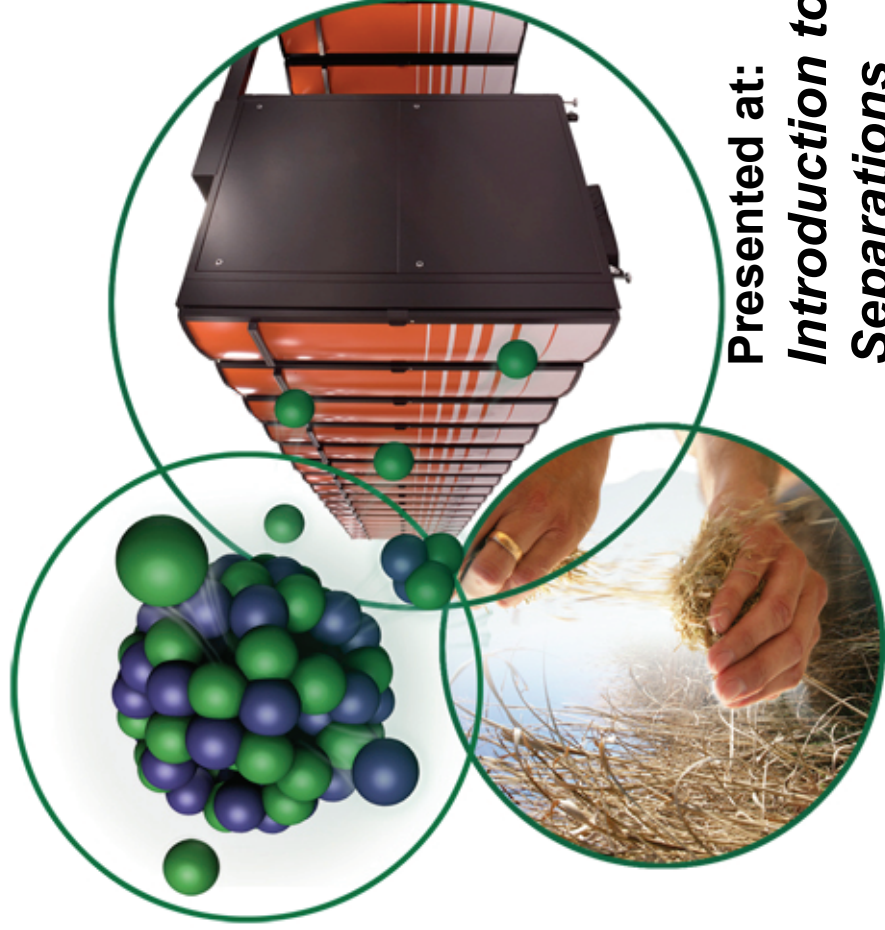


Spent Fuel Recycle



Robert Jubin
**Nuclear Science and
Technology Division**
Oak Ridge National Laboratory

Presented at:
***Introduction to Nuclear Chemistry and Fuel Cycle
Separations***
Vanderbilt University
Dec. 16, 2008

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for the Department of Energy

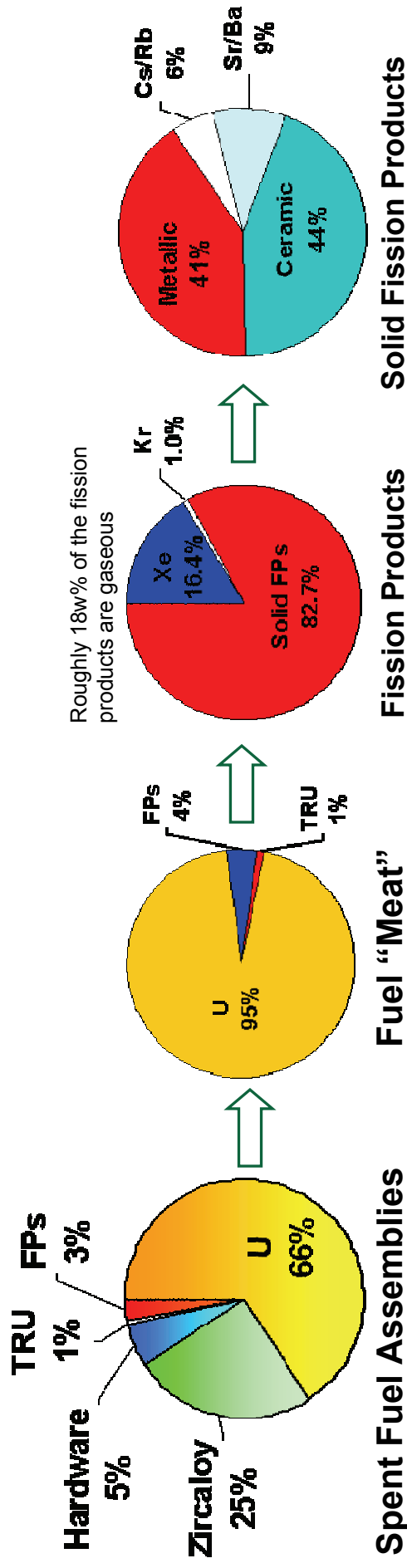
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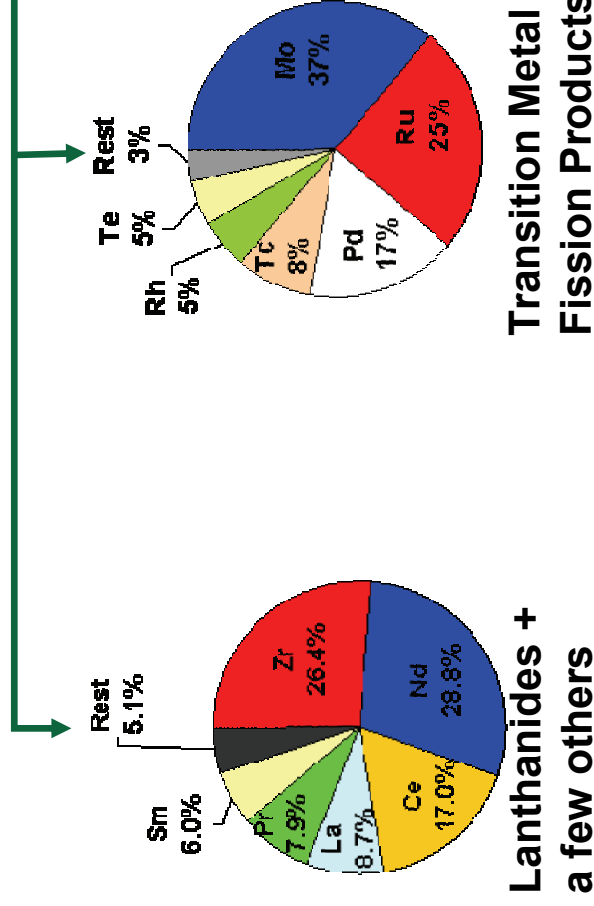
Overview

- Head-end
- Primary separations
- Product conversion
- Supporting separations
- Off-gas treatment

Composition of used fuel



Roughly 18w% of the fission products are gaseous

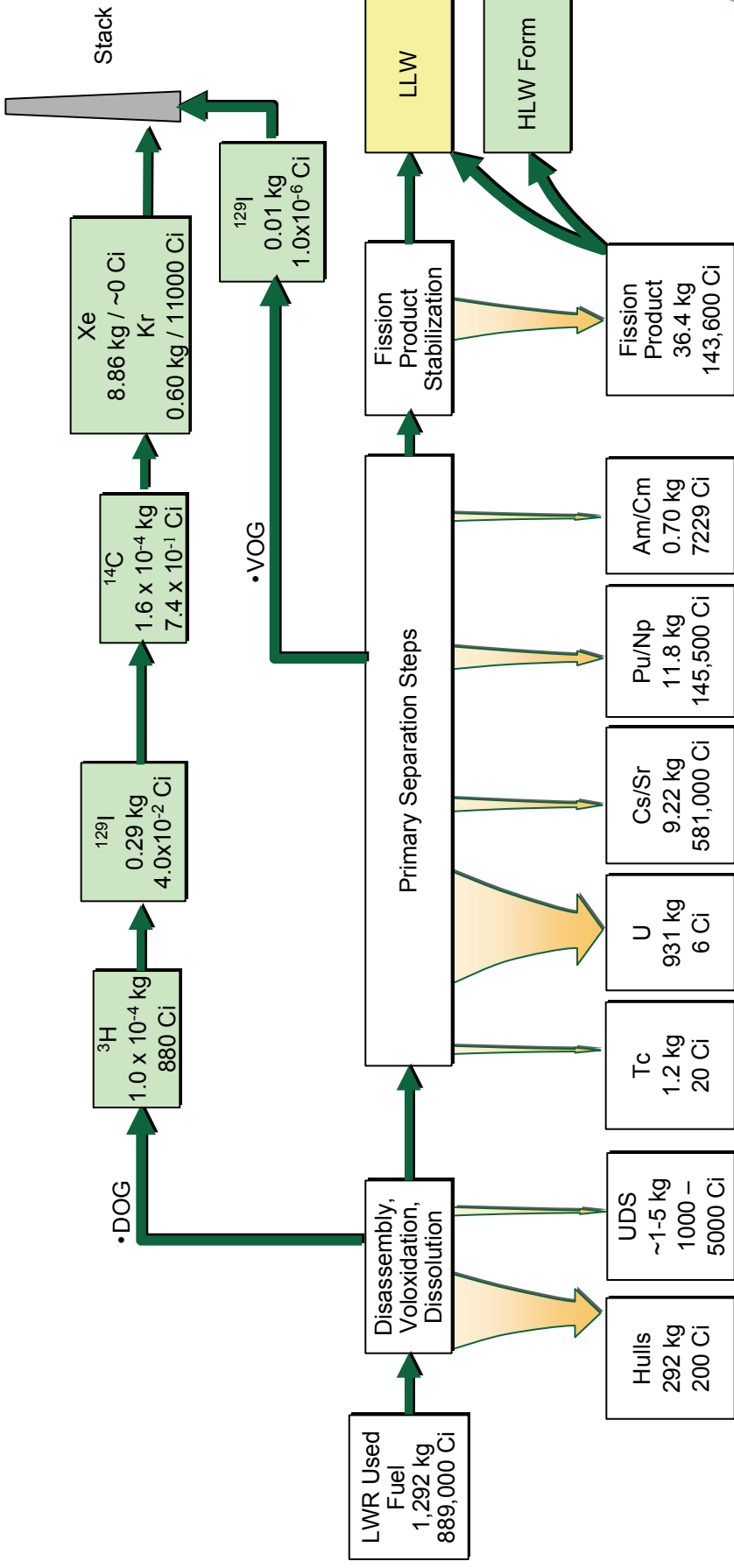


(Del Cul, ORNL)

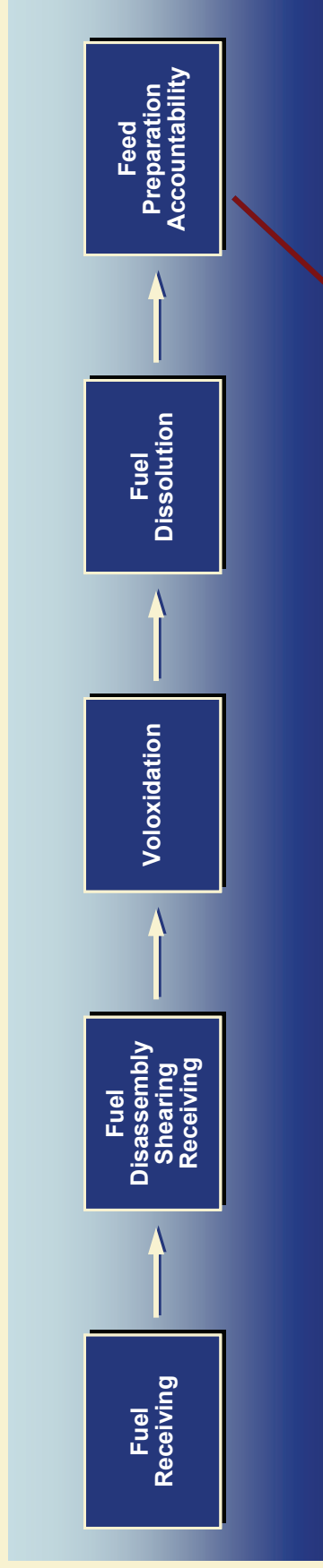
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Simple Reprocessing Demonstration

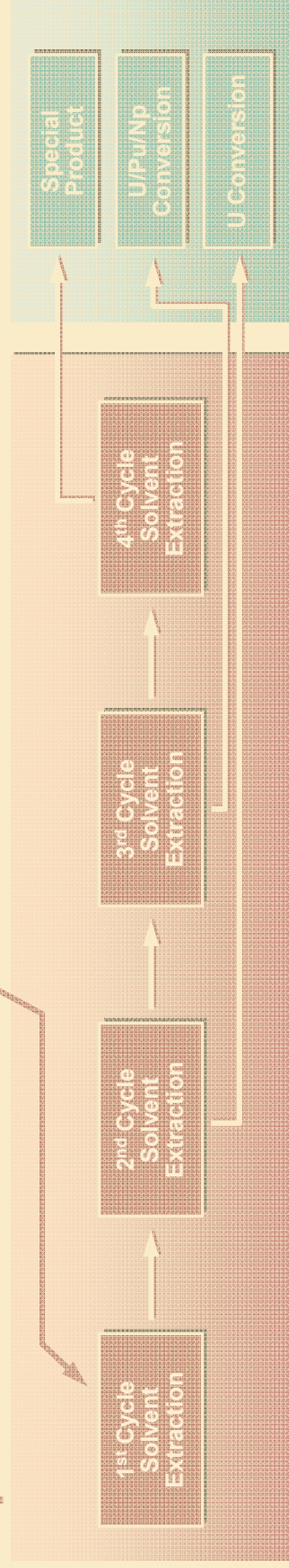
(Mass Basis: 1 MT SNF; 55 GWD/MTIHM; 5 year Cooling)



Head End

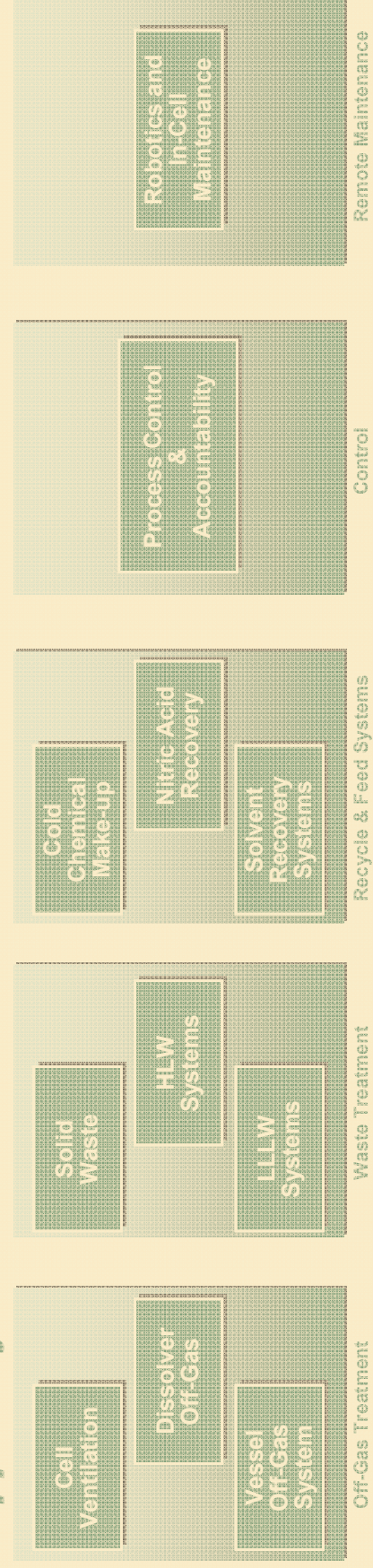


Separation Processes

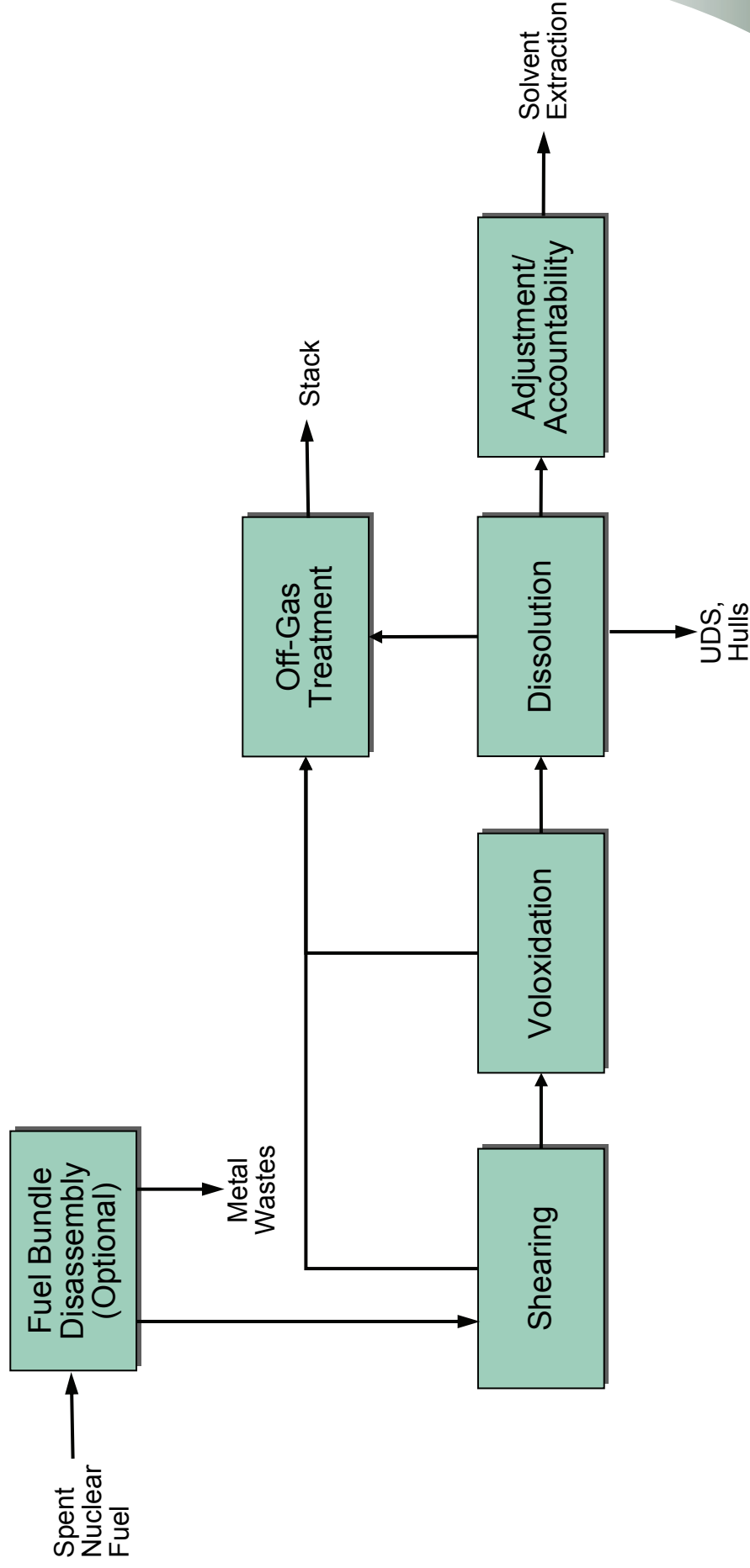


Conversion

Support Systems



Block Diagram of Aqueous Head-end



Exposing Fuel/Target Material

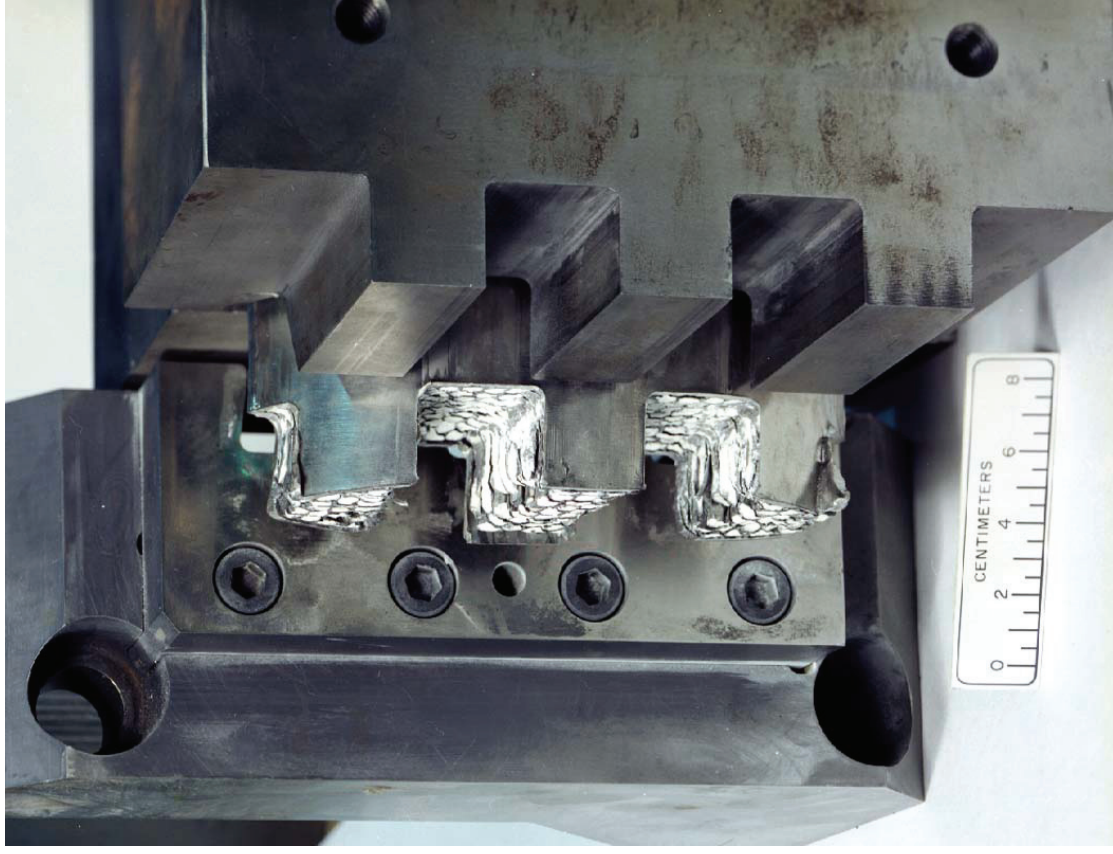
- Preliminary step is to remove nonfuel-bearing hardware
- Process: State-of-the-art for most fuels (oxides) is to create short segments, exposing fuel/target material at the ends of the segments
 - Chemical decladding is uneconomical in most cases because of excessive waste production
 - Mechanical 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

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

Shear with Dummy Fuel Assembly



Sheared simulated fuel



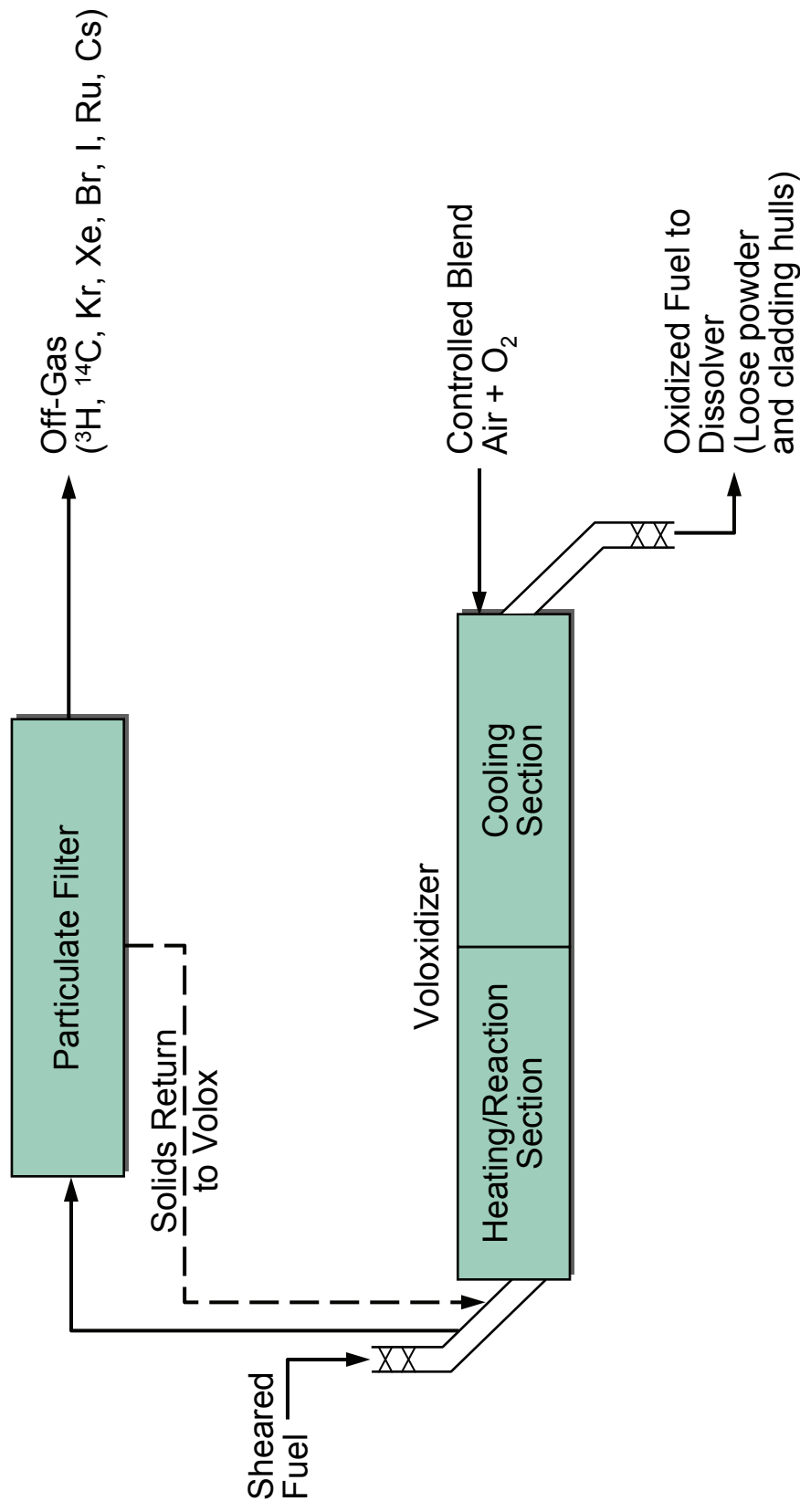
(Croff, K/NSP-121/Part 23/R2)

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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.

