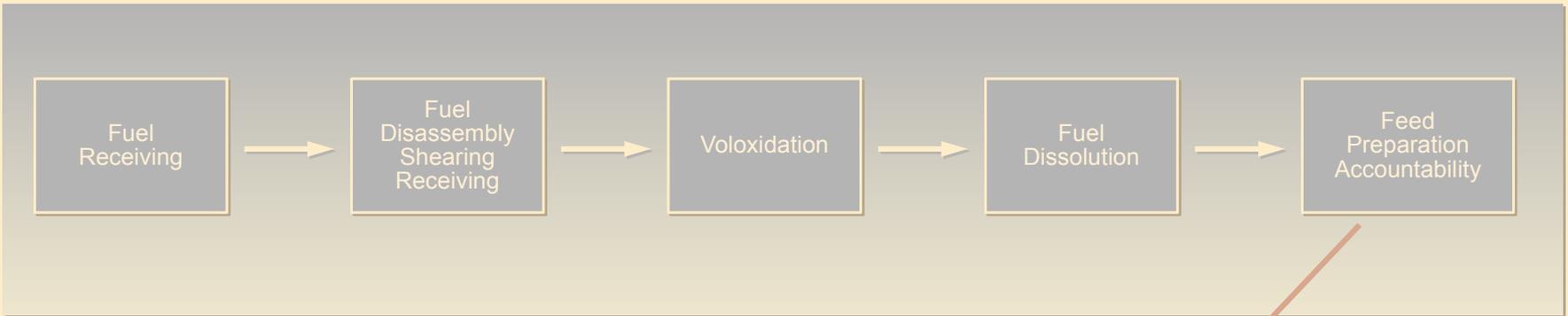
Dissolver Off-Gas



Vessel Off-Gas System



Head End

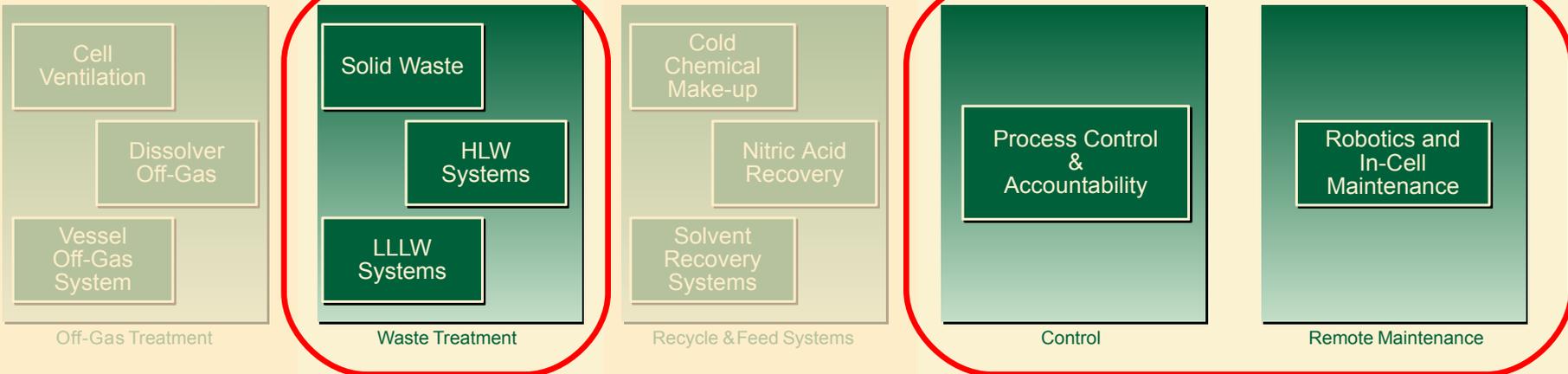


Separation Processes

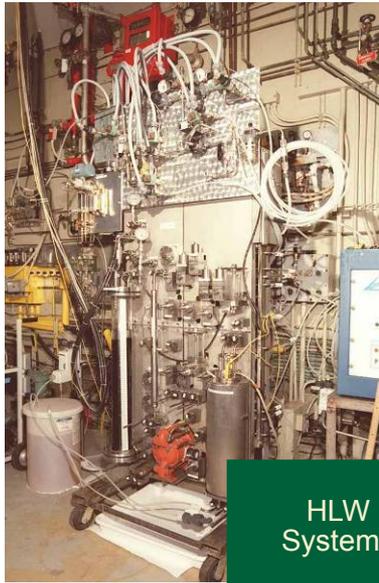


Conversion

Support Systems



Fuel Reprocessing: Waste Treatment



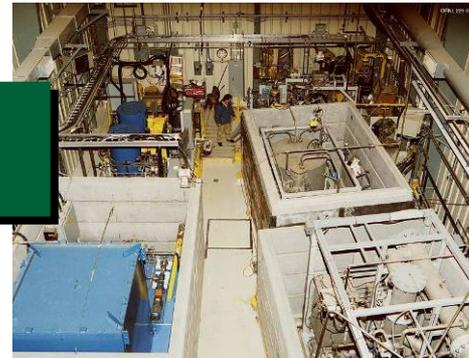
HLW
Systems



Solid Waste



LLLW
Systems



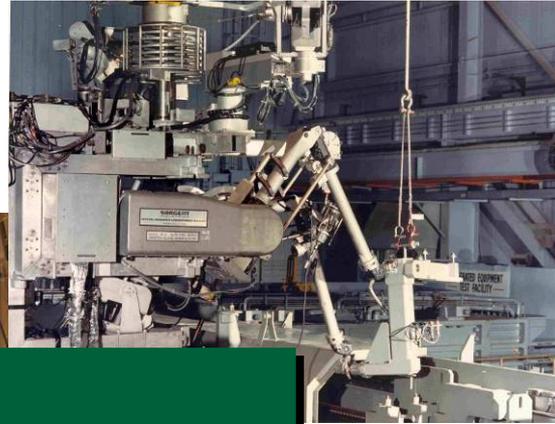
Fuel Reprocessing: Process Control and Accountability



Process Control



Fuel Reprocessing: Remote Maintenance



Robotics and In-Cell
Maintenance



What About Proliferation?

- Proliferation of fissile material (i.e. Pu) has been raised as a concern for several decades
- UREX and pyrochemical technologies were proposed as “proliferation resistant” technologies because Pu could be kept with other TRU or radioactive fuel components
 - Critics do not accept this argument
 - Pyroprocessing now called “reprocessing” rather than “conditioning” by NA-24
 - This has export control ramifications
