

Spent Fuel Recycle

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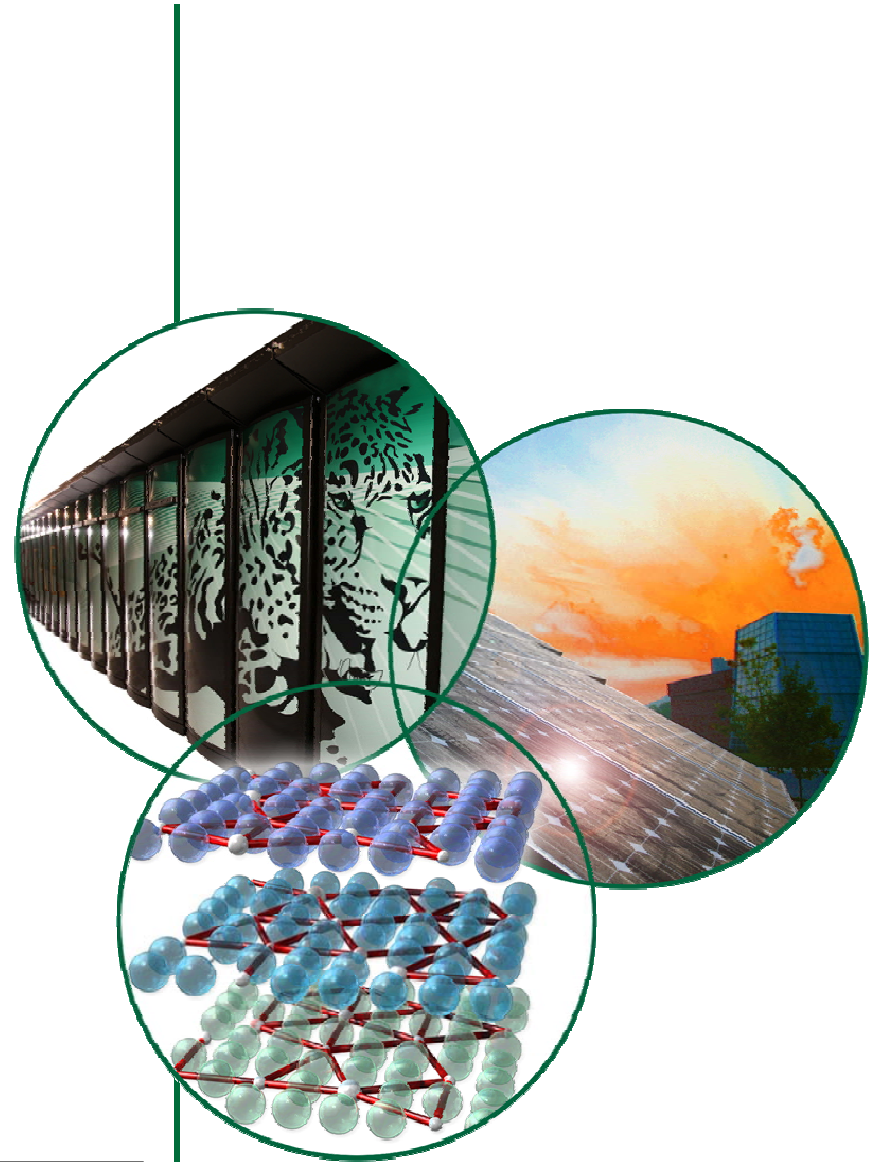
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Nuclear Science and Technology Division
Oak Ridge National Laboratory

Presented at:

*Introduction to Nuclear Chemistry and Fuel Cycle
Separations*

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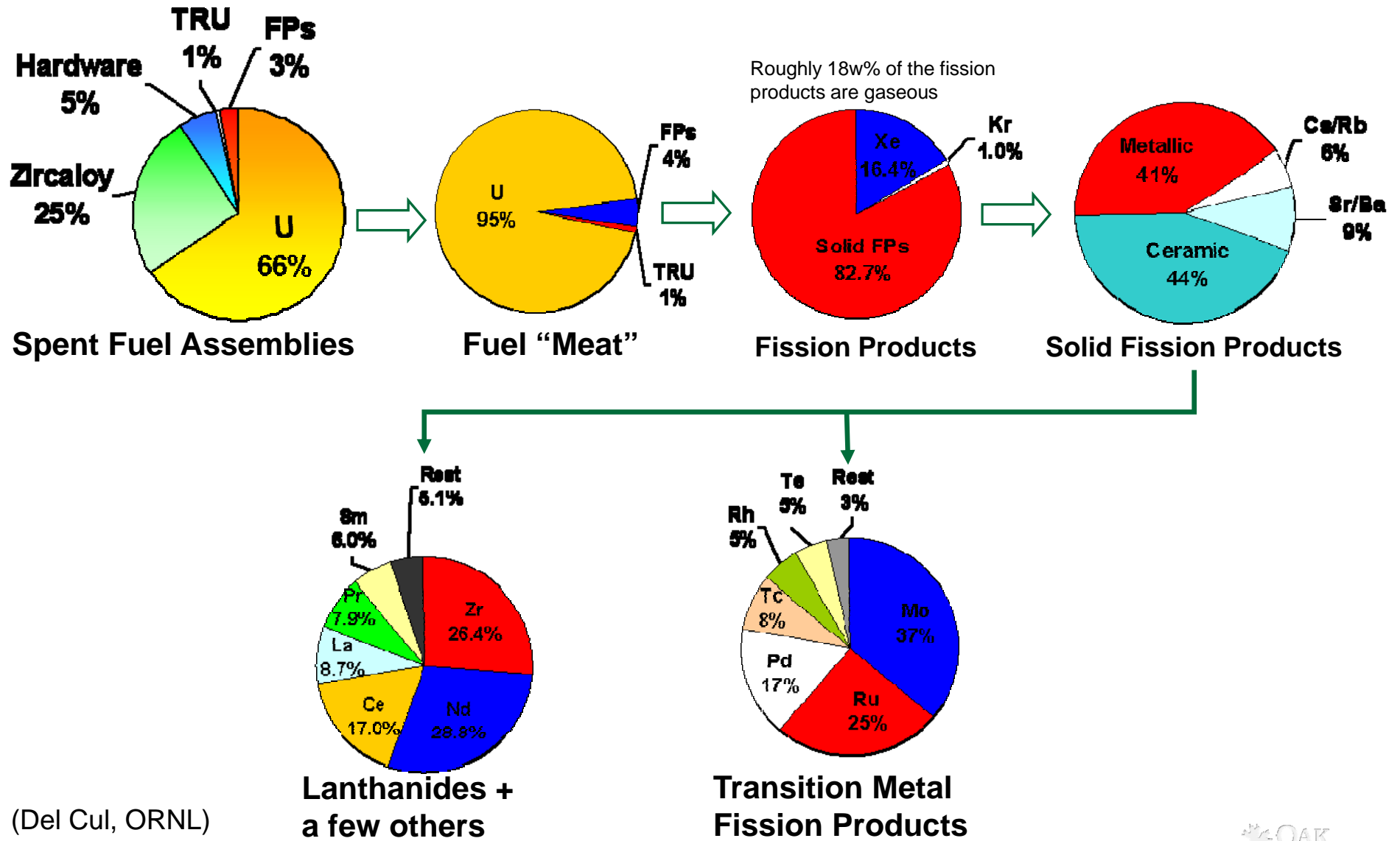
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Overview