Voloxidizer: Standard Operation



Full-scale experimental voloxidizer during installation

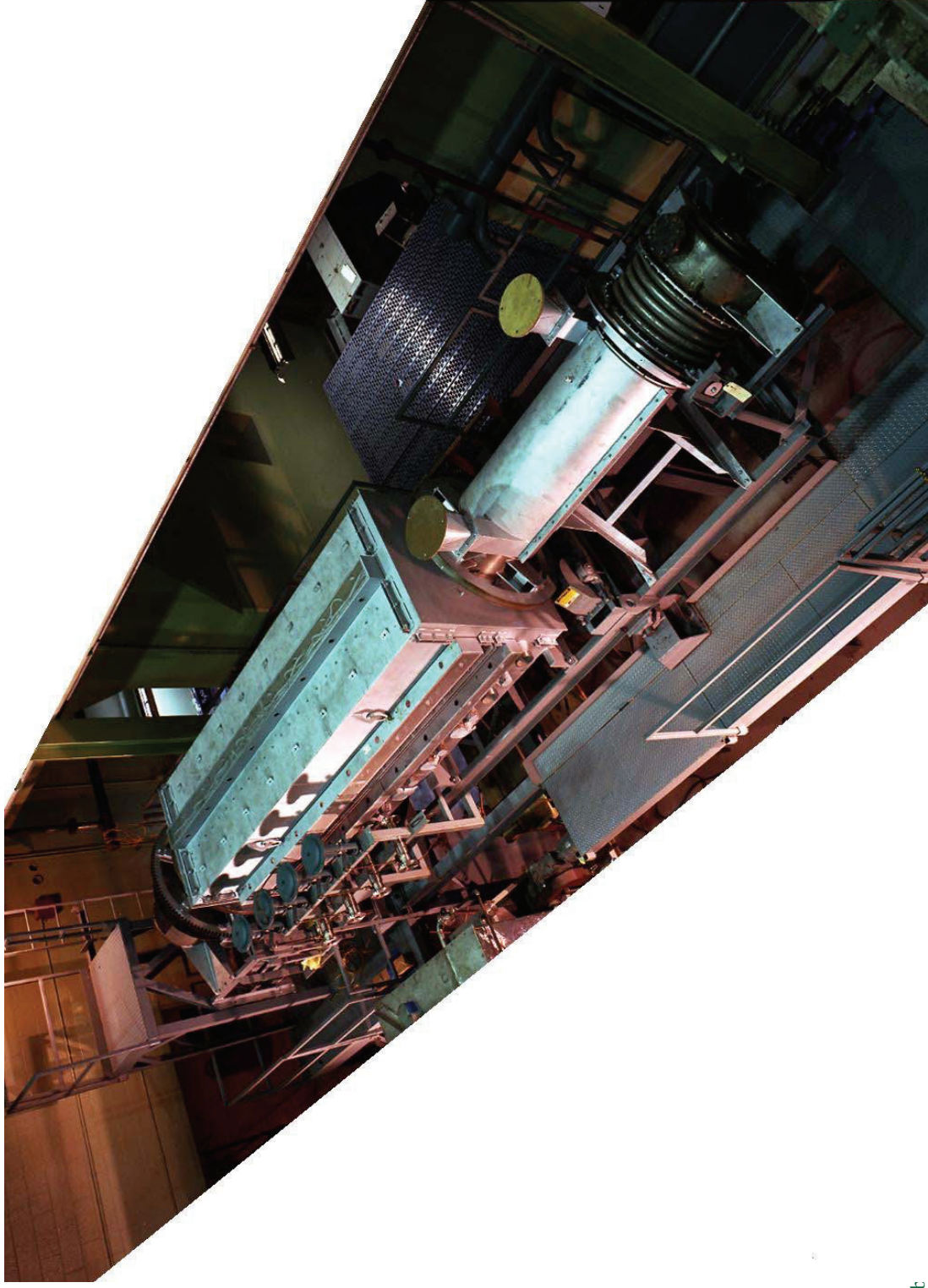
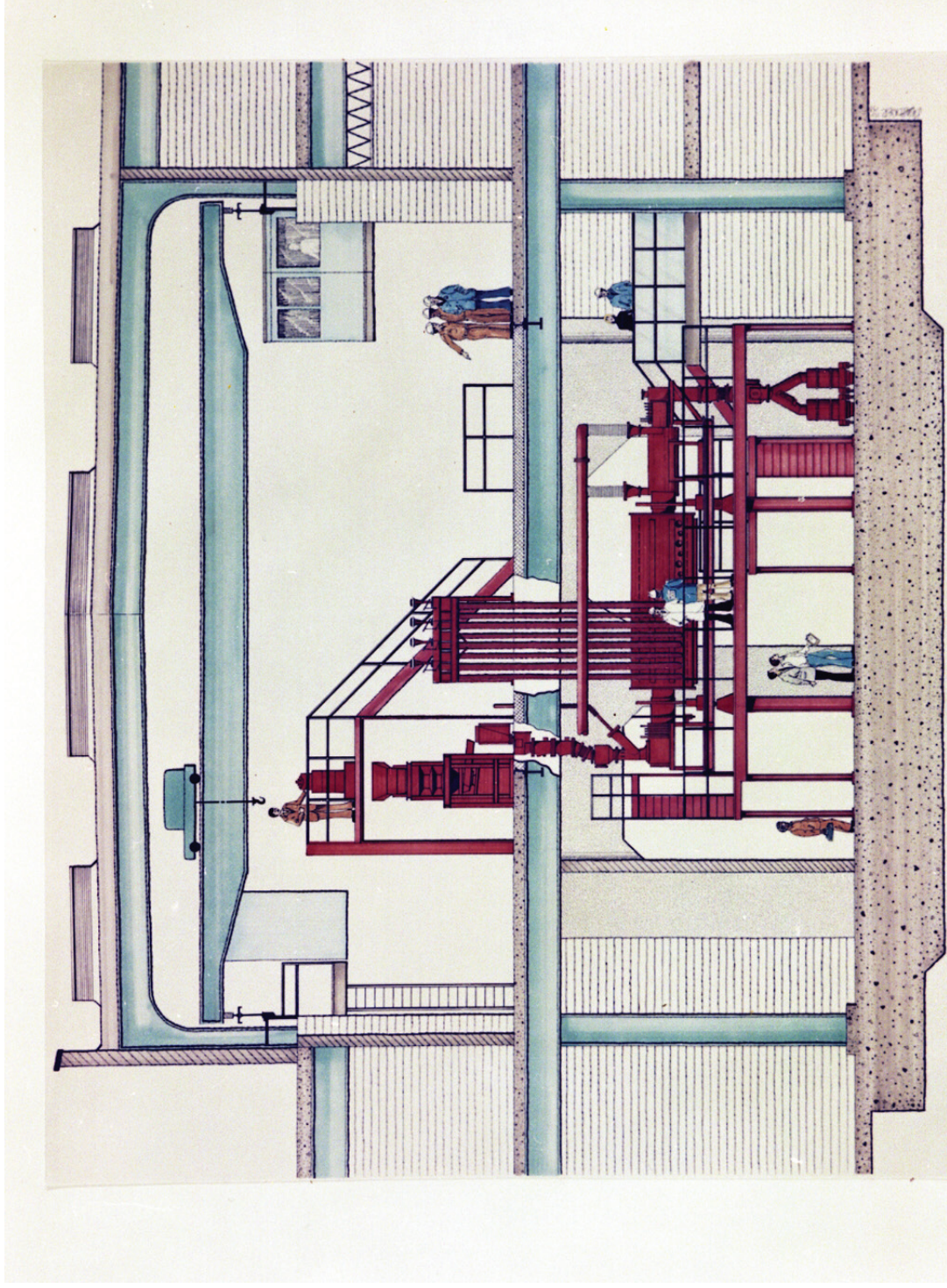
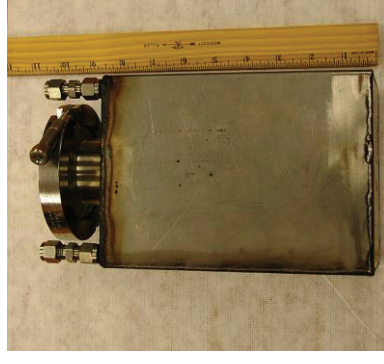
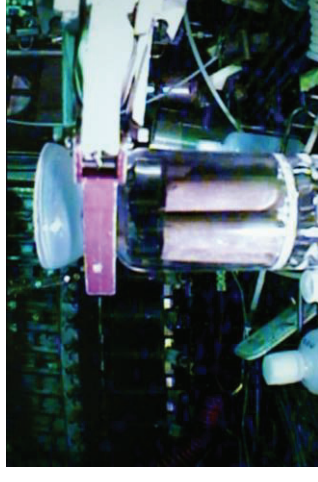


Illustration of installed experimental 0.5 MT/day voloxidizer



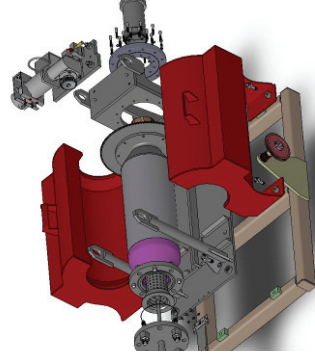
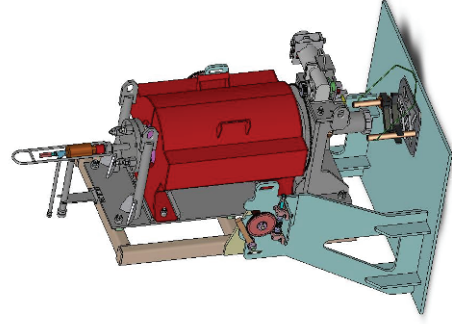
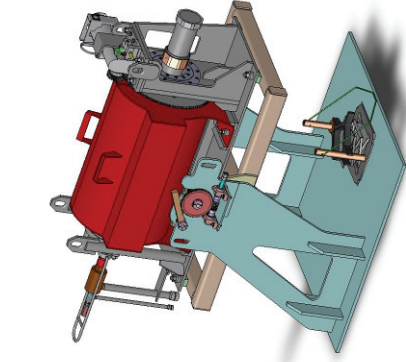
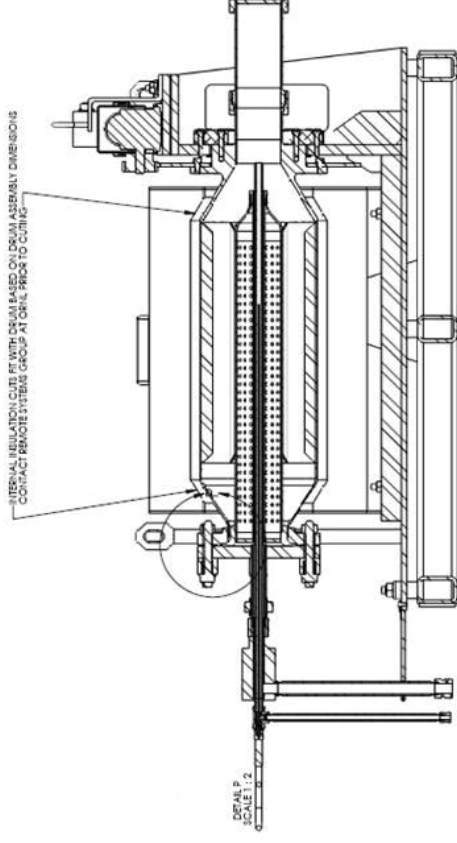
Run 1—Dresden Fuel

- Voloxidized ~3.5 kg of Dresden Fuel at REDC
 - Used very simple vessels for oxidation process
 - 1.268 kg, still in the clad, processed in quartz vessel in several 200 g sub-batches
 - 2.266 kg loose pellets/pellet fragments processed in stainless steel vessel in two sub-batches
 - Product dissolved readily
 - Undissolved residue analyzed
 - Clad/Fuel powder separated cleanly

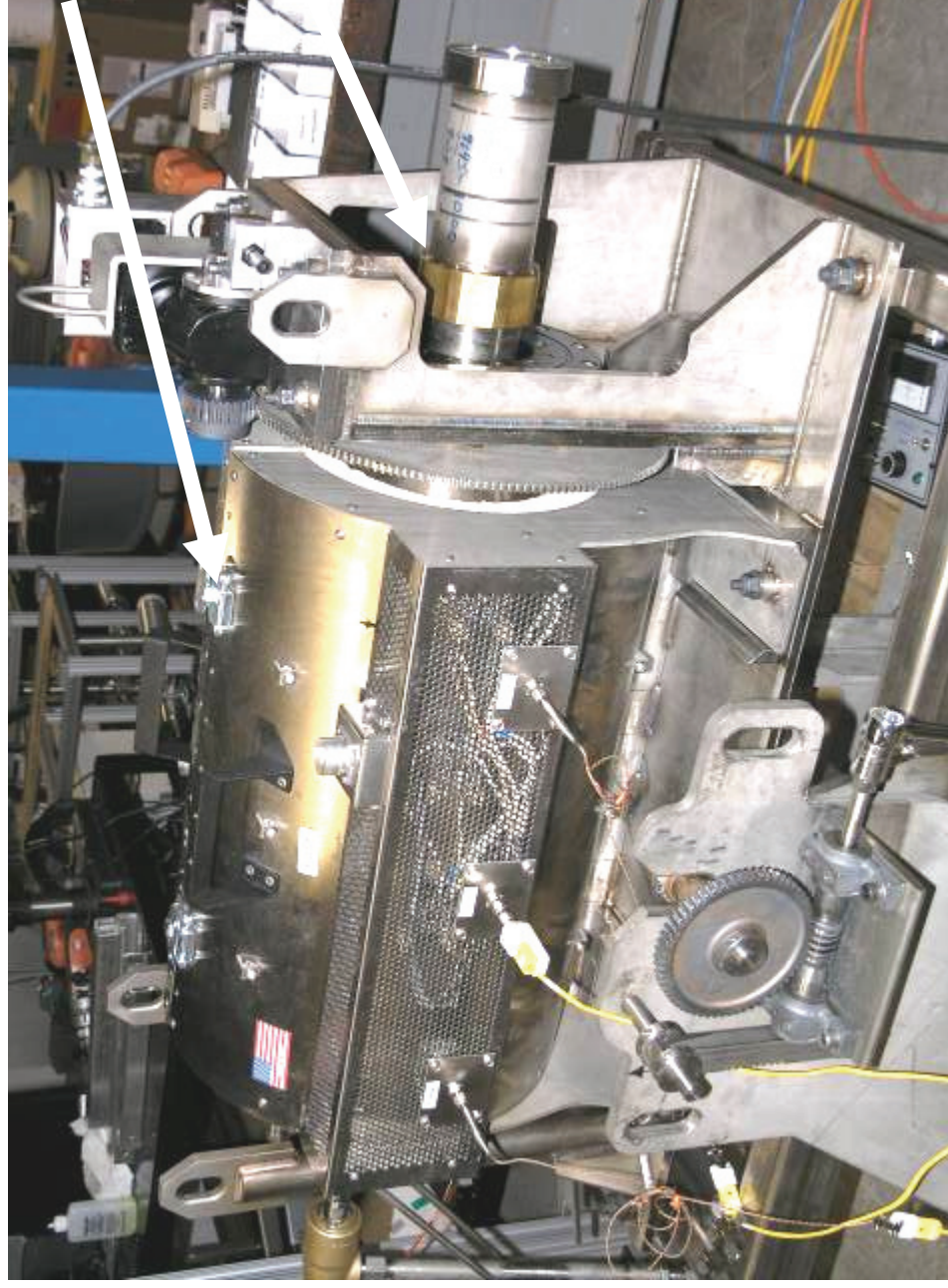


Features of a Small Batch Voloxidizer

- Most of the retort tube is enveloped by the furnace
- Rotating tube
- Variable operating environment
- Removable hulls basket
- Powder transfer can integrated into design
- Tilting platform can force material into hotter zones



Small Batch Voloxidation



Rotary Kiln w/
Heater in Place

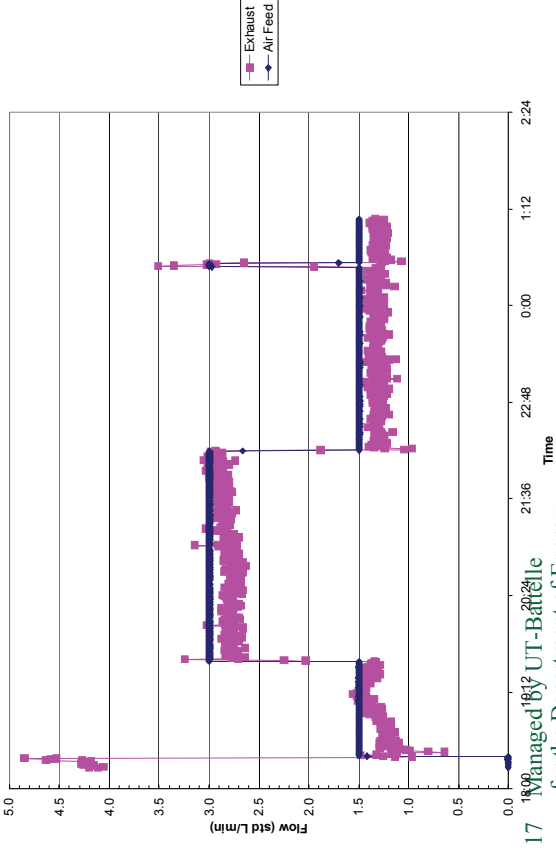
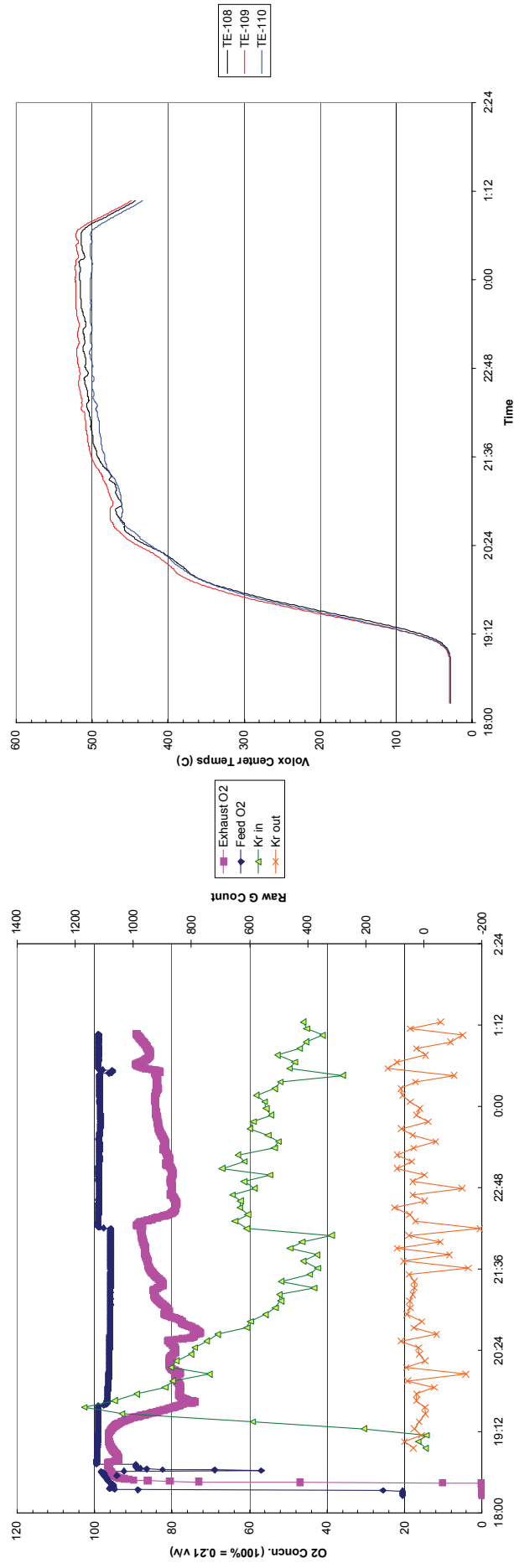
Product Canister

Voloxidation Run 2—Batch 1

- First batch was comprised of Surry-2 fuel
 - Initial enrichment 3.11%
 - Burnup: 36 GWd/MT heavy metal
 - Cooling time: 27 years (discharged from reactor in 1981)
 - Amount: 1704 g (316 g hulls, 1388 g fuel)
- Experiment
 - Fuel was oxidized in air at about 500°C
 - The run was prematurely terminated due to apparent cessation of oxygen consumption
 - Occurred after 4 hours of operation at temperature
 - Weighing of product powder and hulls showed that fuel was only 70% oxidized
 - There was potential for a cold zone near the closure flange, causing slow kinetics
 - Complete batch of fuel was re-run to finish the oxidation
 - Operation at temperature for 4 hours was done to ensure complete oxidation
 - 1542 g fuel powder recovered (indicates DU carry-over from shakedown run)
 - The voloxidizer was periodically tilted from the horizontal to cause fuel to migrate from the cold zone into the hot furnace zone
 - Both oxygen consumption and ⁸⁵Kr evolution was used to monitor progress and reaction endpoint

Run 2—Batch 1—Part A

O₂ and Kr⁸⁵ Concentrations, Air Flow, and Temperatures



Run 2 Voloxidation Products



Post Voloxidation products:
Powder and empty hulls

Enhanced Voloxidation Option: UO_3

- Standard voloxidation of UO_2 at $\sim 500^\circ\text{C}$ produces U_3O_8 as a fine powder due to the great volume expansion
- This black U_3O_8 powder readily reacts with O_3 at lower temperature to form an even finer red colored UO_3 powder
 - Enhanced removal of volatiles (e.g. iodine)
 - Facilitates HNO_3 dissolution
 - Less acid consumption
 - Minimize formation of NOx gases, simpler wet off-gas system

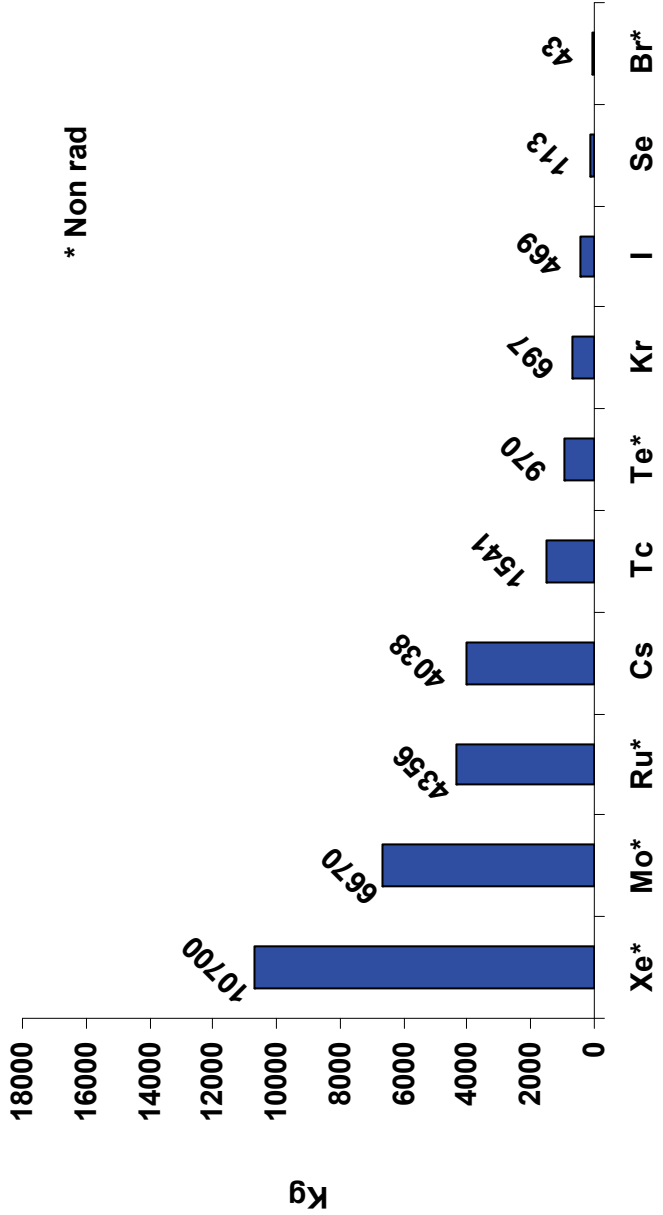
U_3O_8



XRD:
Monoclinic
 UO_3



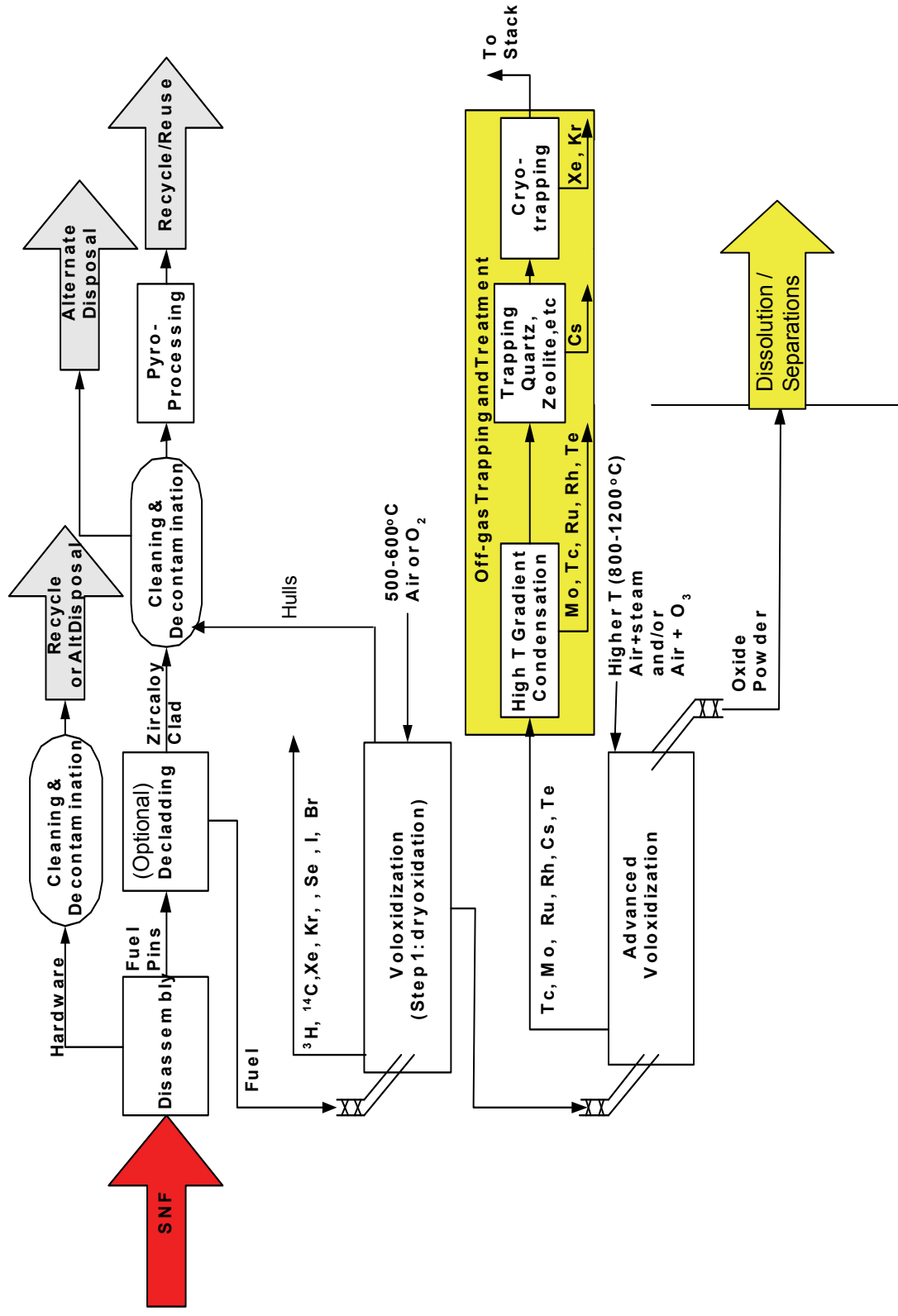
Species that can be partially or totally removed during head-end treatment (Kg per 2000 MT of PWR-SF at 33GWd/MT)



Percent Removal		^{14}C		^{85}Kr	^{129}I	Cs	Ic	Ru	Rh	Te	Mo		
^3H	100	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