- NA-24 is now basing “proliferation resistance” on Attractiveness Level
 - This opens the door to leave U with Pu to dilute it to a lower attractiveness level
 - This is a change from previous policy, that isotopic dilution was necessary (i.e. U-233 or 235)
- No technology by itself is intrinsically proliferation proof
- Technology is one aspect of a multifaceted approach that is necessary to protect fissile material (with safeguards, security, transparency, etc)

Where Are We Today?

- **Solvent extraction is a mature technology used at commercial scale to reprocess spent nuclear fuel**
- **Many new extractant molecules have been developed, but not demonstrated at large scale**
- **High throughput, high separation factors are achievable**
- **Electrochemical methods have been demonstrated for U recovery at engineering-scale**
- **TRU recovery and salt recycle have not been demonstrated at engineering-scale**

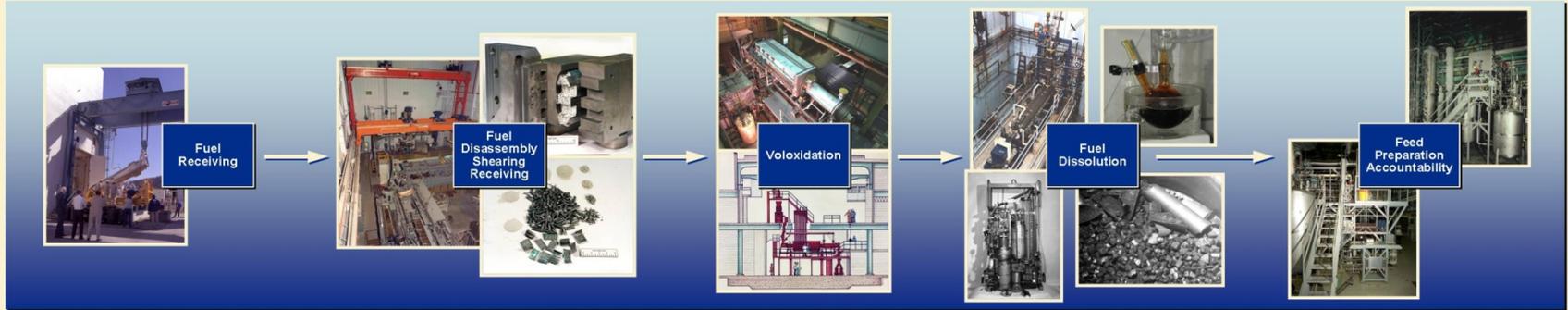
Where Are We Going?