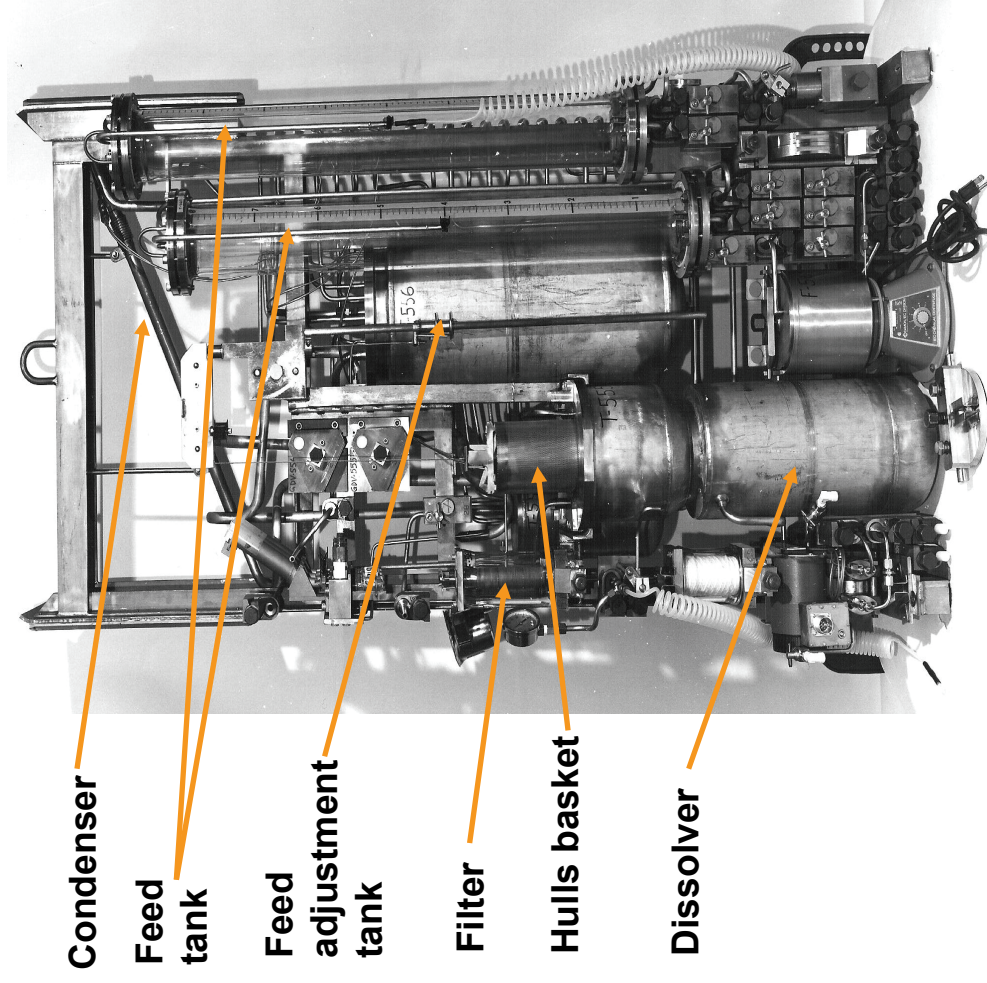
- **Operations**
 - Exposed fuel or target material is placed in a perforated metal basket
 - Basket is immersed into hot nitric acid where essentially all of the fuel or target dissolves
 - Basket containing undissolved cladding is removed and cladding treated as waste
- **Equipment has proven to be 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:
 - $3\text{UO}_2 + 8\text{HNO}_3 \rightarrow 3\text{UO}_2(\text{NO}_3)_2 + 2\text{NO} + 4\text{H}_2\text{O}$
 - At high acid:
 - $\text{UO}_2 + 4\text{HNO}_3 \rightarrow \text{UO}_2(\text{NO}_3)_2 + 2\text{NO}_2 + 2\text{H}_2\text{O}$
 - “Fumeless”:
 - $2\text{UO}_2 + 4\text{HNO}_3 + \text{O}_2 \rightarrow 2\text{UO}_2(\text{NO}_3)_2 + 2\text{H}_2\text{O}$
- For UO_3
 - $\text{UO}_3 + 2\text{HNO}_3 \rightarrow \text{UO}_2(\text{NO}_3)_2 + \text{H}_2\text{O}$
- For U_3O_8
 - Combining UO_2 and UO_3 reactions yields:
 - $\text{U}_3\text{O}_8 + 7\text{HNO}_3 \rightarrow 3\text{UO}_2(\text{NO}_3)_2 + 0.5\text{NO}_2 + 0.5\text{NO} + 3.5\text{H}_2\text{O}$
 - By the approximate equation:
 - $\text{U}_3\text{O}_8 + 7.35\text{HNO}_3 \rightarrow 3\text{UO}_2(\text{NO}_3)_2 + \text{NO}_2 + 0.35\text{NO} + 3.65\text{H}_2\text{O}$

Development / Pilot Scale Dissolution Equipment



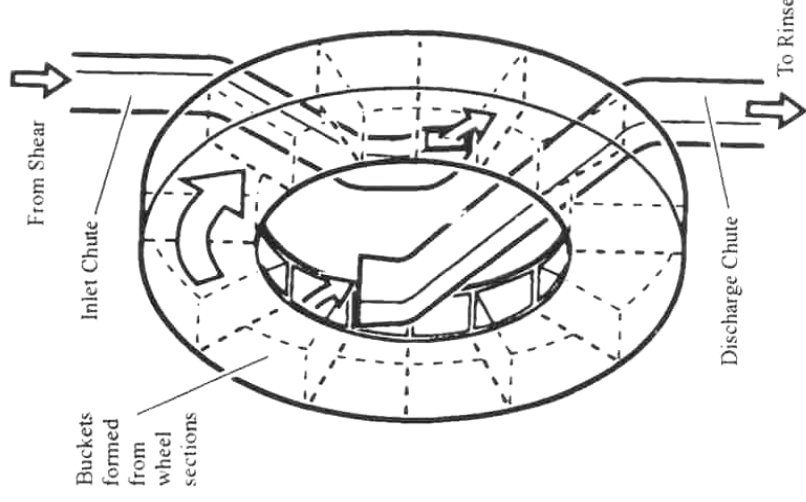
- Utilize existing equipment from previous research with LWR fuel
 - ~14L stainless steel jacketed dissolution tank
 - Metal screen basket insert for sheared fuel pieces
 - ~25L stainless steel SX feed adjustment tank
 - Two 8L feed metering tanks
- Special powder feeder designed to handle voloxidized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

Radiochemical Engineering Development Center Batch Dissolver Rack

Dissolution Equipment

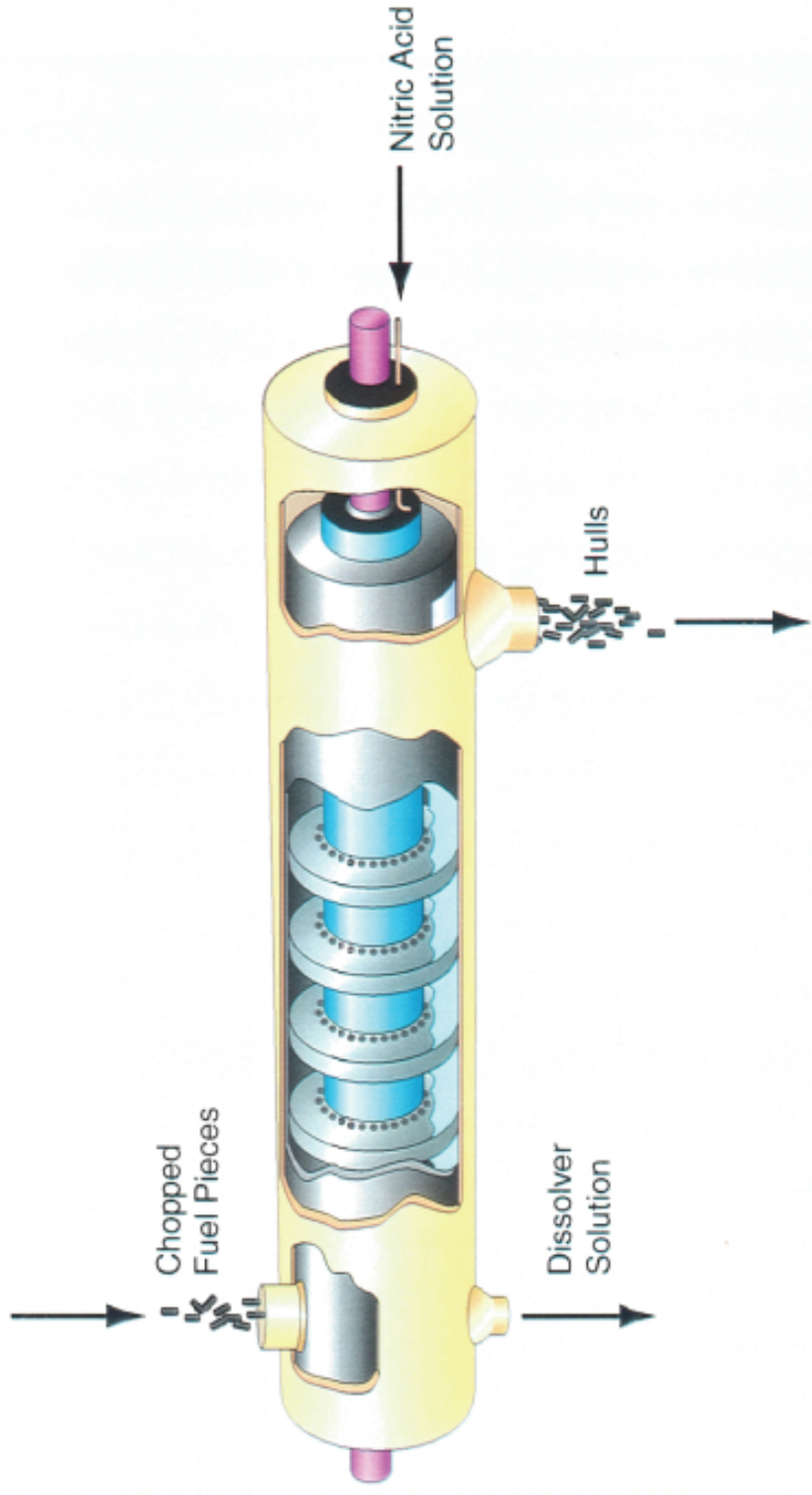
- **Ferris Wheel Dissolver**

- 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)

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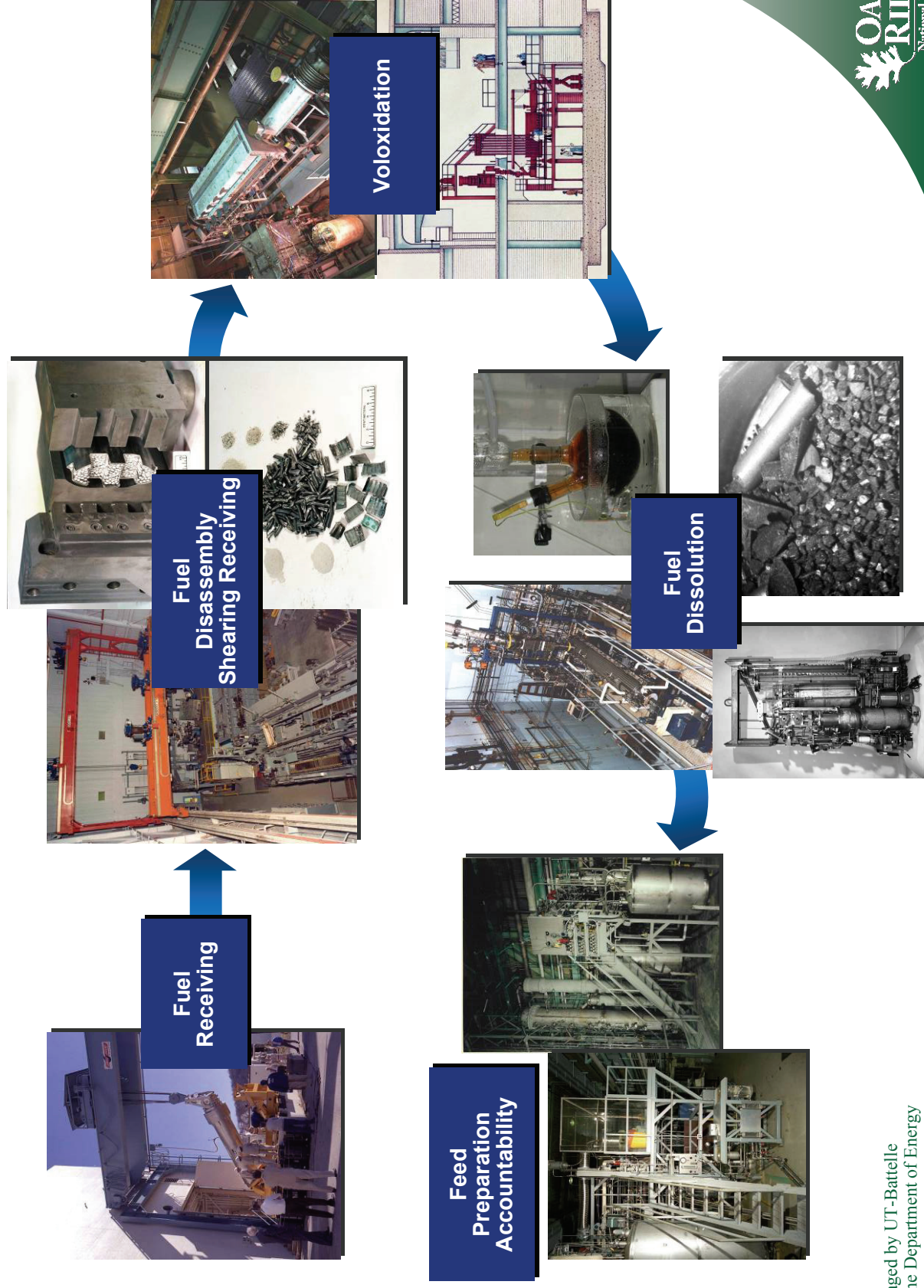
Feed Preparation

- 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



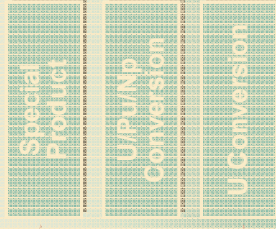
Head End



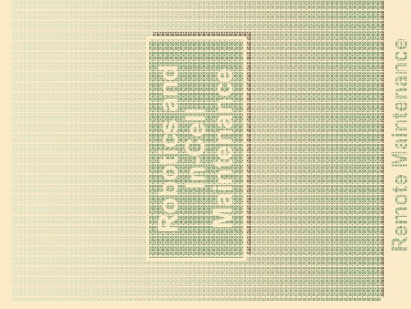
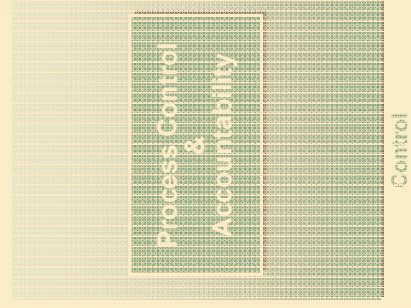
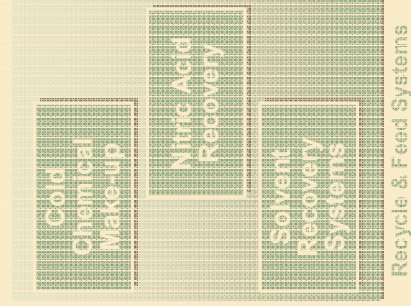
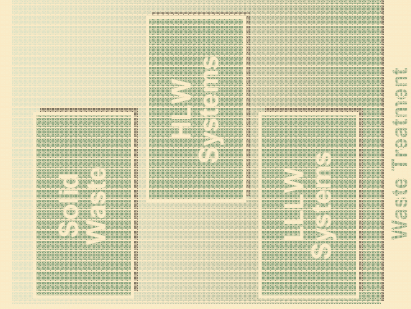
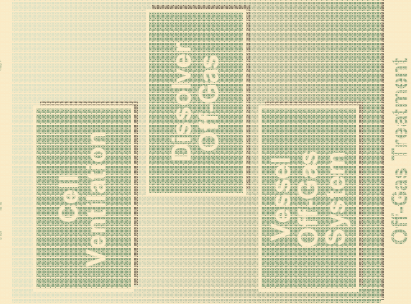
Separation Processes



Conversion



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)

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

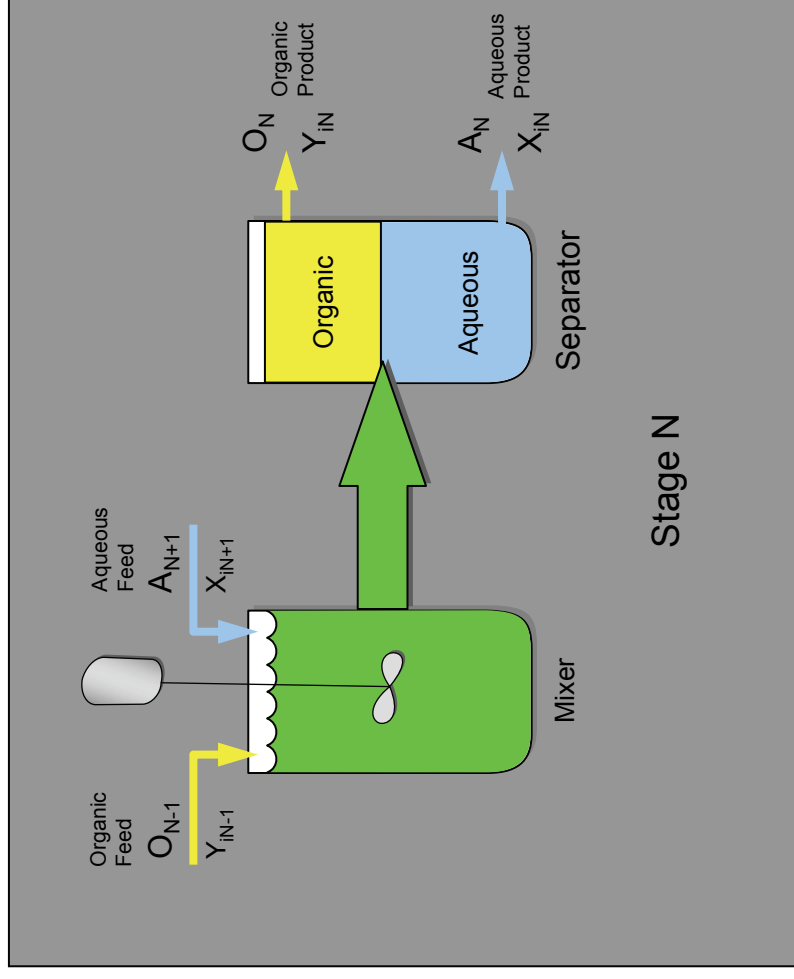
- What's extracted?

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

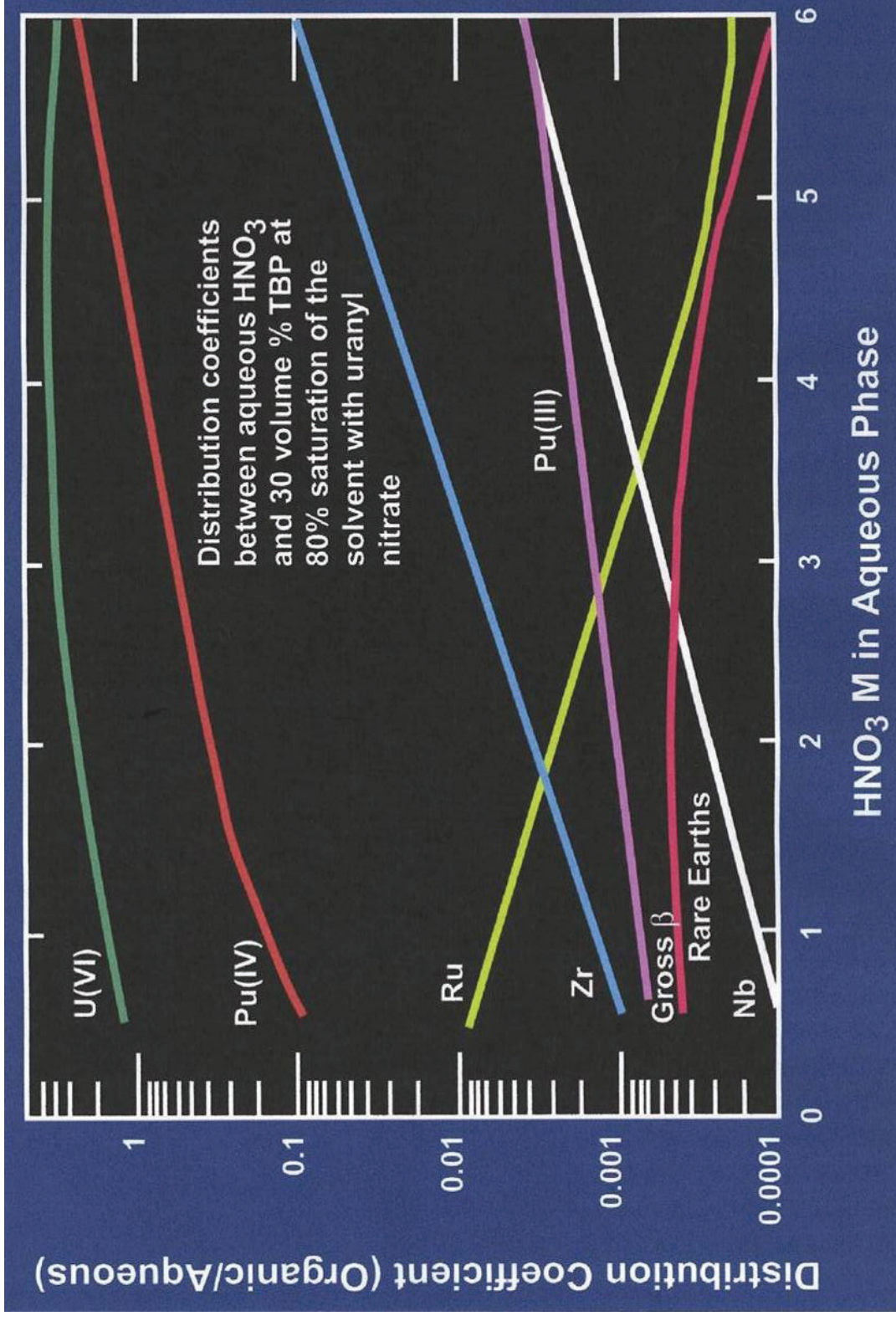
$$y_n = D(x_{n+1}) / (OD/A + 1)$$

The fraction extracted is:

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

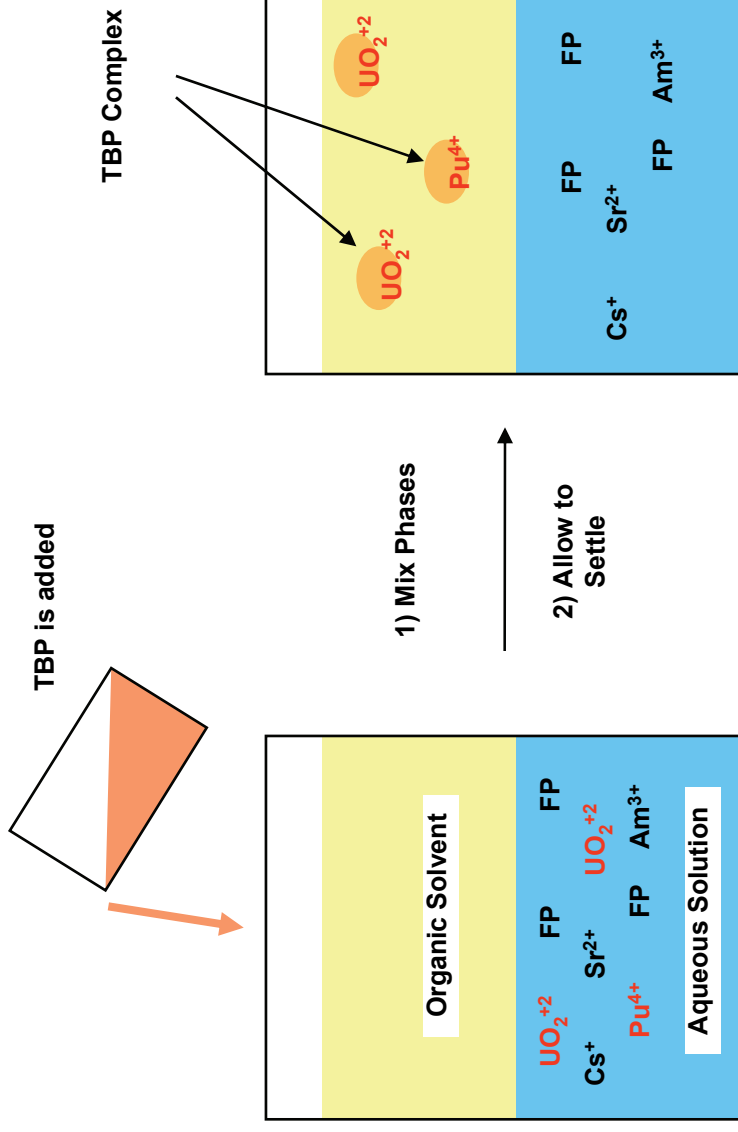


Effect of Nitric Acid Concentration on Extraction by TBP



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

PUREX Process- Basic principles

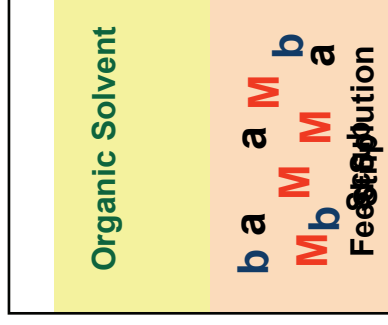


PUREX Process- Basic principles

Extraction

Scrubbing

Stripping

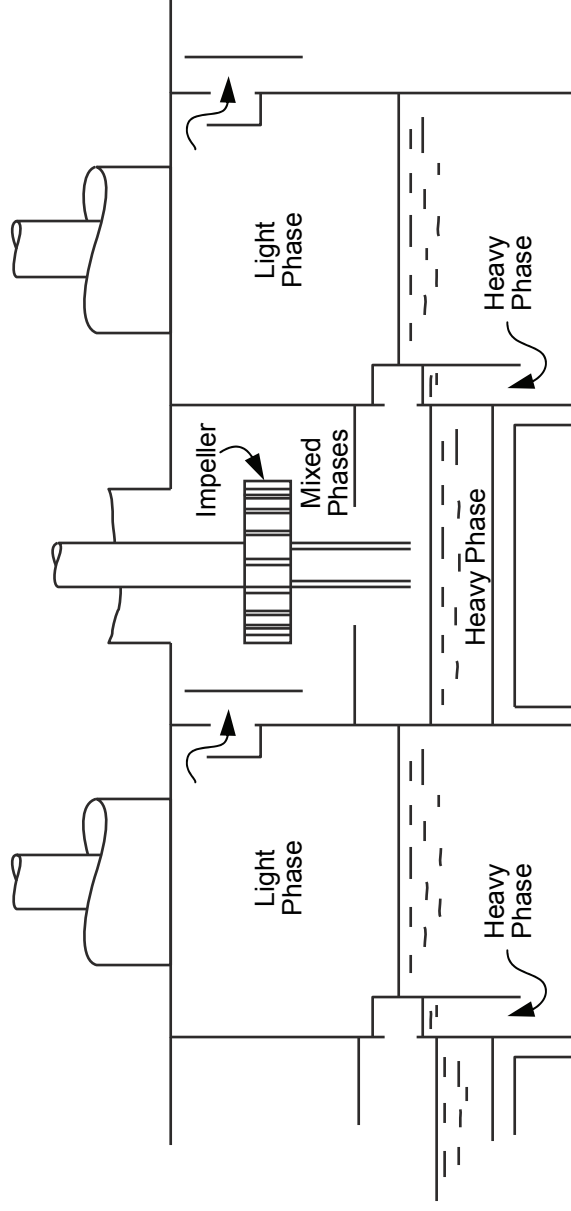
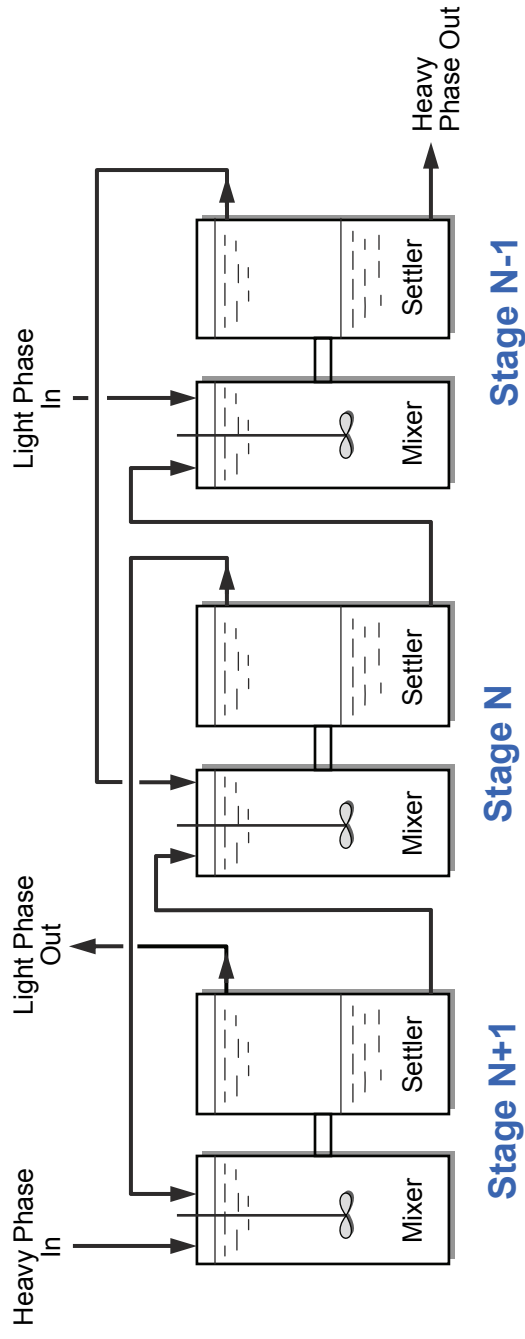


Separates metal to be recovered

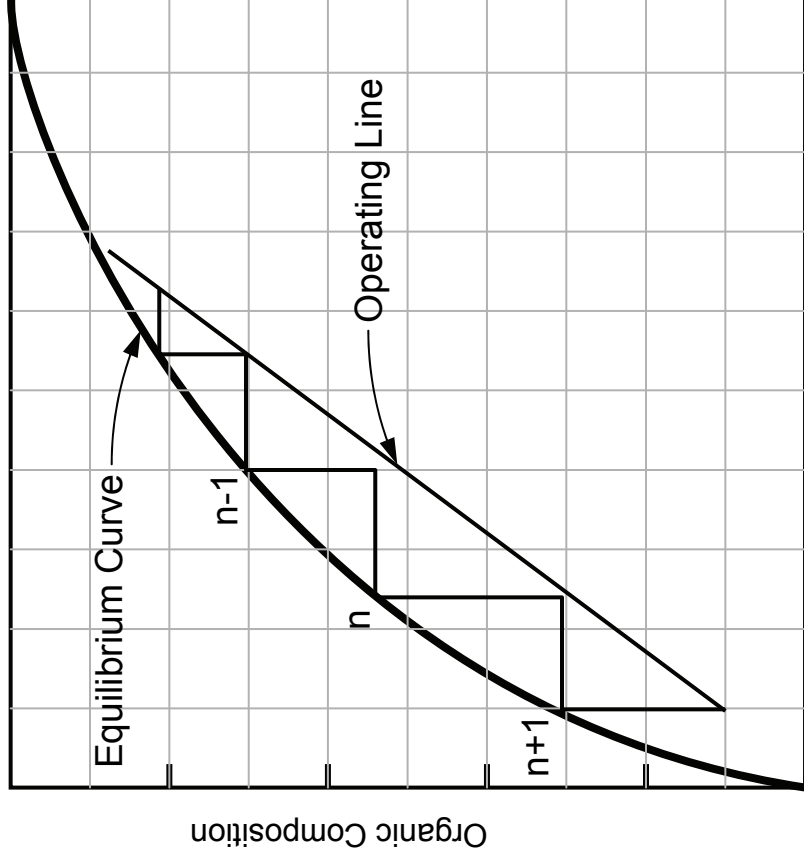
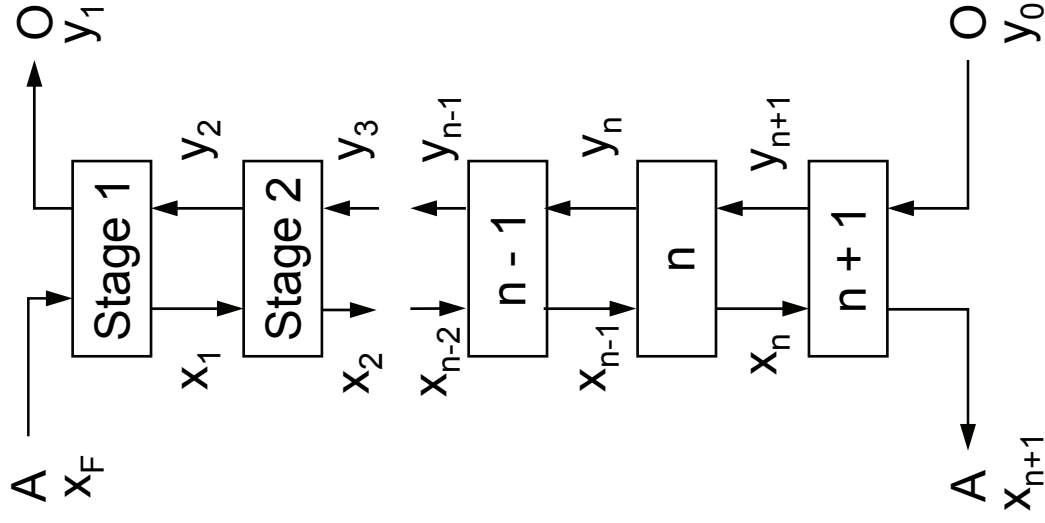
Removes impurities from metal

Recovers product in solution

Multistage Operations



Simple example of multistage SX

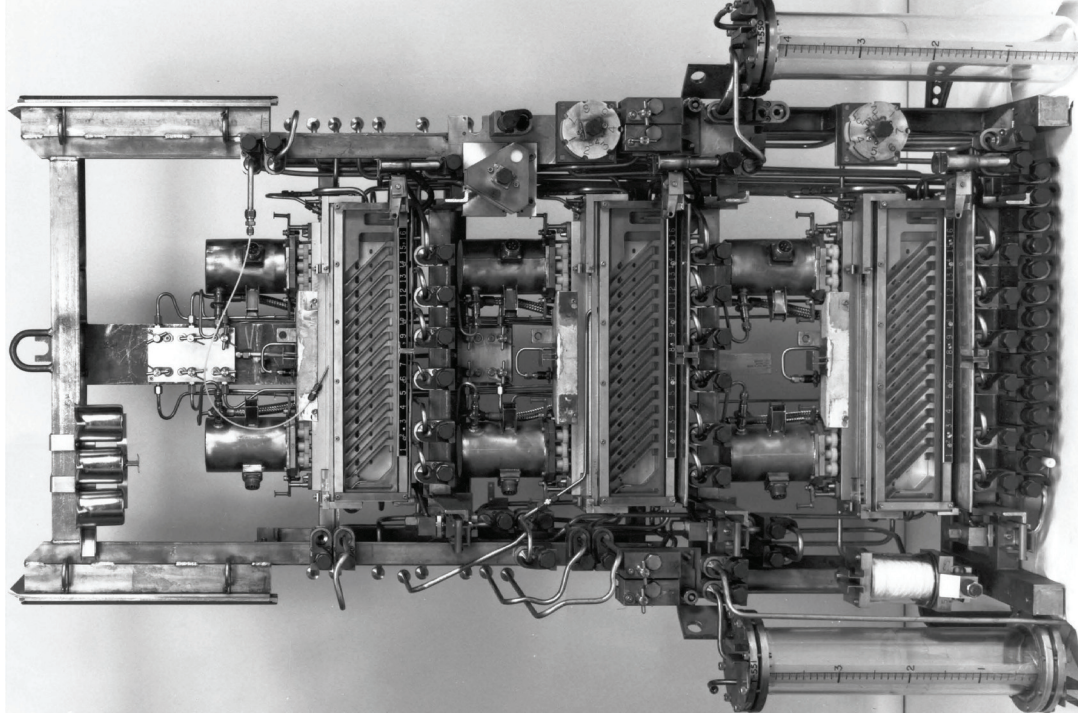


Aqueous Composition

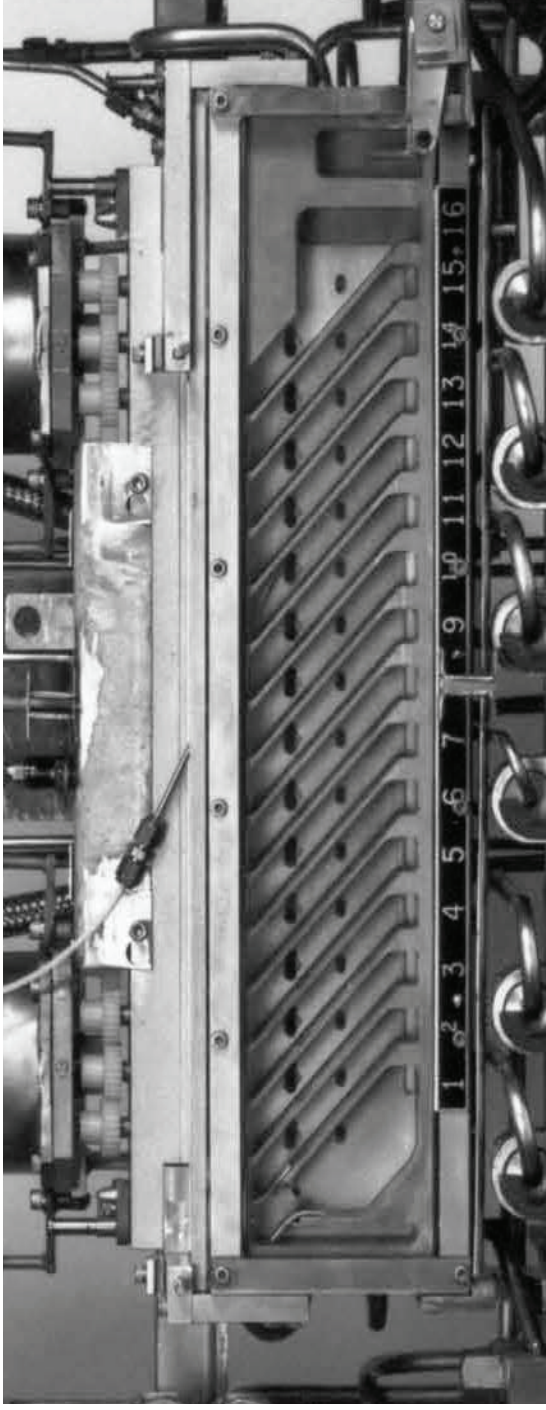
See also A. D. Ryon, ORNL-3045, 1961

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



Solvent Extraction Equipment

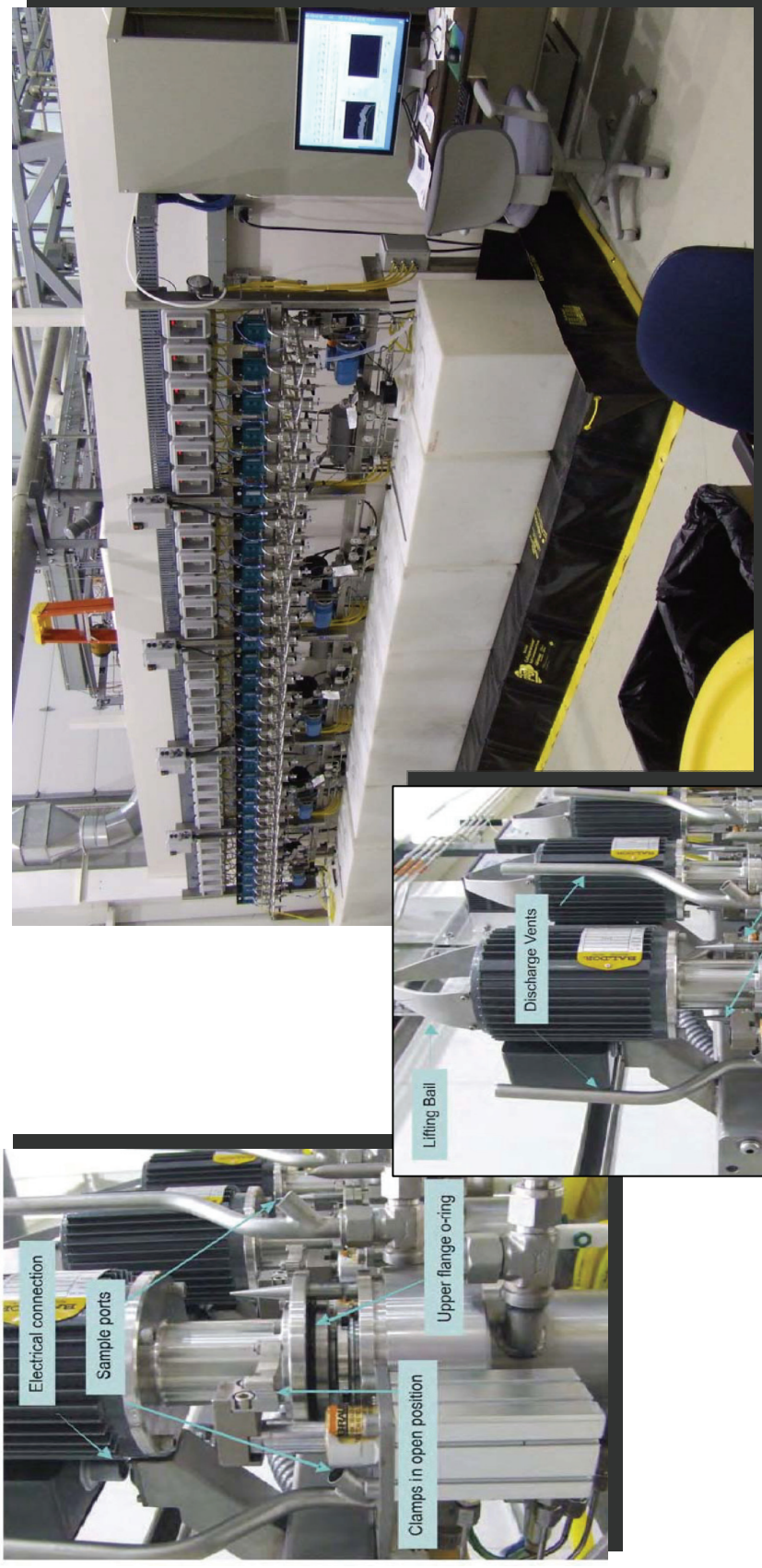


- Quartz window allows viewing of settling stages
- Contactors are open on the top for reagent additions and stage sampling
- Mixer/settler volumes are 30/50 mL, respectively
- Throughput: up to 5L/h total flow

Solvent Extraction Equipment in Operation

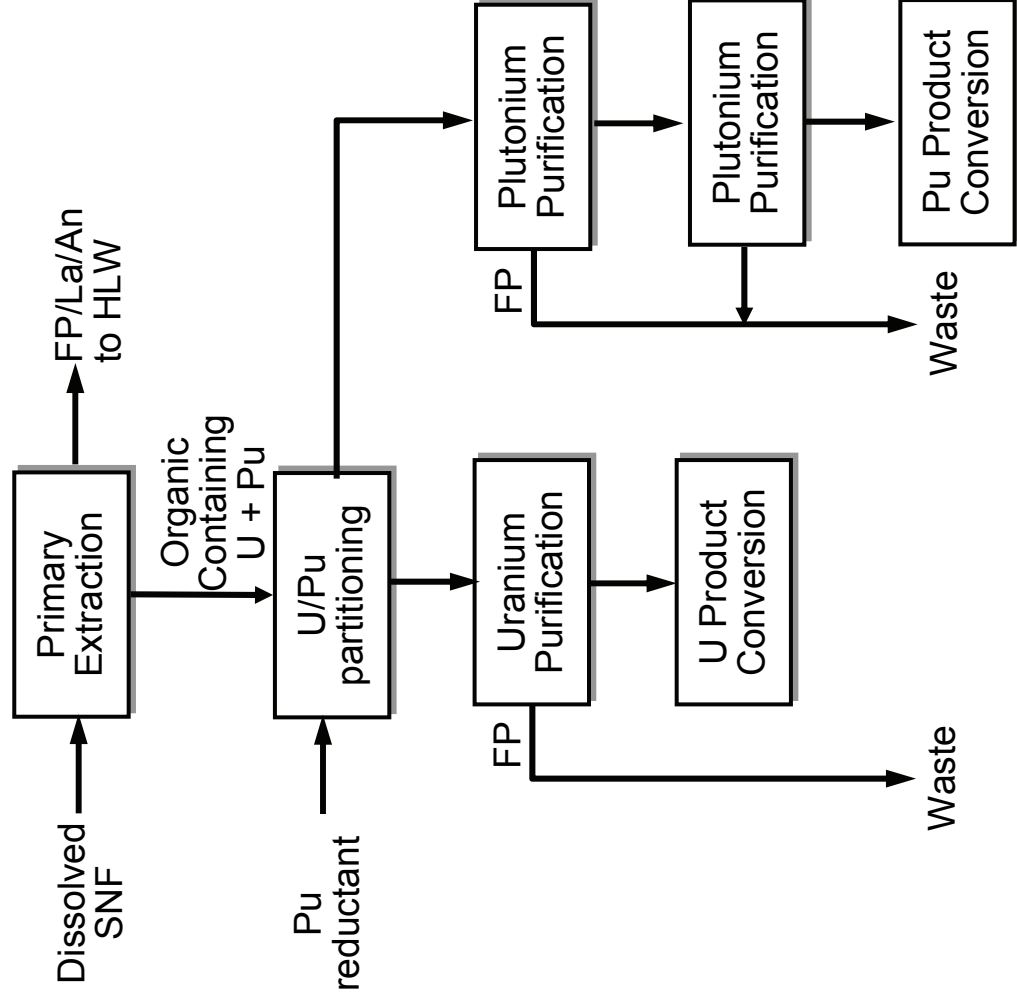


Experimental Scale Equipment

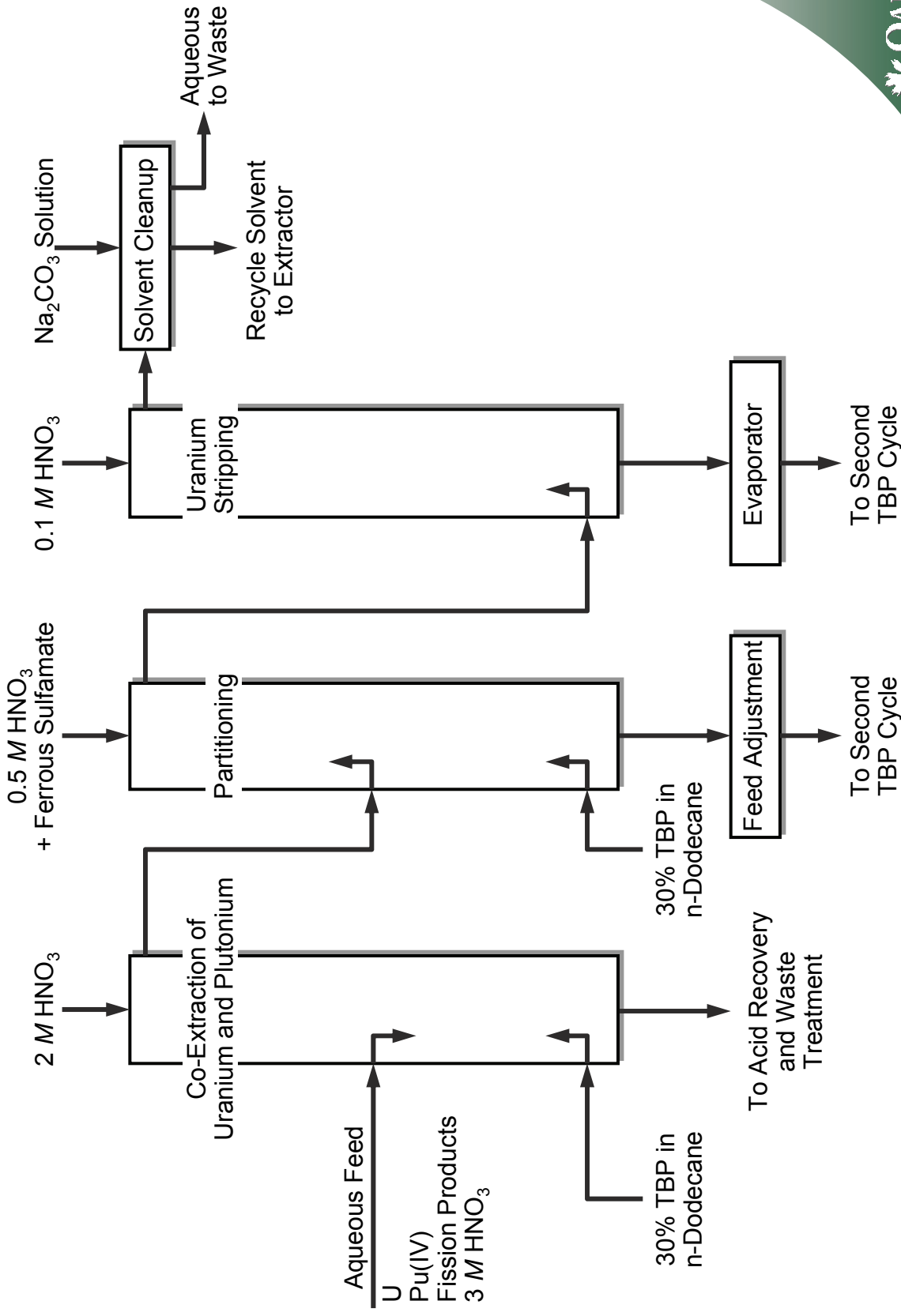


INL Centrifugal Contactor
Engineer Scale System

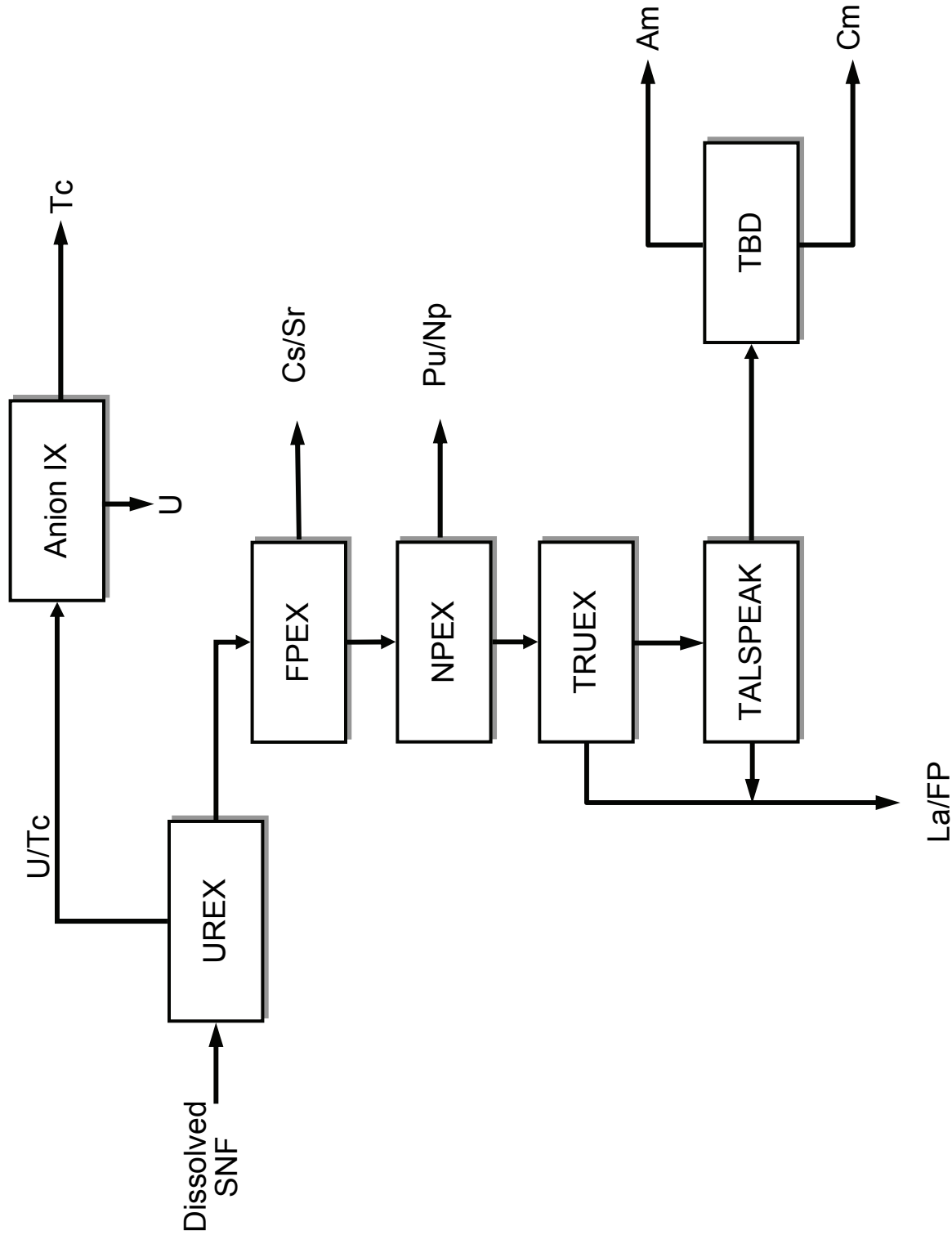
PUREX Process



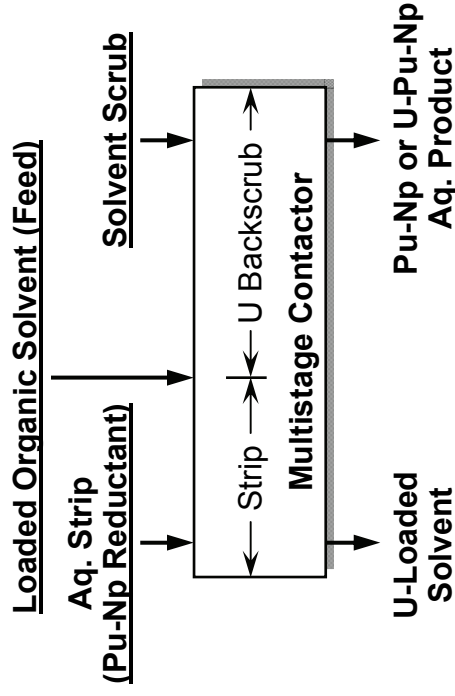
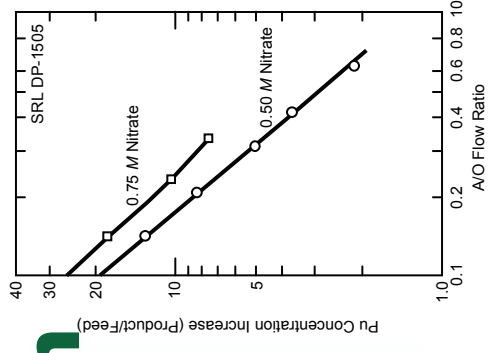
First Cycle PUREX Extraction-Partitioning Flowsheet



Aqueous Separation Flowsheet Option

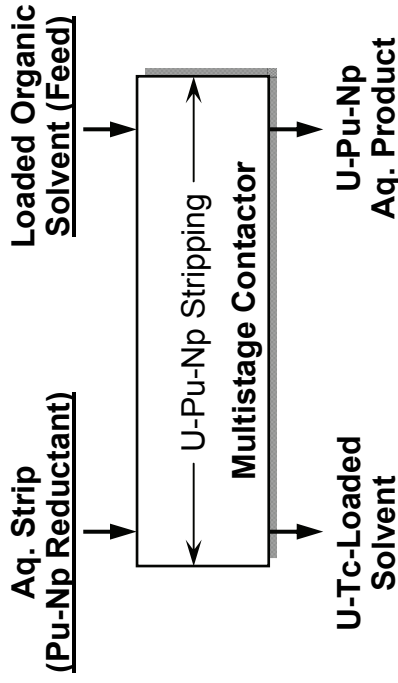


Partial Partitioning of Uranium



PUREX-Type Partitioning Contactor Bank

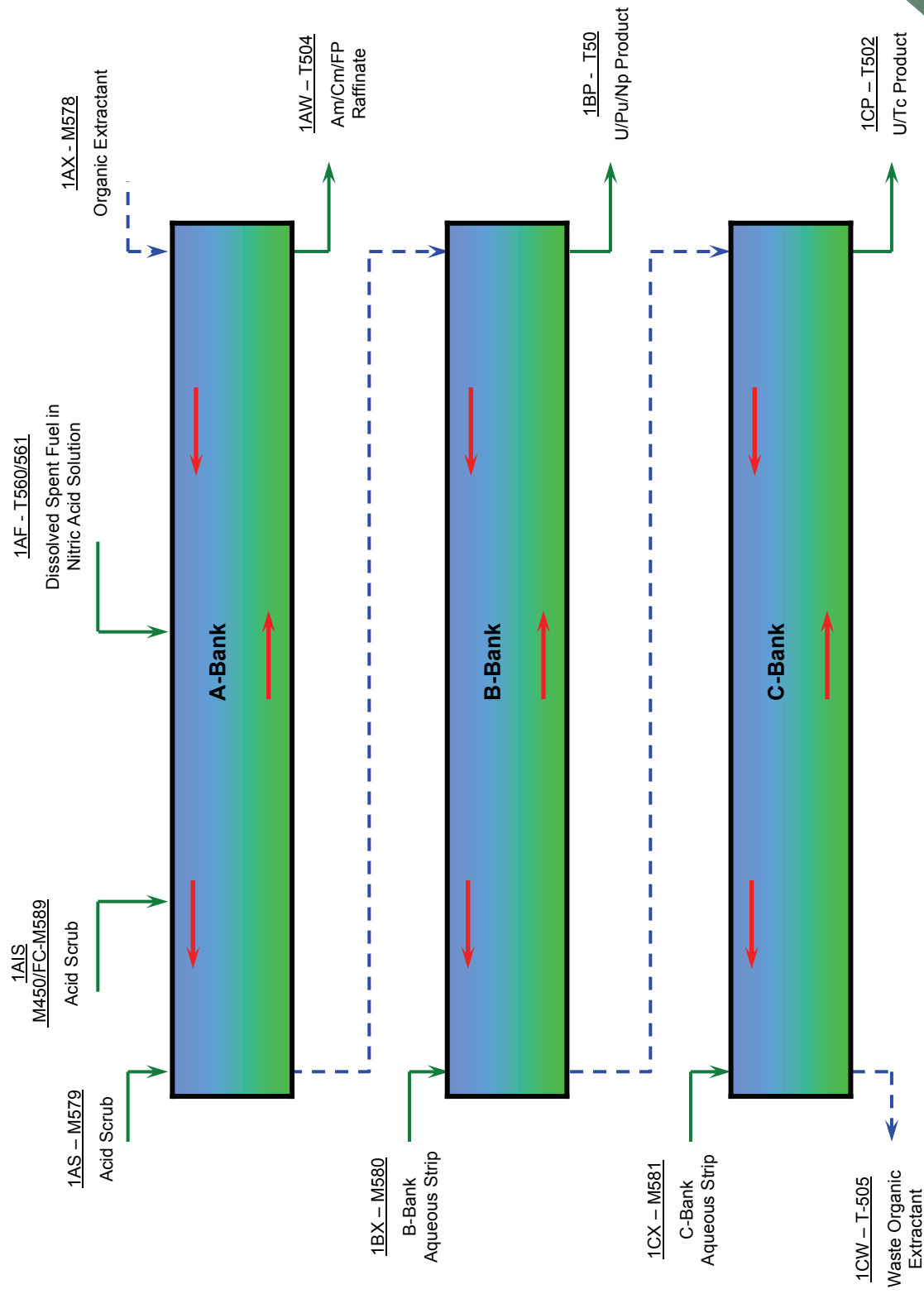
(Complete or partial partitioning is possible)