- **Research into advanced separation methods as part of the Advanced Fuel Cycle program in progress**
 - **New Aqueous methods**
 - **Electrochemical methods**
 - **Transformational methods**
- **Integration of separation R&D efforts with waste form and fuel fabrication is essential**
 - **No more “throw it over the fence approach”**

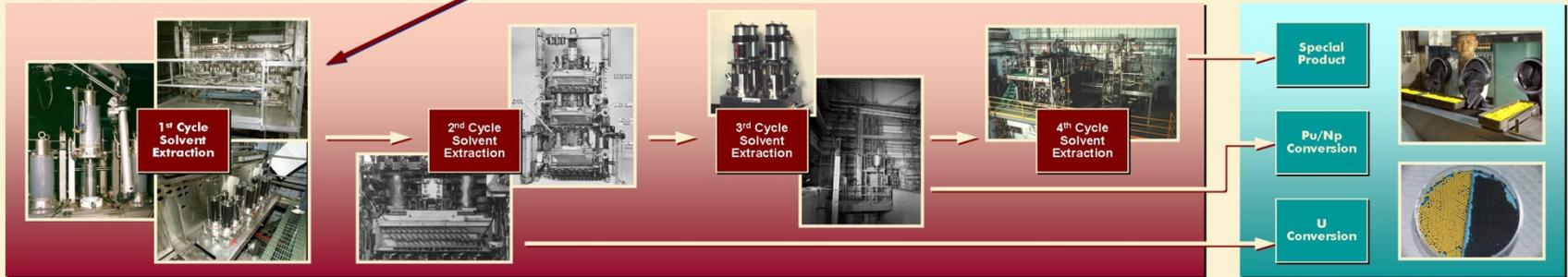
Fuel Reprocessing: The Big Picture

(actually a lot of little pictures)

Head End



Separation Processes



Conversion

Support Systems



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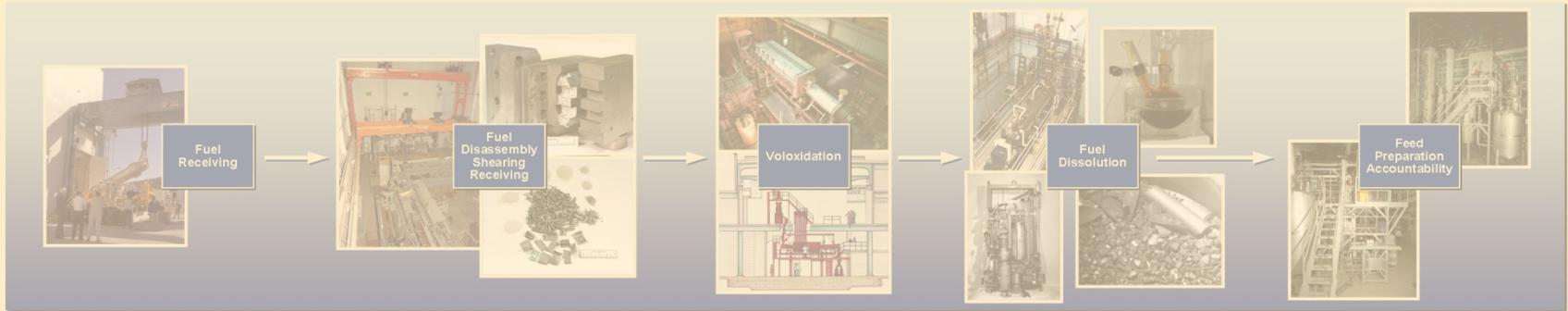
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Fuel Reprocessing: The Big Picture

(actually a lot of little pictures)

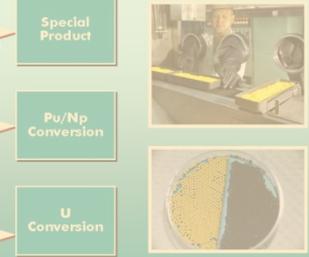
Head End



Separation Processes



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