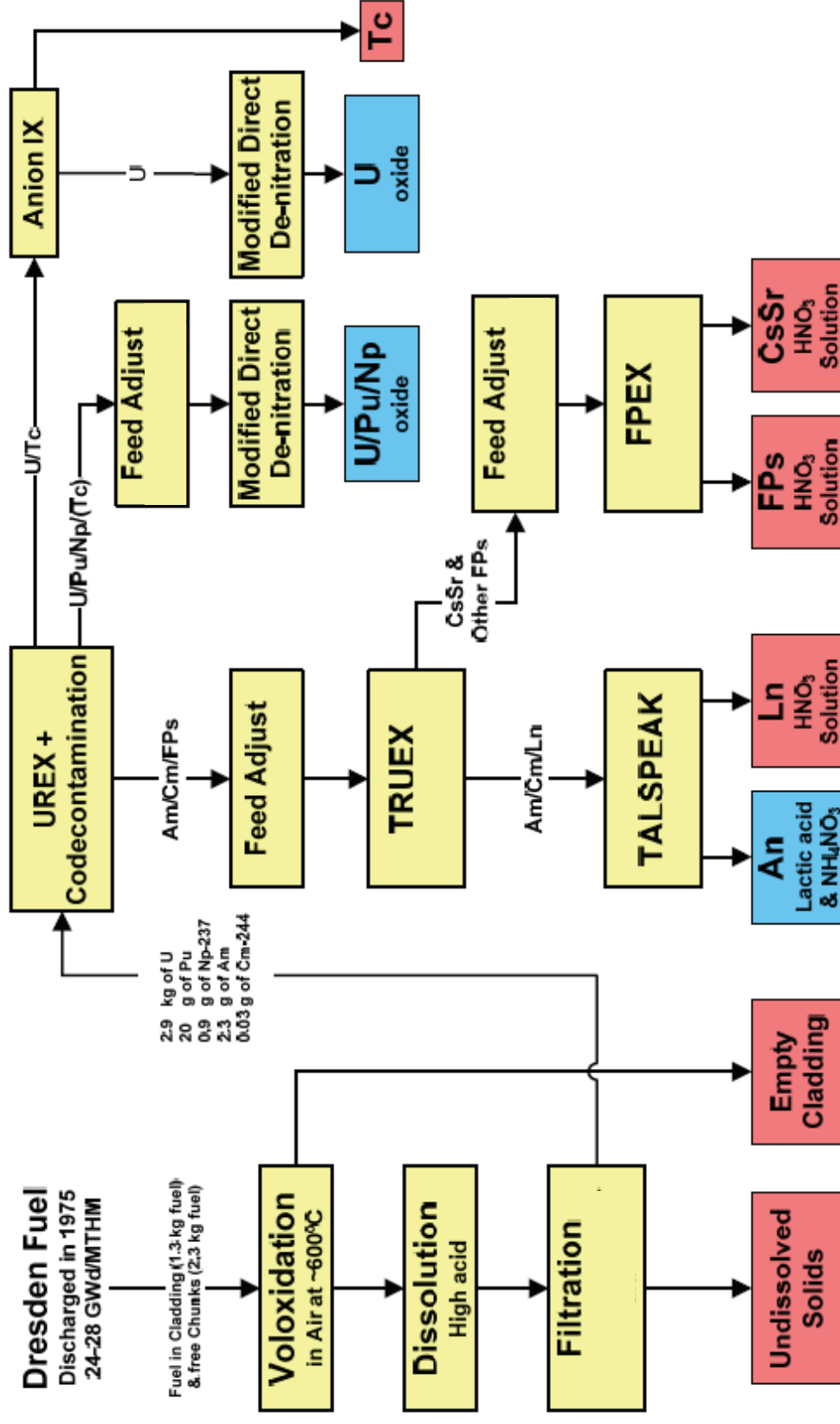
UREX+ Codecon Flowsheet Partial Partitioning Contactor Bank

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

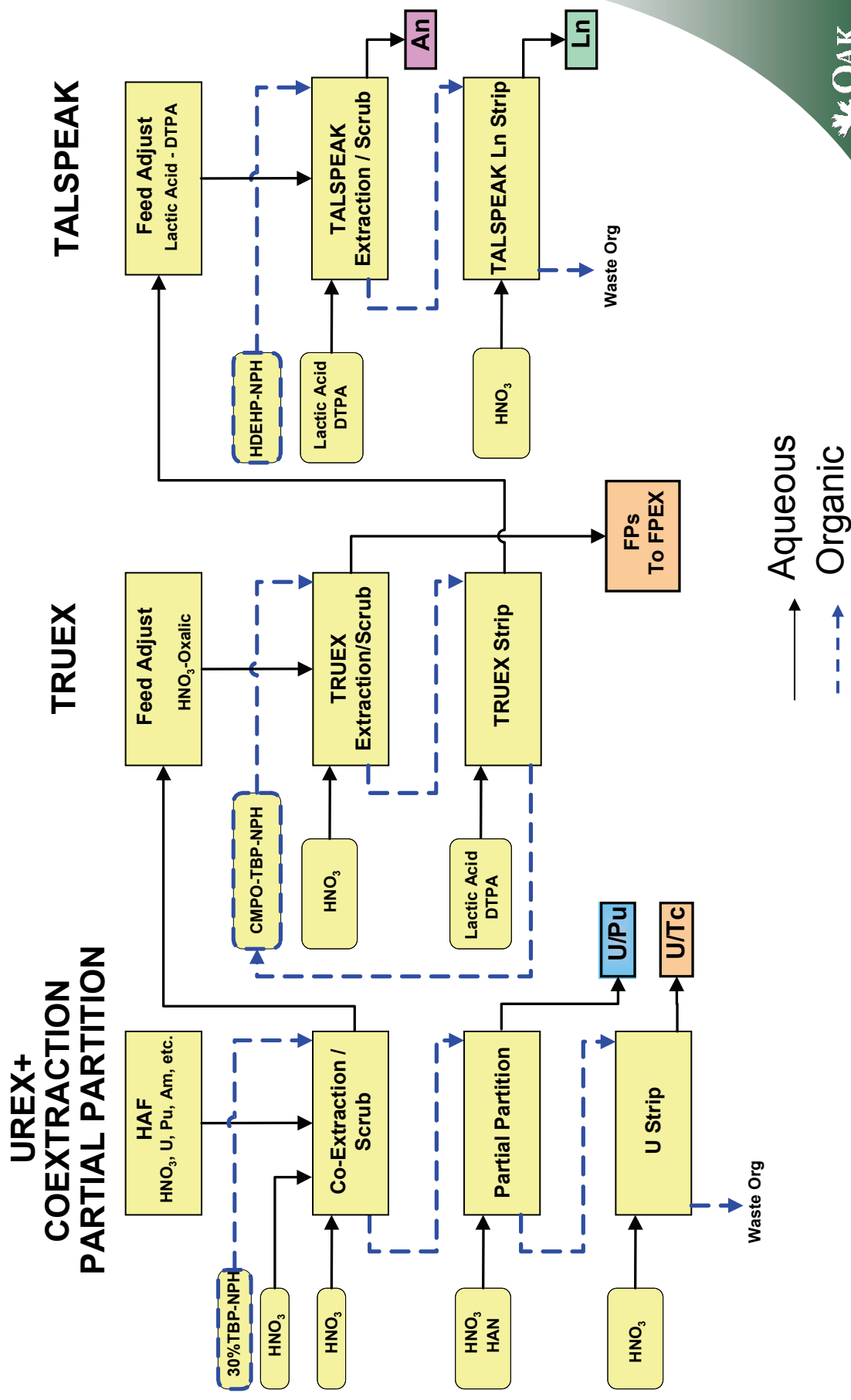
CETE UREX+ Flowsheet



Recent Demonstration Flowsheet



Dresden Separation Flow Sheets

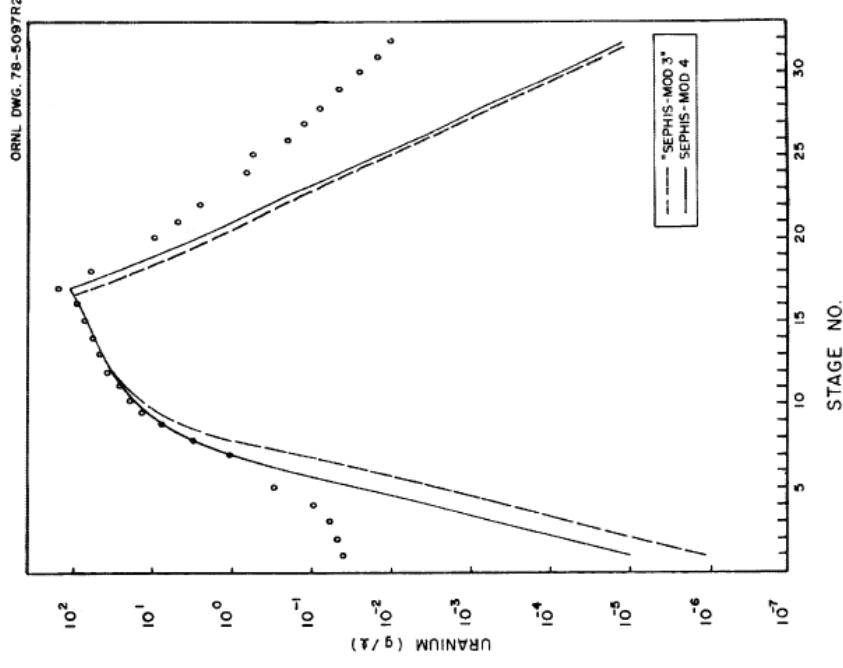


Co-extraction / Partial Partitioning Products

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

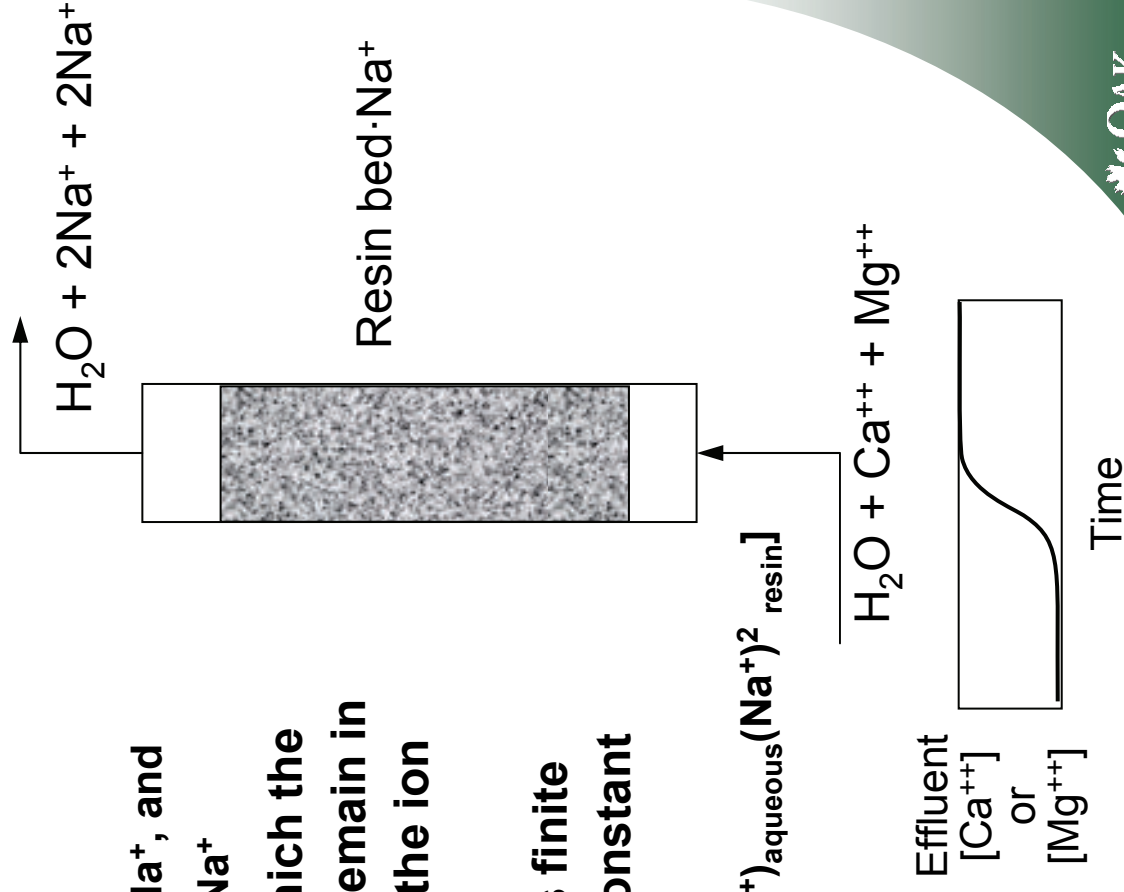
- **Ion exchange:** Passing an aqueous solution over a solid substance that will preferentially remove certain constituents (ions) from the solution by exchanging them with ions attached to the ion exchanger. The removed constituents are recovered by separating the solution from the ion exchanger or 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):

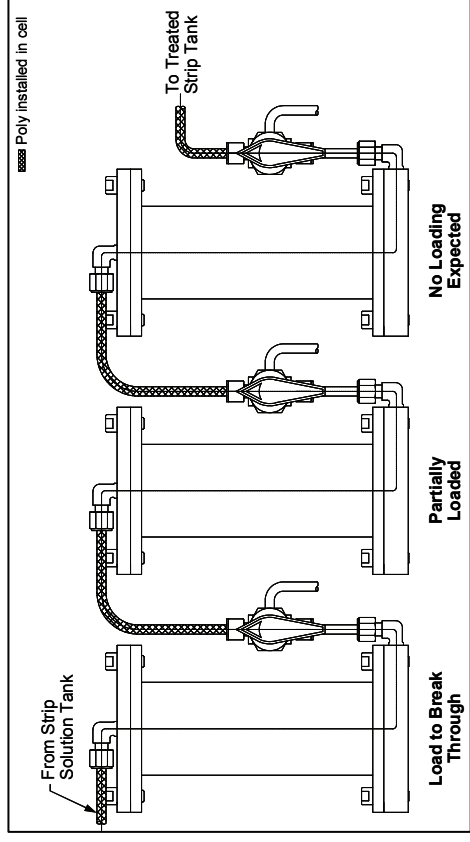
$$K_{\text{Ca}^{++}\text{-Na}^+} = \frac{[(\text{Ca}^{++})_{\text{resin}}(\text{Na}^+)^2]_{\text{aqueous}}}{[(\text{Ca}^{++})_{\text{aqueous}}(\text{Na}^+)^2]_{\text{resin}}}$$



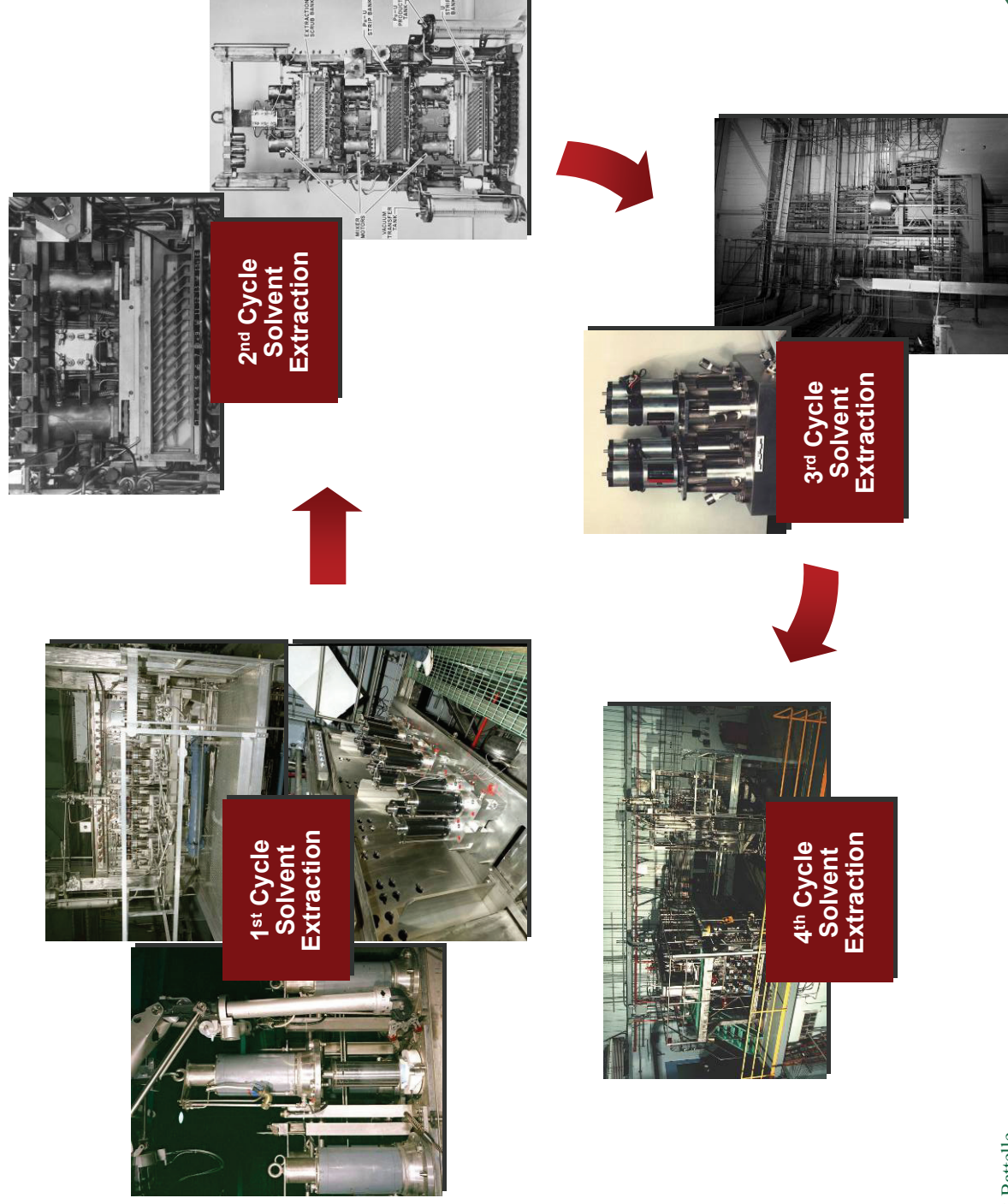
King, C. Judson, *Separation Processes*, McGraw-Hill Book Company, New York, NY, 1971.

Technetium Recovery by Ion Exchange

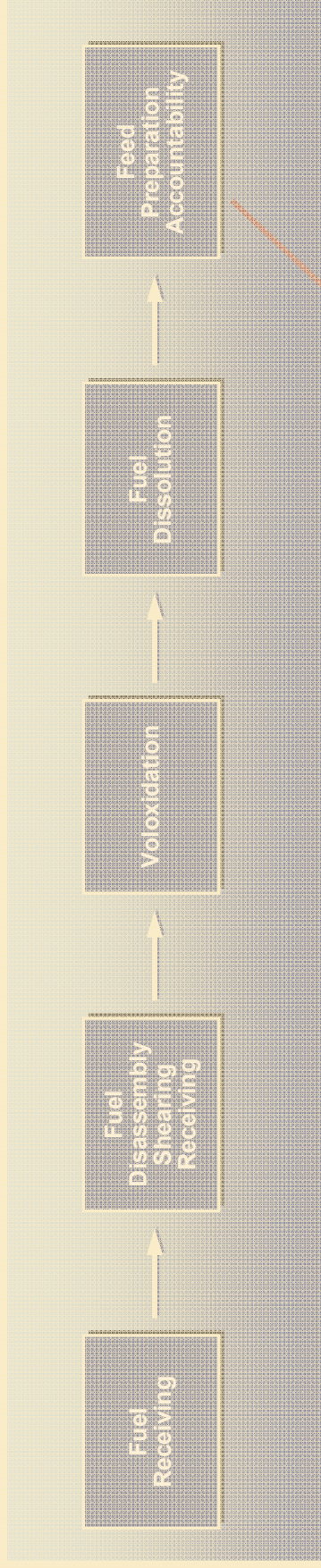
- Worked with LANL to design Tc recovery and solidification system
 - Ion exchange columns fabricated for in-cell loading
 - LANL supplied pretreated Reillex HP resin (80°C HNO_3)
 - Columns installed in REDC Hot Cells
 - Tc recovery operations from CETE Run 1 (Dresden)
 - Uranium retained for conversion to oxide
 - Tc recovered and converted to shippable form (NH_4TcO_4)
 - Evaporation @ $\sim 62^{\circ}\text{C}$ and reduced pressure



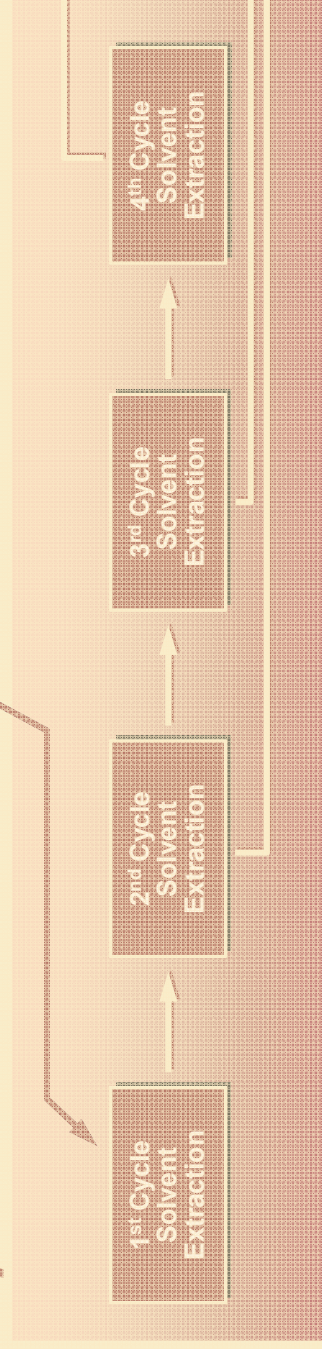
Fuel Reprocessing: Primary Separations Processes



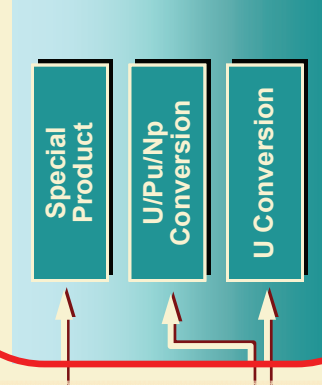
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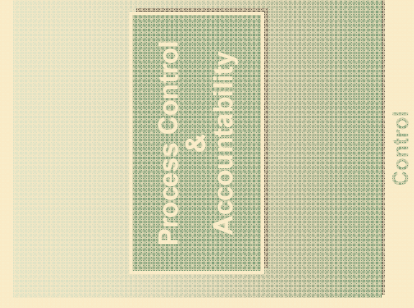
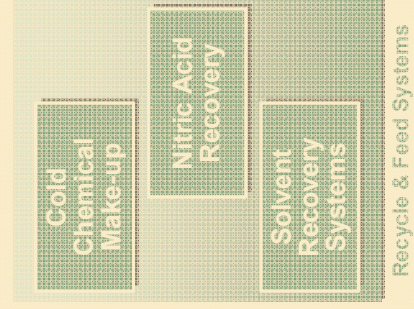
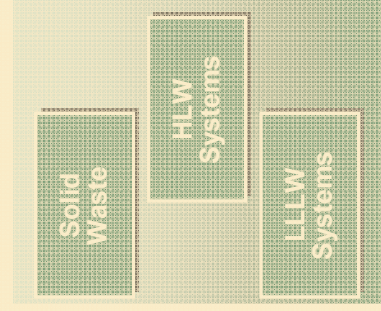
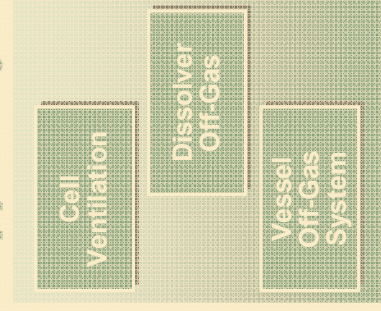
Separation Processes



Conversion



Support Systems



Product Conversion

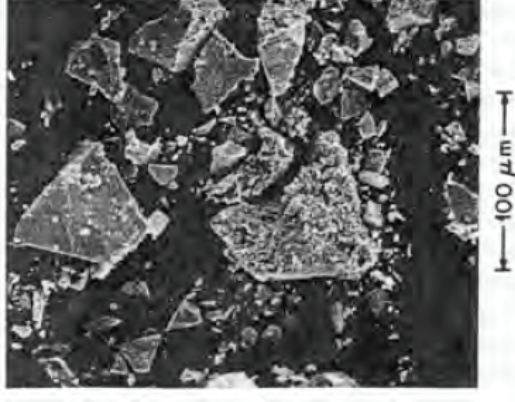
- **Concentrate aqueous plutonium solution and purify:**
Evaporation, ion exchange, solvent extraction
- **Precipitate plutonium:** Trifluoride, oxalate, peroxide
- **Conversion:** Tetrafluoride or oxide-fluoride mix
- **Reduction to metal:** With calcium metal and iodine catalyst in a closed vessel
- **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)

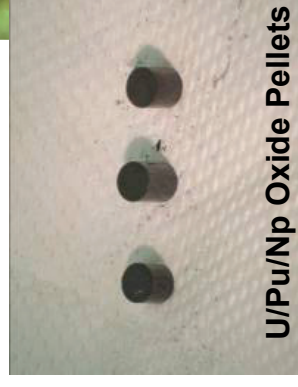
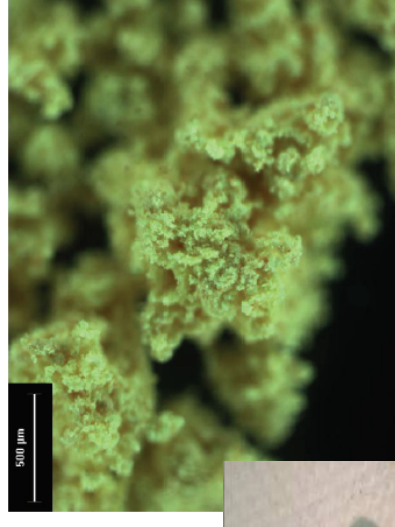
Product Denitration

- **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 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)

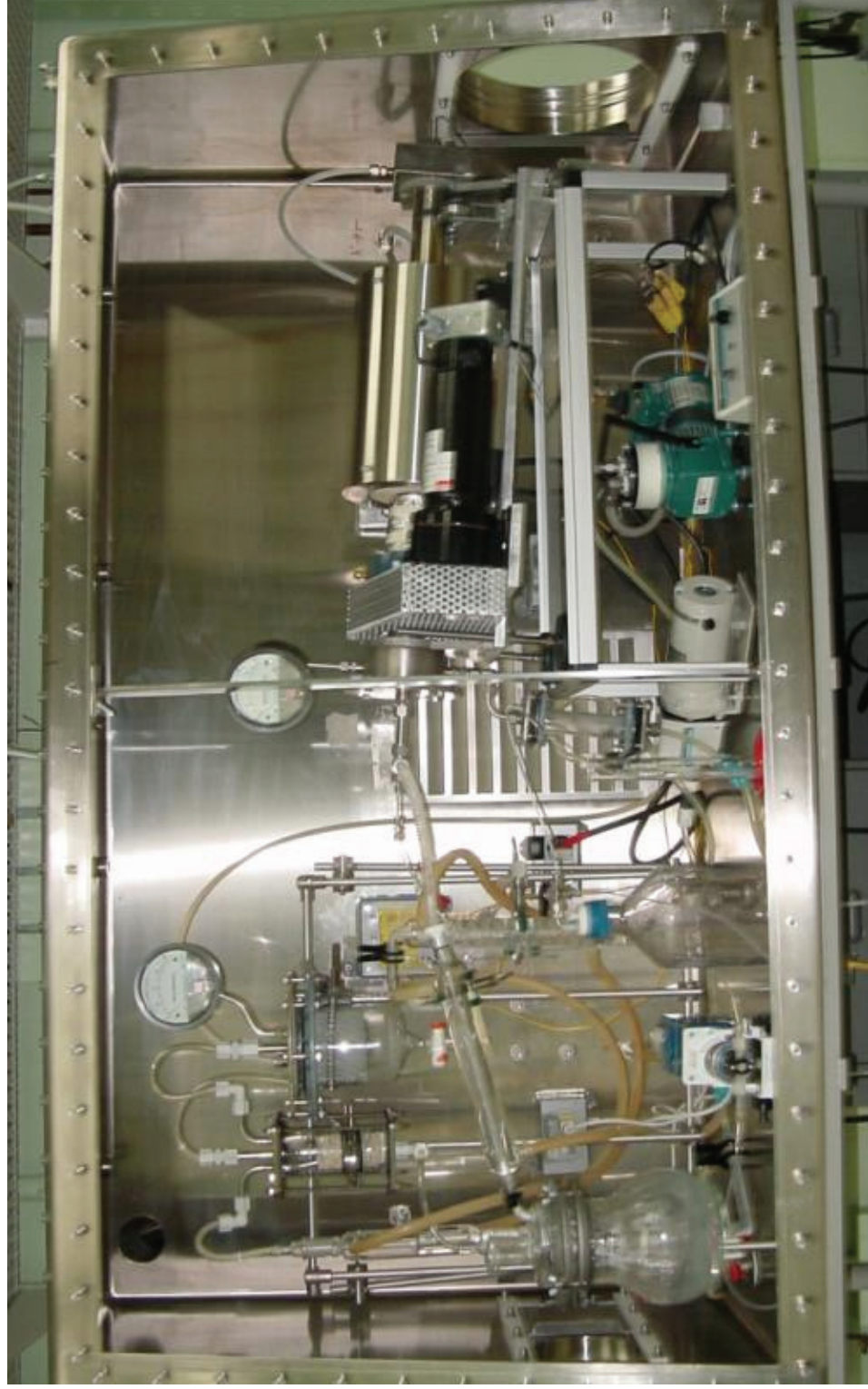


Modified Direct Denitration
(Picture of MDD-produced DU)



U/Pu/Np Oxide Pellets

MDD Equipment in glovebox



Dresden Product Conversions

- **U Product**
 - During Tc anion exchange run, ~4L of “clean” U product collected for MDD conversion
 - Product concentrated in glove box
 - ~200 g converted to oxide for evaluation
 - Remaining uranium product (~2.7 kg) after Tc removal was evaporated (~55L to 8L) and transferred to glove box lab for conversion by MDD
 - Has been converted to UO_3
 - Characterization is underway
- **U/Pu/Np Product**
 - Product from hot cells (~7-8L) transferred to glove box labs for evaporation and U concentration
 - Has been converted to $\text{UO}_3/\text{PuO}_2/\text{NpO}_2$
 - Characterization is underway

Dresden Product Conversions

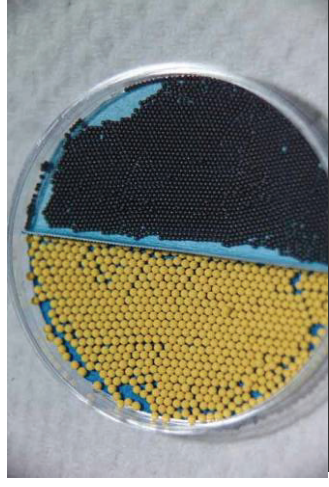
- Lanthanide Product
 - Strip product from TALSPEAK in nitric acid
 - Investigating resin loading on weak acid resin
 - Convert to oxide by calcination
- Am/Cm Product
 - Raffinate from TALSPEAK in lactic acid/DTPA
 - Method for destruction or recycle of complexants needed
 - Plan is to test resin loading on weak acid resin
 - Convert to oxide by calcination
 - Resin loading could provide feed for sphere-pac type of target

Fuel Reprocessing: Product Conversion

Special
Product

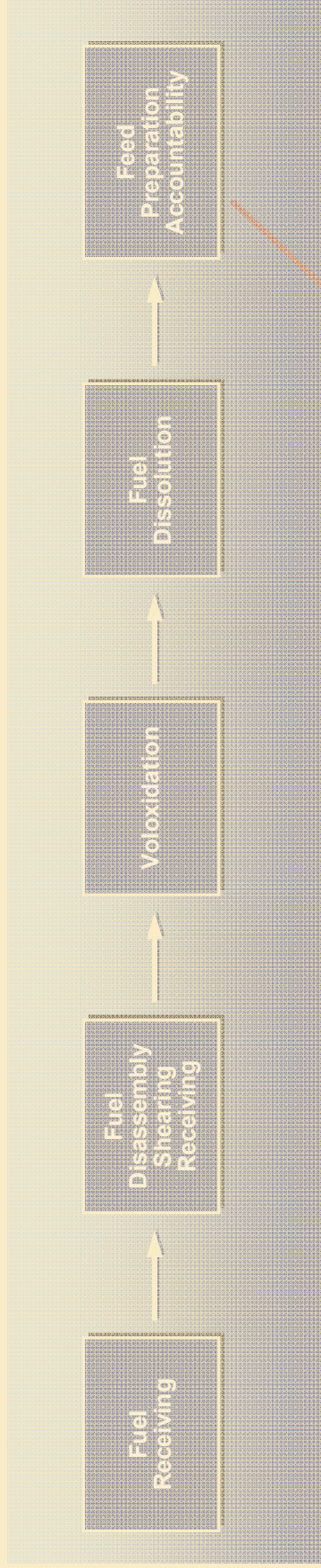


Pu/Np
Conversion

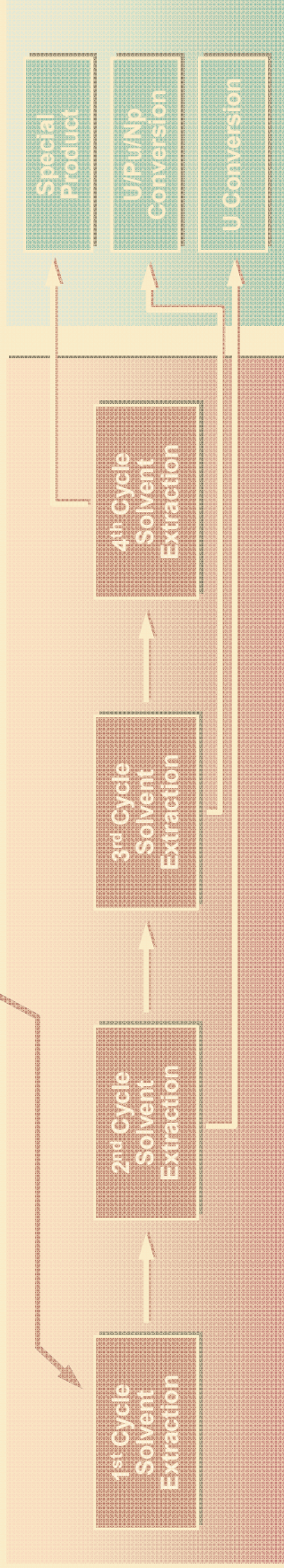


U Conversion

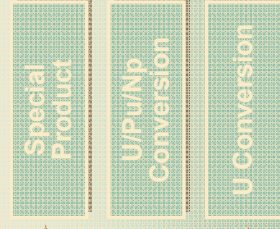
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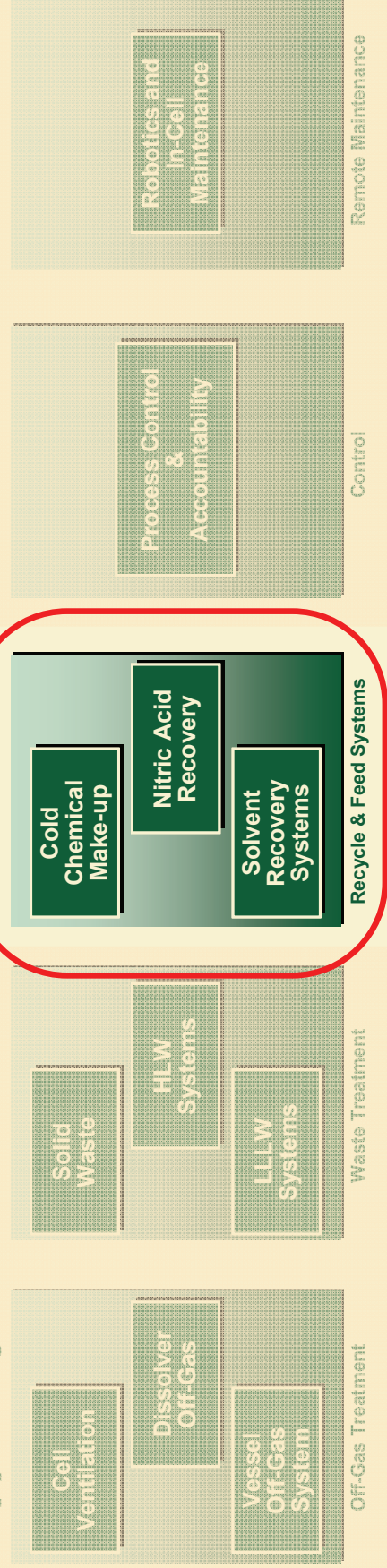
Separation Processes



Conversion



Support Systems



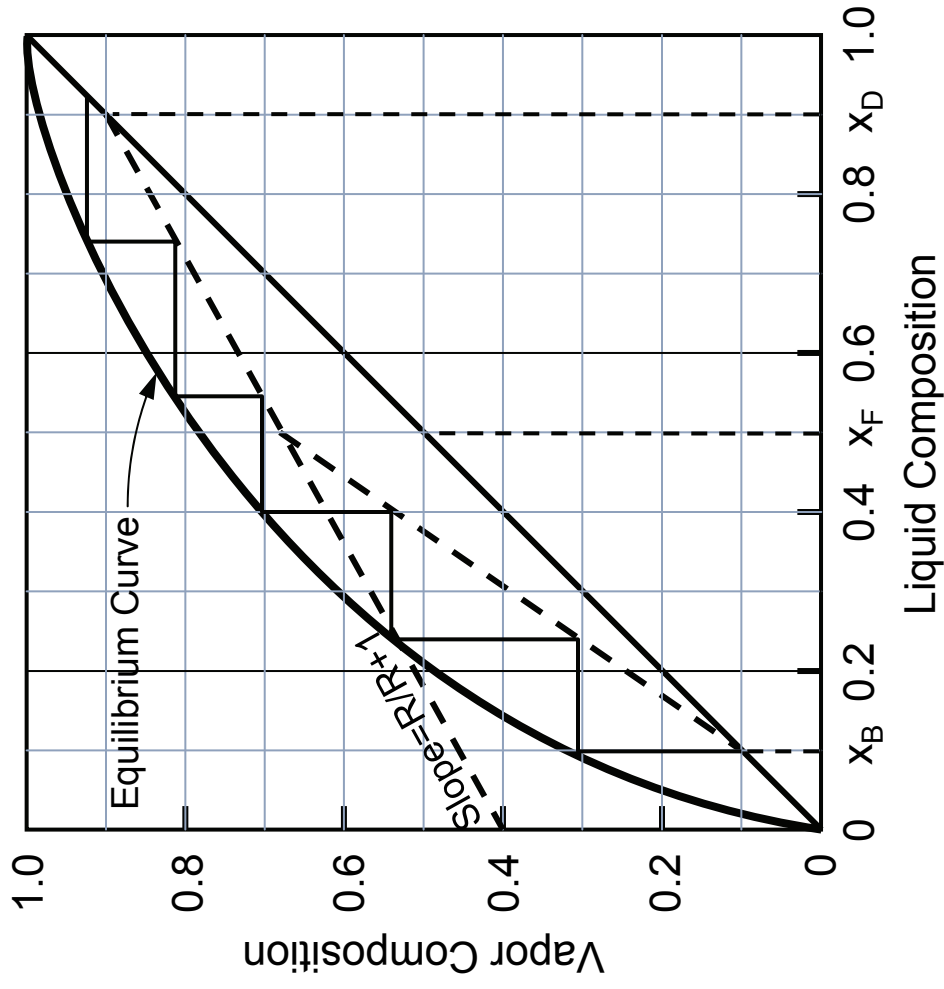
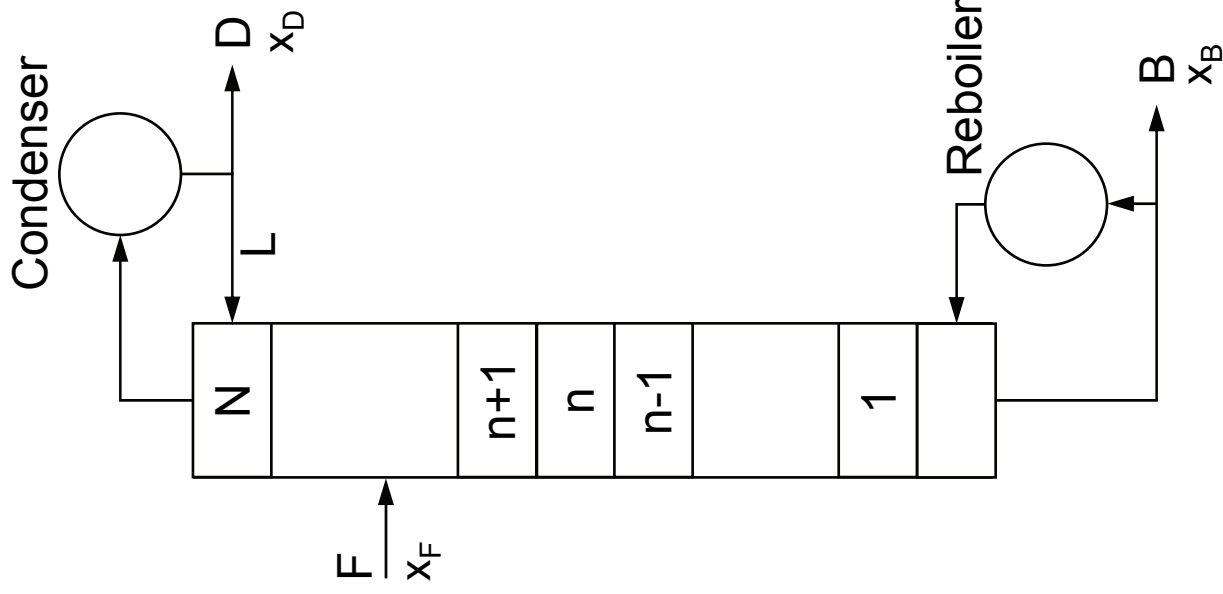
Recycle / Recovery Systems

- 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 vapors, 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 ratio 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

McCabe-Thiele Diagram



$$R = \text{Reflux Ratio} = \frac{L}{D}$$

Applications of Distillation / Evaporation

- **Acid recycle**
 - Nitric acid recovery from off-gas and waste processing
 - Dissolution in 800MT/yr plant requires ~ 10⁶ 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 nitric acid concentration and temperature
- 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
- 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 HNO_3
 - 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

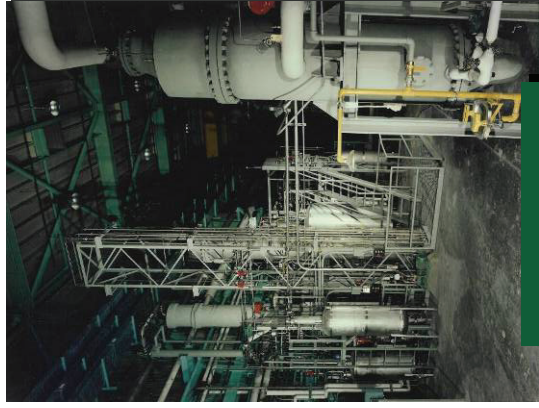
- The use of an organic diluent to recover dissolved and entrained TBP from aqueous streams
- Mixer Settler or Centrifugal contactor running at high A/O ratio
- 1 or more stages may be used to obtain desired recovery

Solvent Treatment / Washing

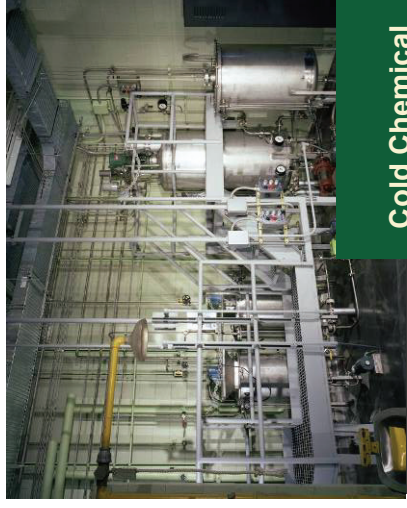
- Solvents are degraded by radiolysis and chemical hydrolysis
 - If allowed to accumulate, the organic phase will have increased retention of U, Pu, Zr, Nb, Ru.
 - At high levels changes in physical properties will occur
- Solvent treatment
 - Sodium carbonate scrub is used to remove primary degradation 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.

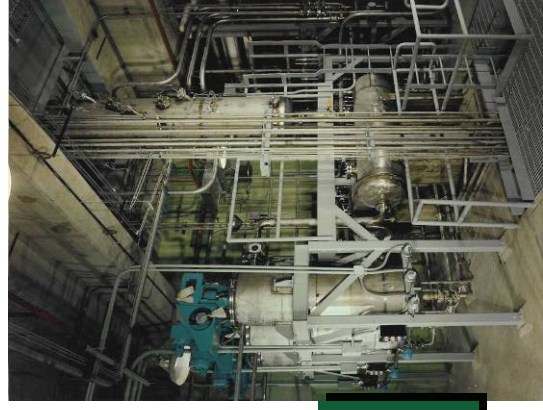
Fuel Reprocessing: Recycle and Feed Systems



Nitric Acid
Recovery

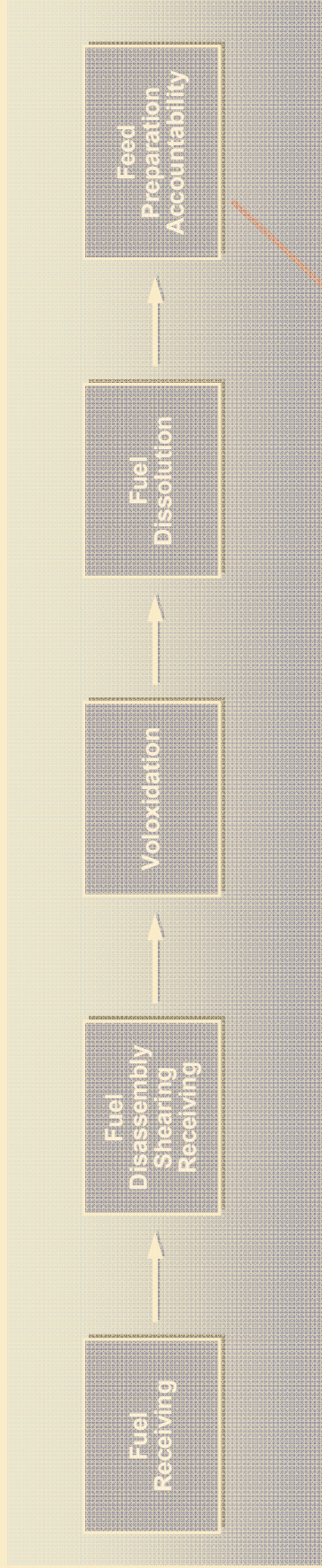


Cold Chemical
Make-up

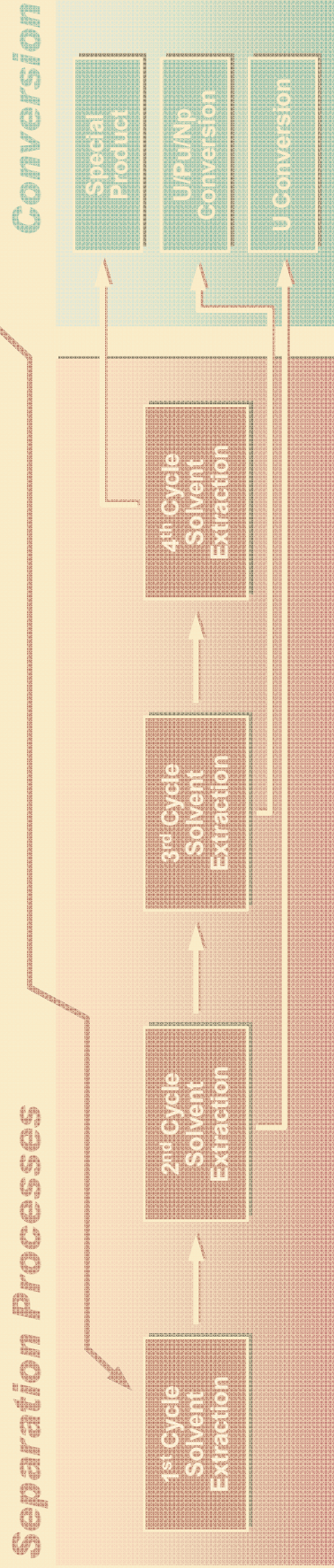


Solvent
Recovery
Systems

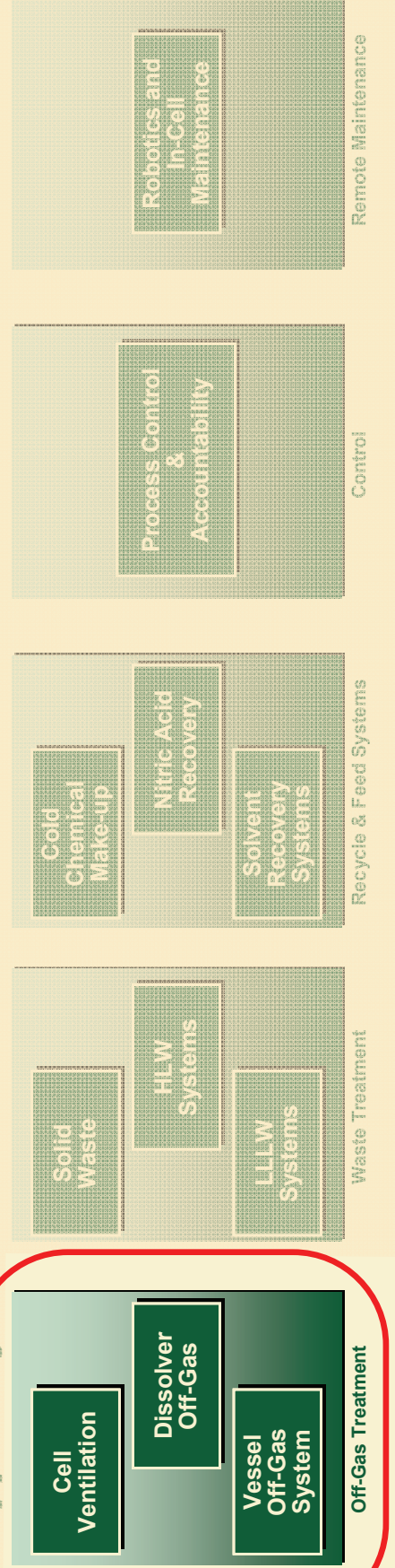
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Separation Processes



Support Systems

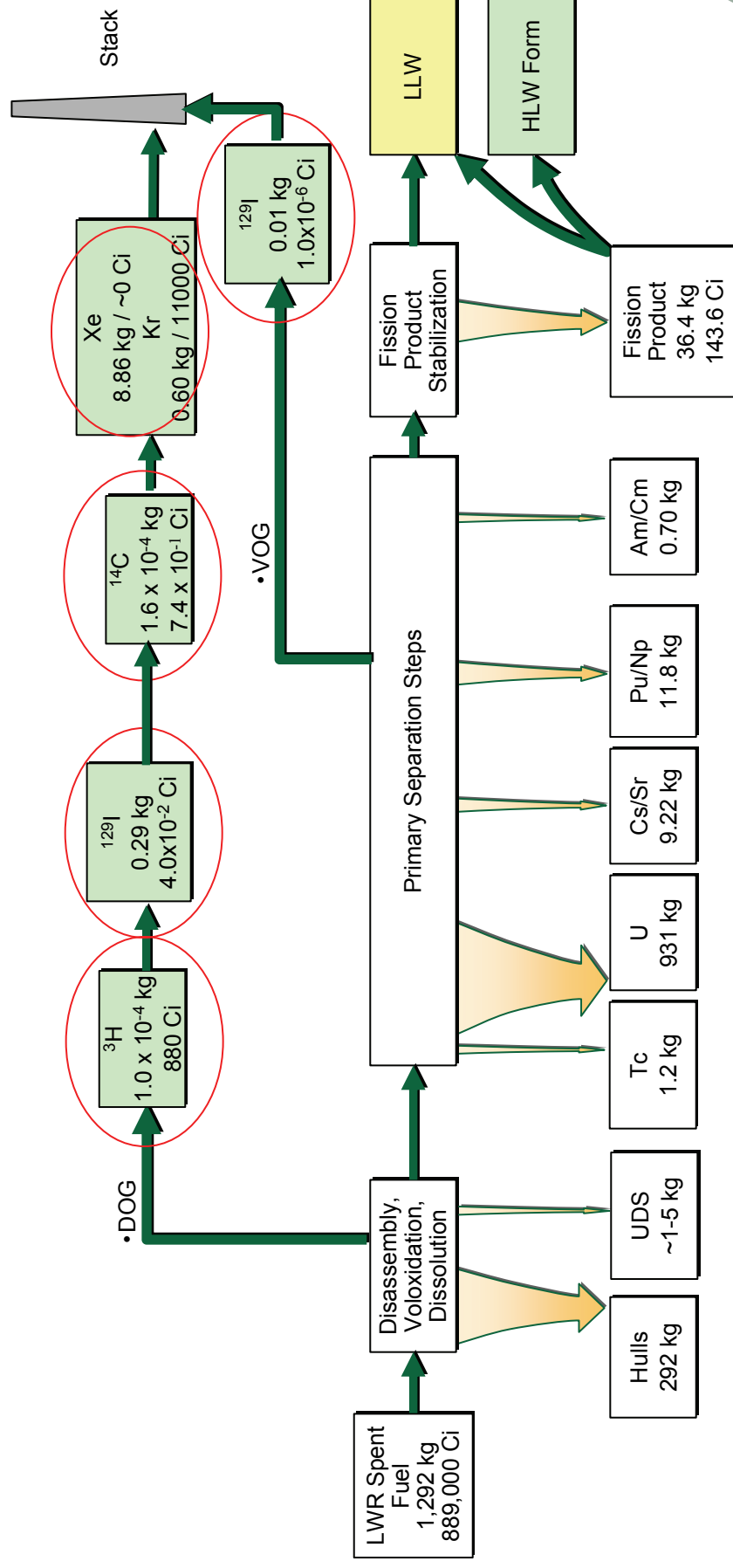


Off-gas treatment

- 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

Simple Reprocessing Demonstration

(Mass Basis: 1 MT SNF; 55 GWD/MTIHM; 5 year Cooling)



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

40 CFR 190 Derived Process Requirements

Isotope	Ci/MTIHM	Ci/GW(e)-yr	Min Required DF
¹²⁹ I	0.02648	0.89	178
⁸⁵ Kr (5 year cooled)	7121	239,000	4.77
⁸⁵ Kr (10 year cooled)	5154	173,000	3.45
⁸⁵ Kr (30 year cooled)	1414	47,000	0.95

Note: Burn-up: 33 GWd/MTIHM

Isotope	Ci/MTIHM	Ci/GW(e)-yr	Min Required DF
¹²⁹ I	0.04149	0.83	167
⁸⁵ Kr (5 year cooled)	11620	234,000	4.67
⁸⁵ Kr (10 year cooled)	8413	169,000	2.38
⁸⁵ Kr (30 year cooled)	2309	46,000	0.93

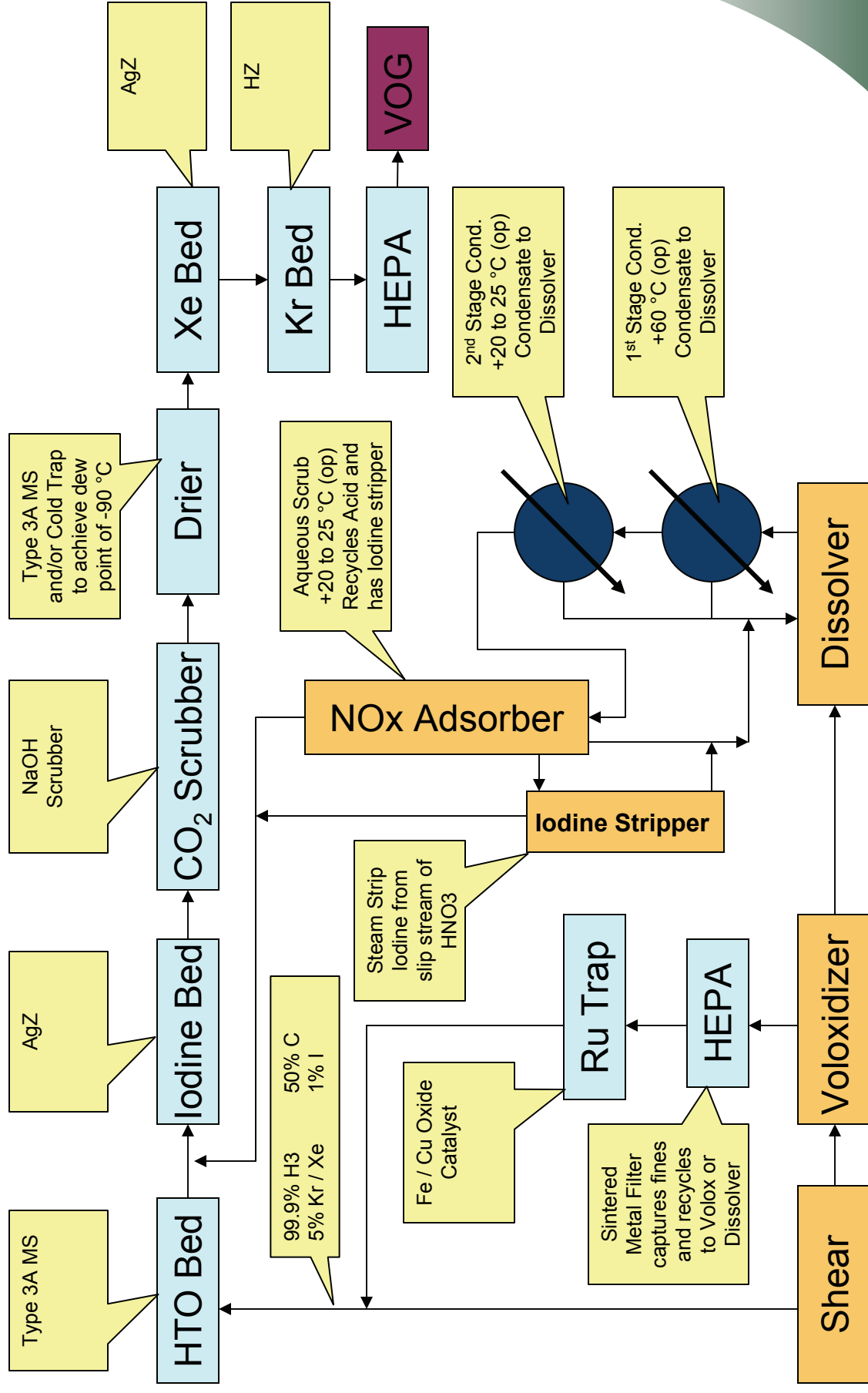
Note: Burn-up: 55 GWd/MTIHM

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

Notional Combined VoxOG / DOG System



Can gaseous FP emissions control technologies meet control requirements?

- We estimated maximum individual nuclide emissions that ensure compliance to 10 mrem/yr limit
 - <0.1 mrem/yr dose per nuclide to the maximally exposed individual (MEI)
- We estimated individual nuclide control efficiencies for
 - <0.1 mrem/yr MEI dose (10 CFR 20, 40 CFR 61)
 - Compliance to fuel cycle emission limits (40 CFR 190)

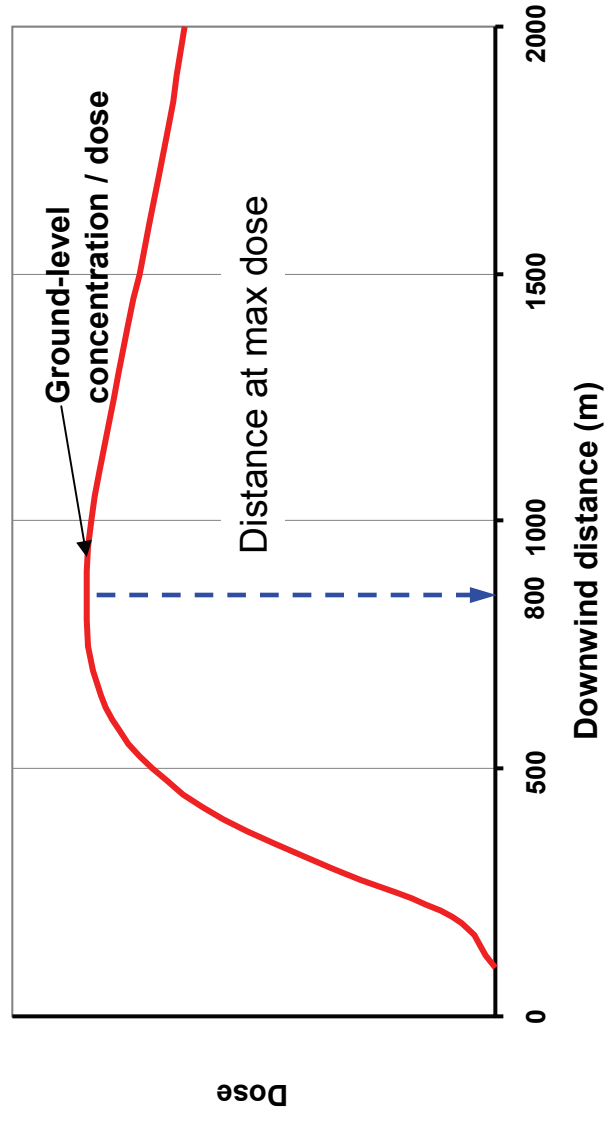
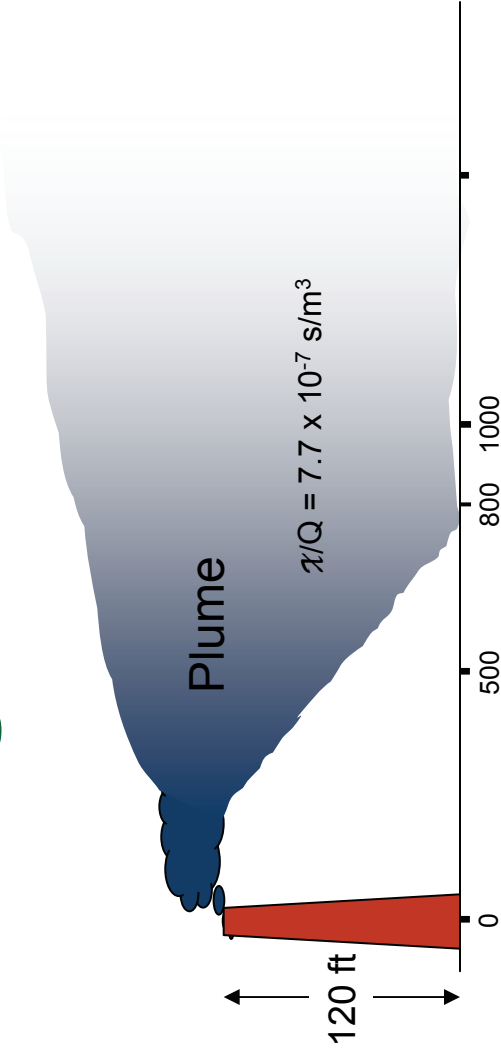
Compliance to 10 CFR 20 is met with <0.1 mrem/yr MEI dose (the ambient-air concentration limits are based on 50 mrem/yr dose)

Air dispersion modeling of stack releases and dose calculations estimated dose to MEI

- CAP88-PC3 is the latest multipathway dose assessment code provided by U.S. EPA to determine compliance to 40 CFR 61 NESHAPS
- Spent fuel source term:
 - 51 GWd/MTIHM burnup, 10 year cooling
 - ORIGEN model estimated the spent fuel composition
- Hypothetical stack parameters: 120 ft high, typical plume rise
- Conservative rural CAP88 agricultural input maximized ingestion dose (significant for ^3H and ^{129}I)
- Model included full progeny dose calculation
- 10-yr meteorological data from INL was used
 - Other locations could result in different dispersion factor (X/Q) and results
 - X/Q was $7.7\text{E-}07$ s/m³, conservatively high and consistent with other sites

The model estimates MEI direction and distance, where ground-level air concentrations are highest

- Hypothetical MEI: 800 m downwind (SSW) of the hypothetical stack.
- The plume “hits the ground” just upwind of this point.
- Ground-level dose is maximum at this point.

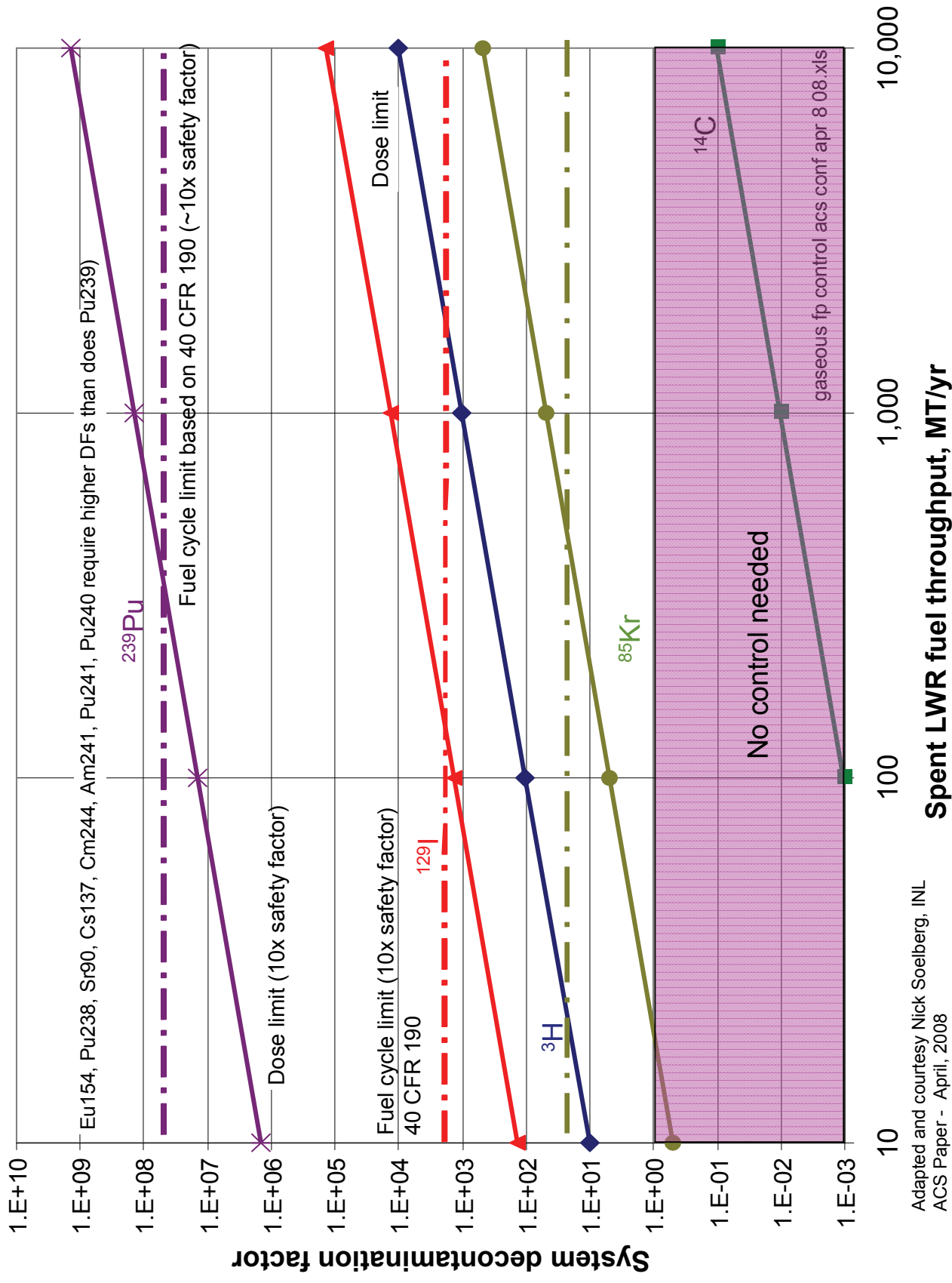


Adapted Courtesy Nick S
ACS Paper - April, 2008

Reasonable release factors and off-gas control efficiencies were assumed

- **Release factors (Decontamination Factors, DFs) to offgas:**
 - All dissolved non-volatile elements (Pu, etc.): 1000 (0.1% release)
 - All dissolved semivolatile elements (Cs, etc.): 100 (1% release)
 - All gaseous FP: 1 (100% release)
- **Offgas control DF for non-gaseous elements ($10E+7$) was estimated based on these units in series:**
 - Mist eliminator or roughing filter: 10
 - Prefilter: 10
 - HEPA filter #1: 1,000
 - HEPA filter #2: 100

Estimated gaseous fission product and ²³⁹Pu DFs required to meet dose and fuel cycle regulations



Adapted and courtesy Nick Soelberg, INL
ACS Paper - April, 2008

AFCI R&D to support gaseous fission product control

- Gaseous fission products require ranges of emissions control depending on SNF processing rate and applicable regulations:
 - I-129: 99-99.99%
 - H-3: 90-99.9%
 - Kr-85: 0-99%
 - C-14: perhaps none
- Small-scale offgas control system, part of the Oak Ridge National Laboratory (ORNL) Coupled End-to-End (CETE) demonstration of aqueous separations processes
- Bench-scale I-129 test system located at the Idaho National Laboratory (INL)

Dissolver Off-gas

- Composition and flowrate of the DOG was estimated based on data from tests conducted at the ORNL on the Integrated Equipment Test Facility (Birdwell, 1991).
- This facility was a test bed for evaluation of nuclear fuel reprocessing using prototypic equipment sized to process 0.5 tonne/day of heavy metal.
 - Measured DOG rate ranged from 500 to 1000 SLM on a dry gas basis
 - NO concentration varied from 0 to ~0.1%
 - NO₂ concentration ranged from 0.5 to 1.25%.

Off-Gas Source Terms

	VoxOG (gm/MTIHM)	DOG (gm/MTIHM)	VoxOG (mol/l)	DOG (mol/l)	Combined after Tritium removal (mol/day)
Tritium (as HTO)	0.10756	--	1.40×10^{-8}	--	--
H₂O (from inleakage or air sparges/purges)	5.60	58,100	4.00×10^{-7}	1.12×10^{-3}	3227
¹⁴CO₂	0.0829	0.0829	Combined with DOG	9.85×10^{-10}	0.00360
¹²CO₂ (from inleakage or air sparges/purges)	---	1311	Combined with DOG	1.05×10^{-5}	29.8
I	---	308.2	Combined with DOG	3.27×10^{-7}	1.19
Kr	29.84	566.9	Combined with DOG	1.95×10^{-6}	7.12
Xe	442.5	8407	Combined with DOG	1.84×10^{-5}	67.4

Basis:

55GWd/MTIHM, 5 year cooled
 VoxOG rate 540 L/min for 1 MTIHM
 DOG rate 2000 L/min for 1 MTIHM
 Plant size 200 MTIHM / yr
 Gas to Voloxidizer has -60°C dew point and is CO₂ free
 Air cell at 15°C dew point
 DOG cooled to 25°C after leaving dissolver
 5% Kr/Xe release in Voloxidizer
 50% CO₂ release in Voloxidizer

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-live iodine from the relatively short half-live 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

HTO Recovery Step: Molecular Sieves (Linde Type 3A)

Process Conditions	Temperature ~25°C
Removal Efficiencies	Drying to ~-50°C dewpoint
Issues	Recovery efficiency at very low dewpoints
Capacity of Adsorbent	~0.11 kg HTO/kg Adsorbent
Level of Development	Extensive Industrial Use in Non-Nuclear Applications Some Uses in Nuclear Applications
Regeneration	270°C – 30+ cycles

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 outgassing (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

Iodine Recovery Technology

Material / Process	Process Conditions	Decontamination Factor	Capacity of Adsorbent	Level of Development	Regeneration
Silver Exchanged Faujasite (AgX)	Preheating of inlet gas to 150°C Operating Temp 150°C NOx removal needed	10 – 10000	80 – 200 mg I/g	Laboratory Scale Studies Prototype and Large-Scale Application	Not stable (50% loss on capacity after 5 cycles)
Silver Exchanged Mordenite (AgZ)	Preheating of inlet gas to 100 - 200°C Operating Temp 100-200°C Pretreat AgZ with hydrogen to improve loadings	10 – 10000	~140-180 mgI ₂ /g AgZ 230 mgI ₂ /g AgZ max Laboratory regeneration of beds has been demonstrated	Laboratory Scale Studies	400 to 500°C with H ₂ (20% loss on capacity after 13 cycles)

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

Carbon Recovery Technology

Material / Process	Process Conditions	Decontamination Factor	Capacity of Adsorbent	Level of Development
Caustic scrubbing	NO _x and iodine should be removed to avoid added waste volume and disposal complications	10 - 100		Common industrial process
Caustic Slurry Scrubbing	NO _x and iodine should be removed to avoid added waste volume and disposal complications	Ba(OH) ₂ •8H ₂ O has 10 times DF of Ca(OH) ₂		Technology has proceeded through several generations of pilot-scale development
Solid sorbent adsorption (4A)	NO _x and water should be removed. Must be coupled with caustic scrub to recover trapped CO ₂	>100 Does not absorb Kr like 5A sieve at ambient temps		Packed bed adsorption is common industrial practice Has not been applied to nuclear applications

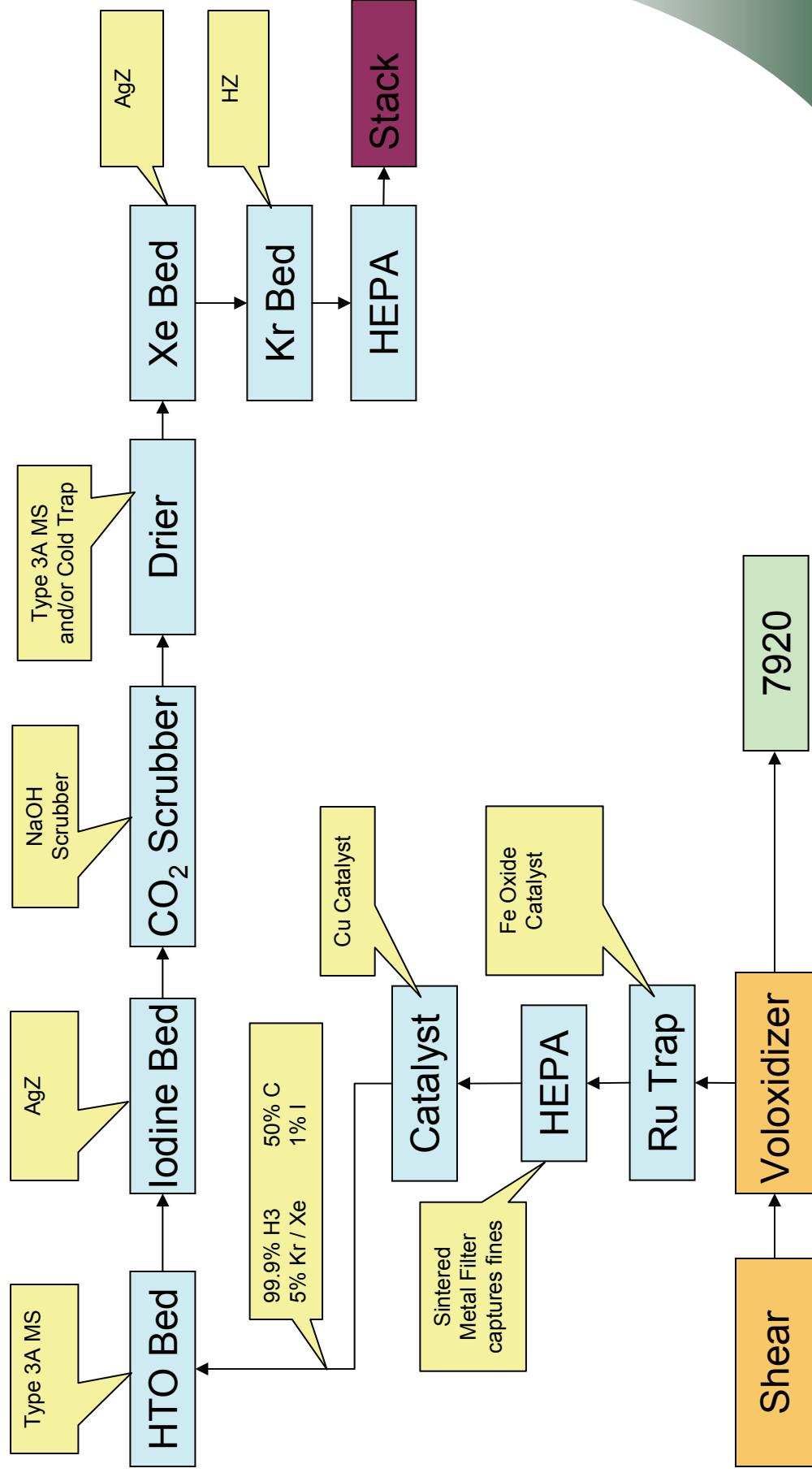
Krypton Recovery

- 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

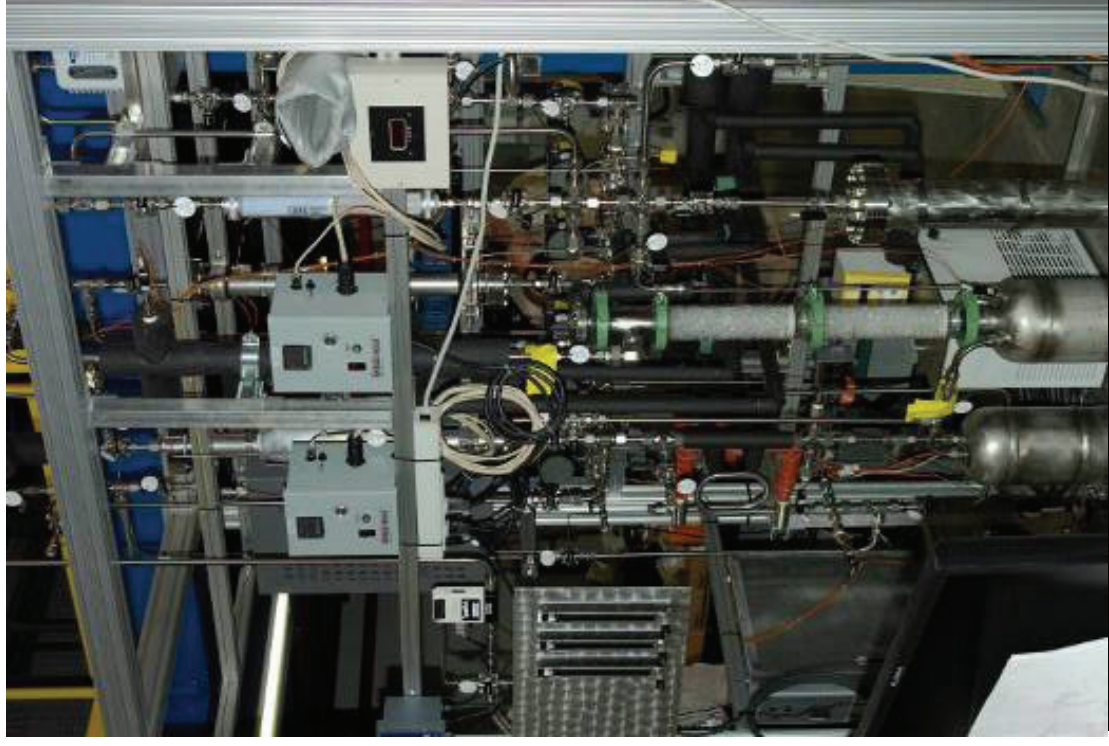
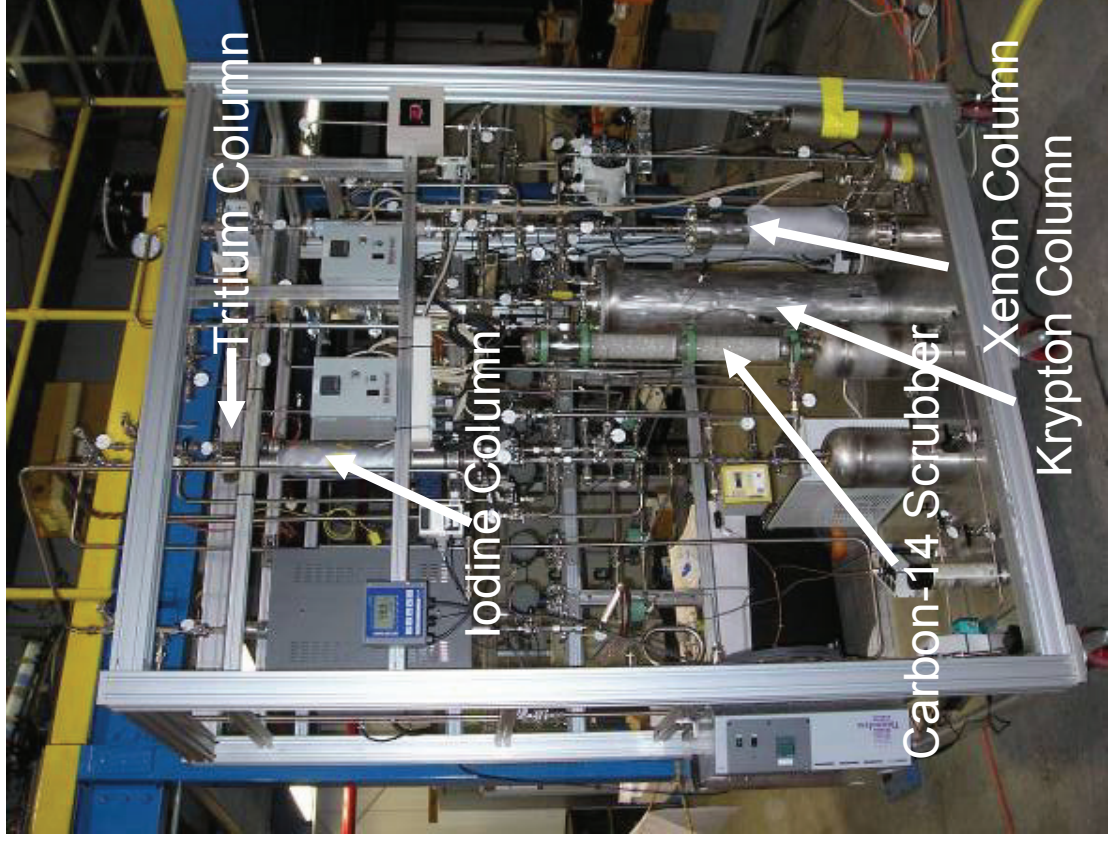
Krypton Recovery Technology

Material / Process	Process Conditions	Decontamination Factor	Capacity of Adsorbent	Level of Development
Cryogenic Distillation	All gas components that are subject to freezing must be removed (NO_x , H_2O and CO_2). Oxygen must be removed prior to operation Pretreat to $\sim 170^\circ\text{C}$ Pressurized system	$100 - 10^3$	Very High Kr inventory	Cryogenic distillation for rare gases is commercial technology Pilot-scale cryogenic units for Kr recovery in the absence of O_2 have been tested
Fluorocarbon Absorption (CCl_2F_2 , R-12)	Three unit operations are required – absorption, intermediate stripping, and final stripping. Pretreat to -150°C Atmospheric or below	$100 - 1000$ for Kr Xe/Kr separation factor of $> 10^6$ Kr purity of $> 99\%$ Also recovers CO_2 , NO_x	Low inventory	Technology has proceeded through several generations of pilot-scale development.
Solid sorbent adsorption [Silver and Hydrogen mordenite (AgZ) and (HZ)] and activated charcoal	Cool to -80°C Atmospheric pressure or below	$10^3 - \text{Kr}$ (charcoal at -150°), $400 - \text{Kr}$ (HZ at -80°C) Separations factors $\sim 5\%$ of Kr retained with Xe – Further separations may be required	Very low inventory (2.5×10^{-5} mol Kr/gm HZ at -25°C)	The technology has been tested at small engineering scale Selectivity is an issue

VoxOG System



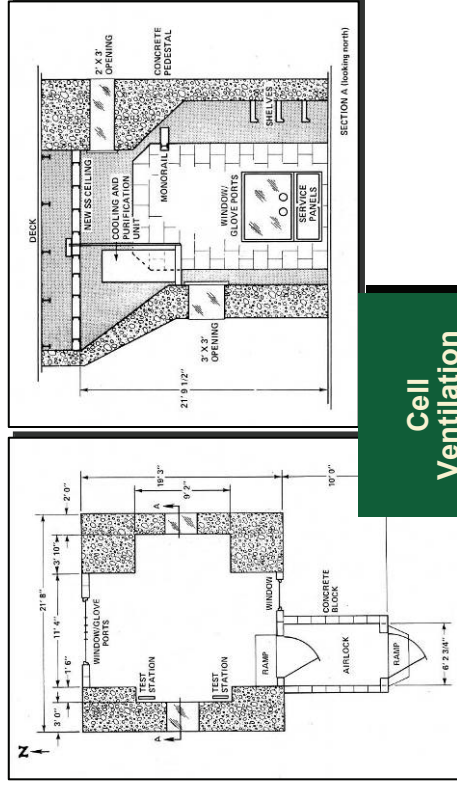
A word on complexity – What looks simple on a block diagram isn't!



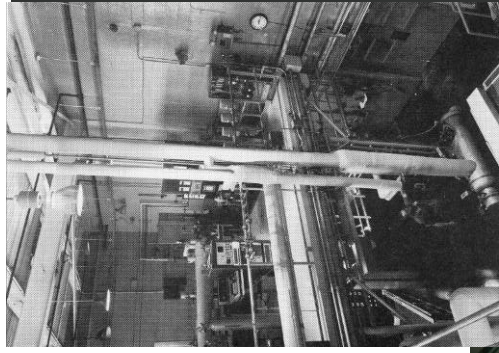
But wait there's more---

- **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

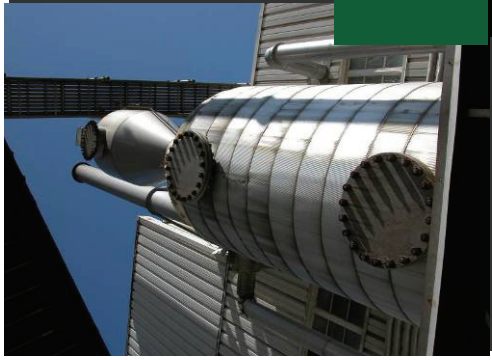
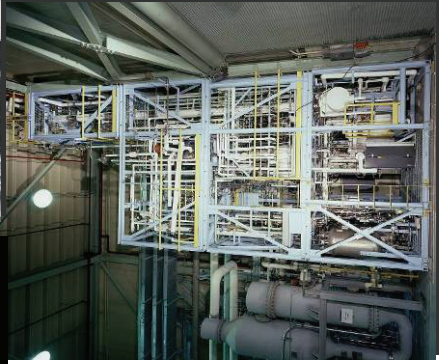
Fuel Reprocessing: Off Gas Treatment



Cell Ventilation

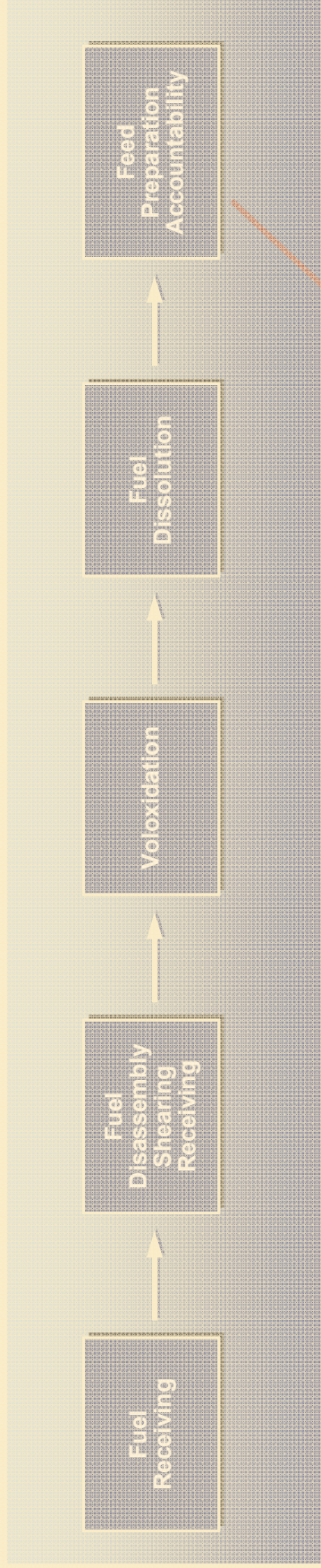


Dissolver Off-Gas

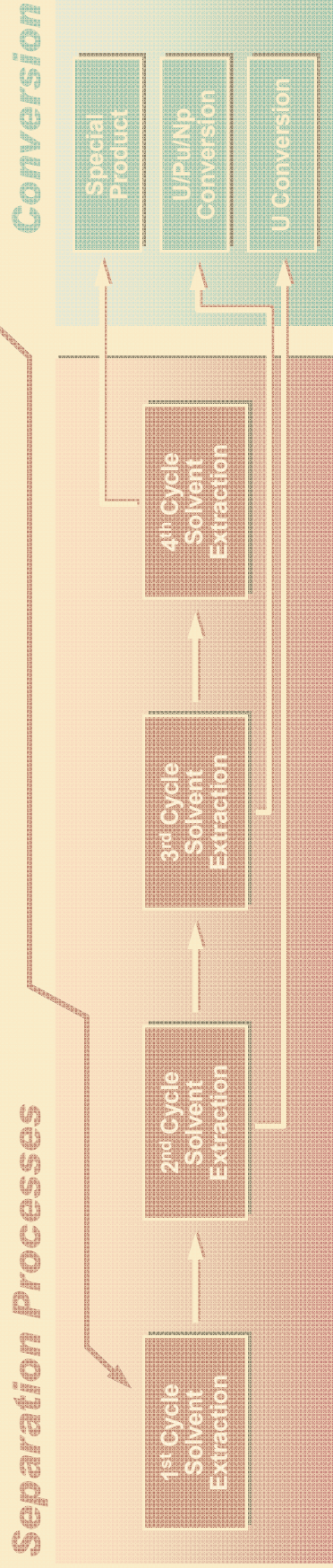


Vessel Off-Gas System

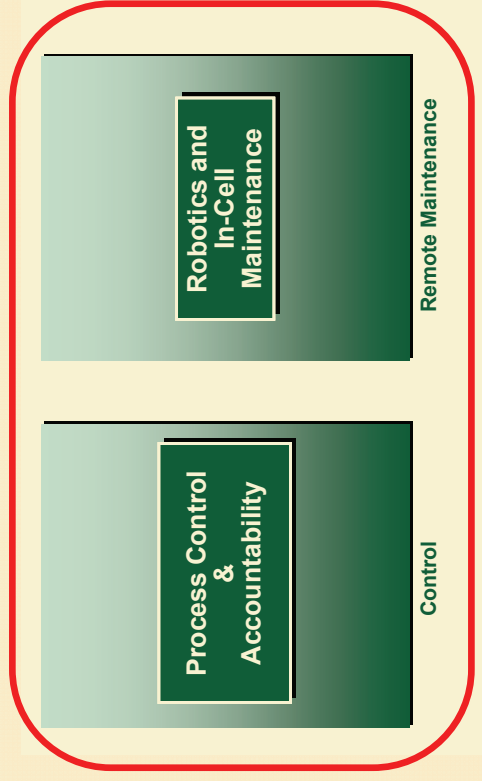
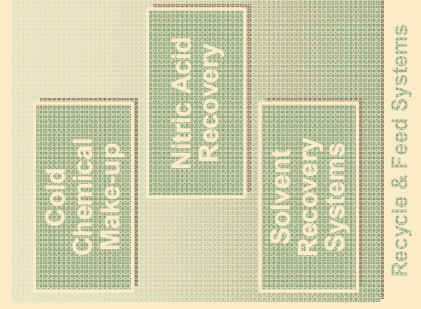
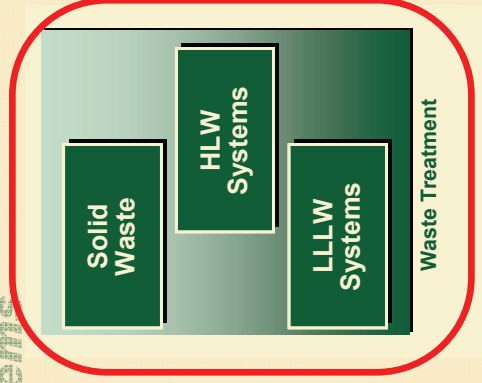
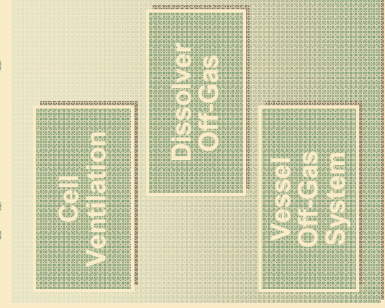
Head End



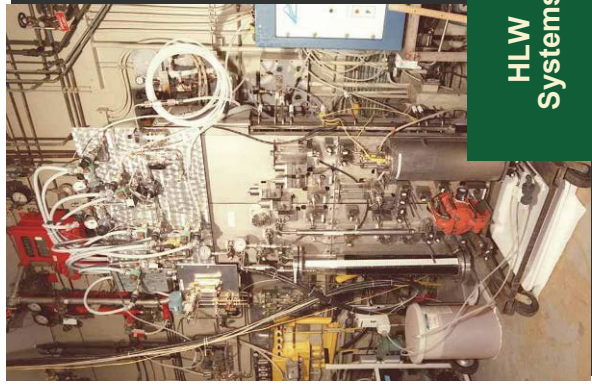
Separation Processes



Support Systems



Fuel Reprocessing: Waste Treatment



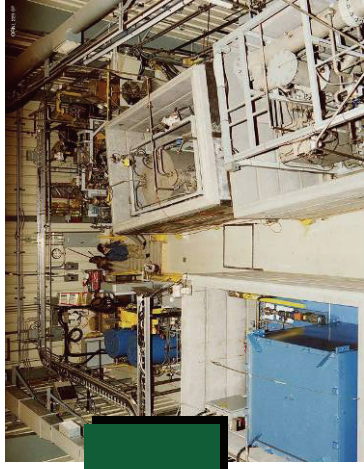
HLW
Systems



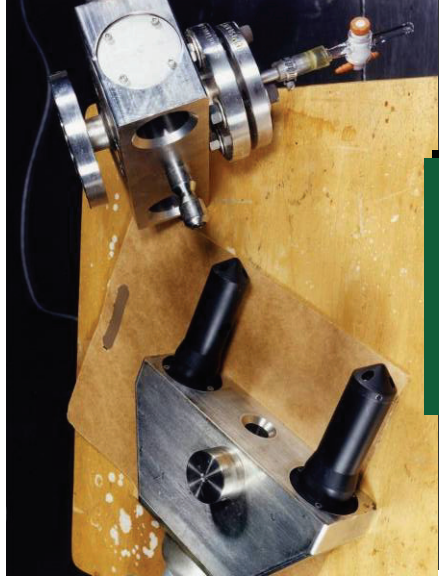
Solid Waste



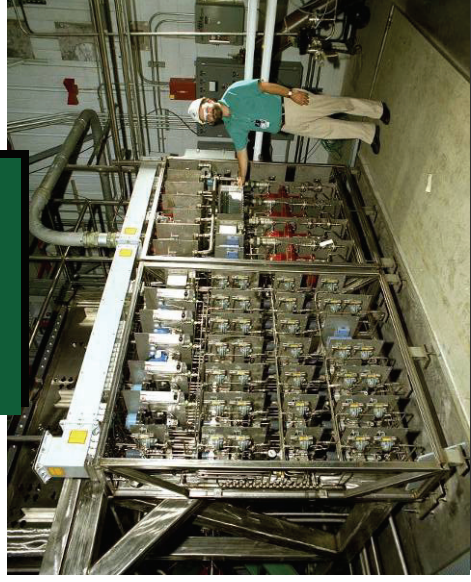
LLW
Systems



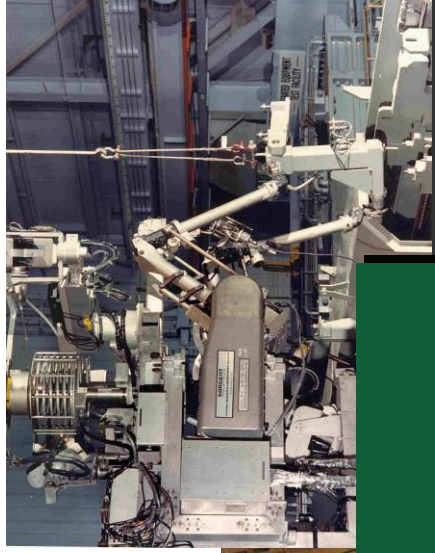
Fuel Reprocessing: Process Control and Accountability



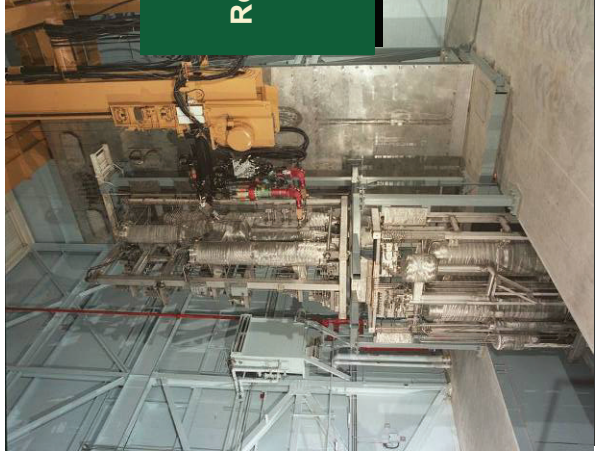
Process Control



Fuel Reprocessing: Remote Maintenance



Robotics and In-Cell Maintenance



So where do we go from here?

- I'm glad you asked that question

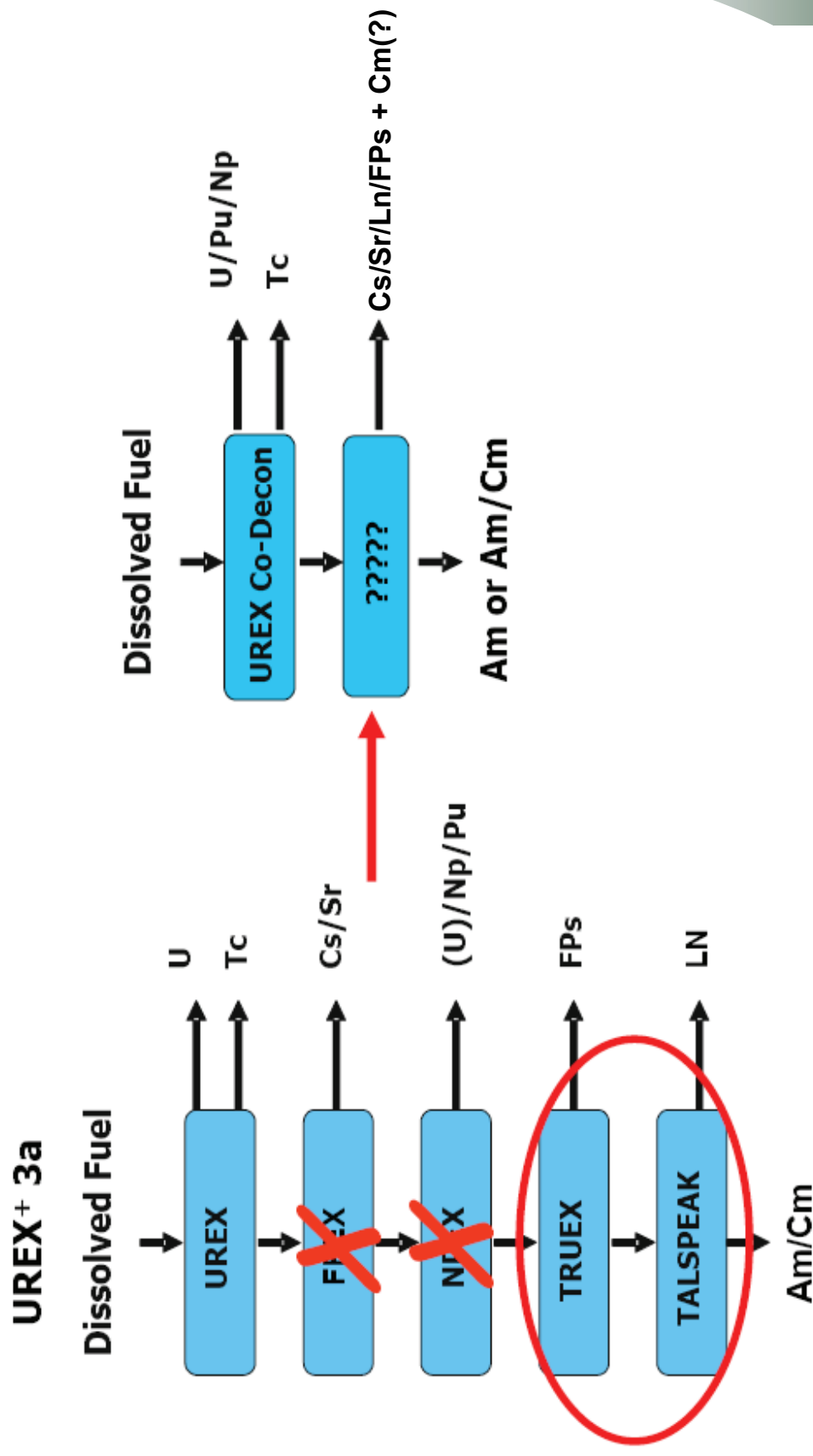
AFCI Separations Campaign FY-08 Major Accomplishments

- **Revised campaign research strategy for aqueous processing**
 - De-emphasize repetitive testing of separation process at lab-scale using small amounts of used nuclear fuel
 - Focus on head-end operations
 - *Voloxidation to separate tritium*
 - *Off-gas capture and immobilization of I, Xe, Kr, ³H, ¹⁴C*
 - Demonstrate product conversion using modified direct denitration
 - Transition development activities from laboratory testing to engineering development
 - *Incorporate industry input into campaign development activities*
 - *Increase Technology Readiness Levels (TRL's) > 6*
 - *Incorporate solvent recycle effects into testing*
 - Integrate Waste Form development with Separations development

Separations Campaign FY-08 Major Accomplishments

- Revised campaign research strategy for aqueous processing
 - Focus on *simplification* of separation processes
 - Decay store HLW rather than separate Cs/Sr
 - Reduce number of separation steps and separated products
 - Separate U/Pu/Np together by manipulating valance states
 - Combine TRUEX/TALSPEAK or use alternative technology
 - Avoid dependence on rigid pH control
 - Develop science-based approach to develop alternative Am/Cm separation process
 - Formation of “SIGMA TEAM”
 - Multi-lab team focused on development of robust separation process for separation of Am or Am/Cm in a single step

Separations strategy evolution



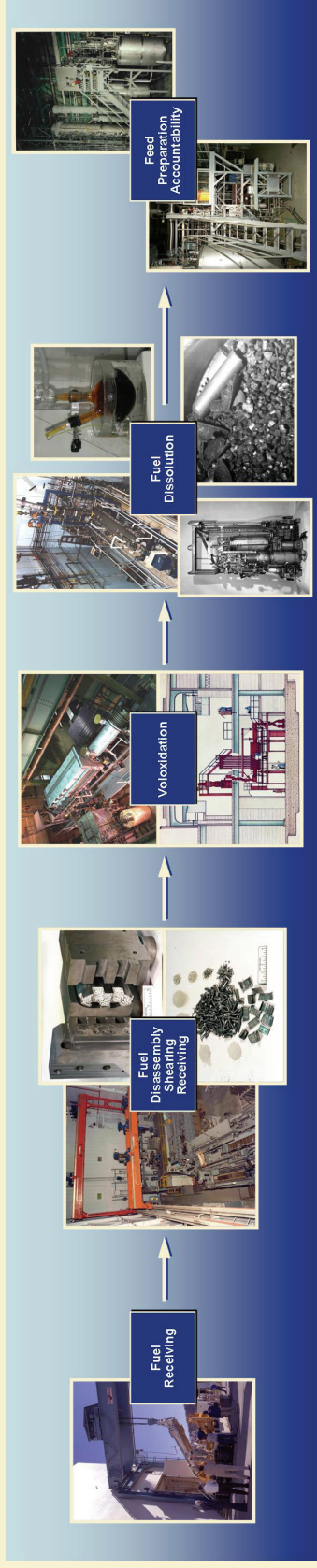
Development Focus on Aqueous Technologies

- Focus on simplification of process is key objective to improve operation and reliability and reduce cost
 - Largest challenge is separation of Am/Cm or Am alone
- Capture and immobilization of volatile off-gas (Iodine, Kr, ^3H , ^{14}C ?)
- CETE Run 2 (focus on off-gas capture and MDD)
- Testing at scales larger than laboratory scale, in prototypic equipment w/ solvent recycle (increase TRL's)
- Integration of separations and waste form development activities (each affects the other)
- Process monitoring and control improvements
- Collaboration with industrial teams to identify and resolve design data needs

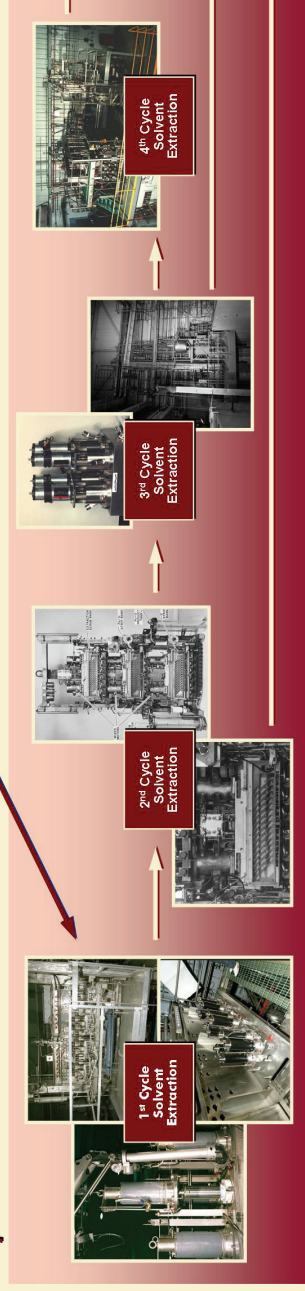
Fuel Reprocessing: The Big Picture

(actually a lot of little pictures)

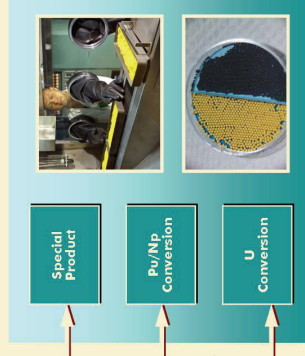
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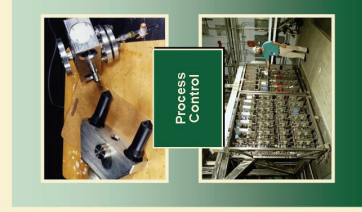
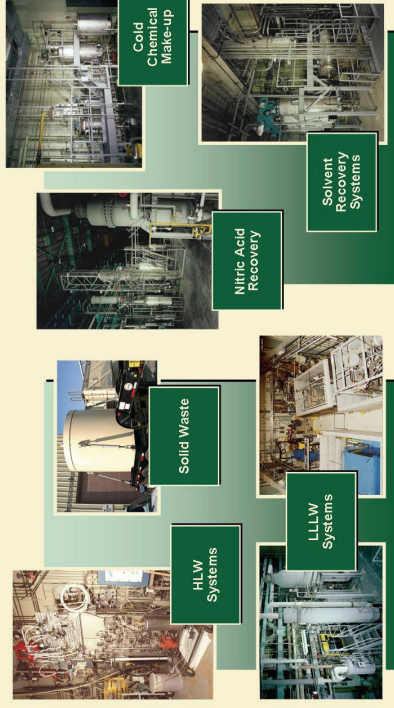
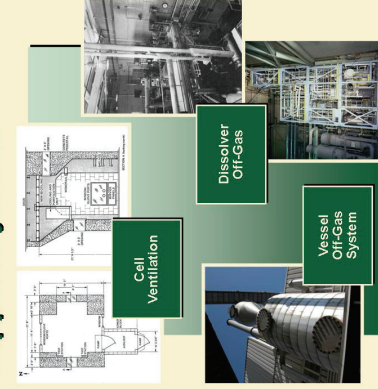
Separation Processes



Conversion



Support Systems



Off-Gas Treatment

Waste Treatment

Recycle & Feed Systems

Control

Remote Maintenance

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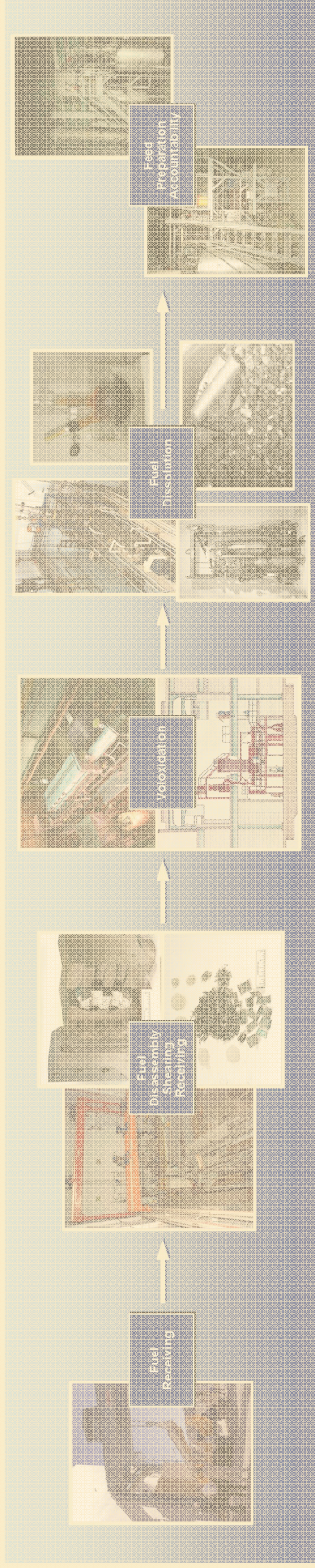
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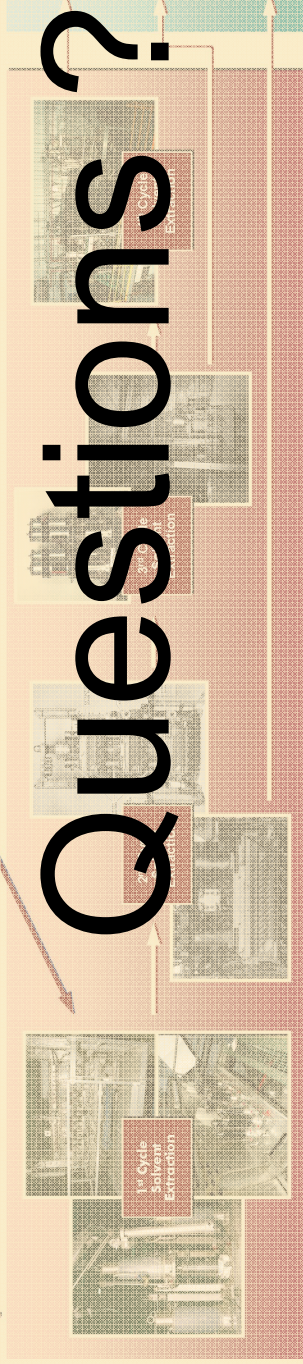
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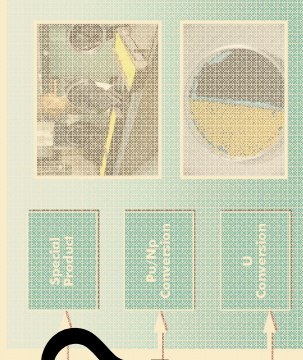
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Separation Processes



Conversion



Support Systems