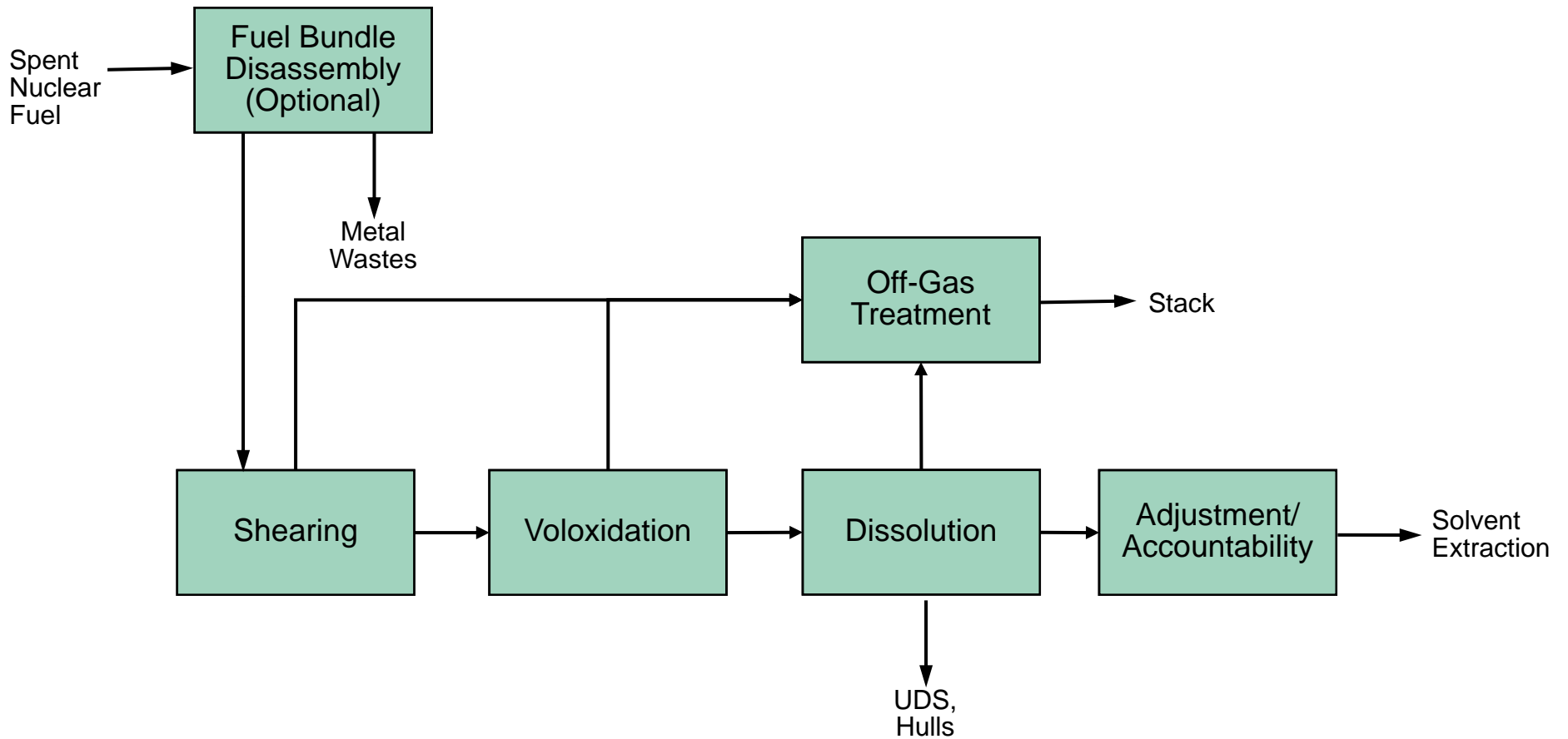
- Head-end
- Primary separations
- Product conversion
- Supporting separations
- Off-gas treatment

Composition of Used Fuel



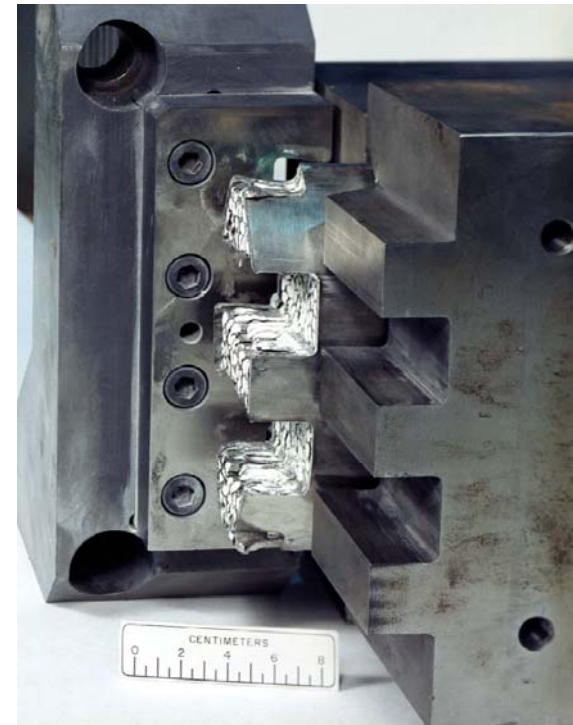
(Del Cul, ORNL)

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



Sheared simulated fuel

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

Voloxidation May Help with Fission Gas Removal - 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.

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.

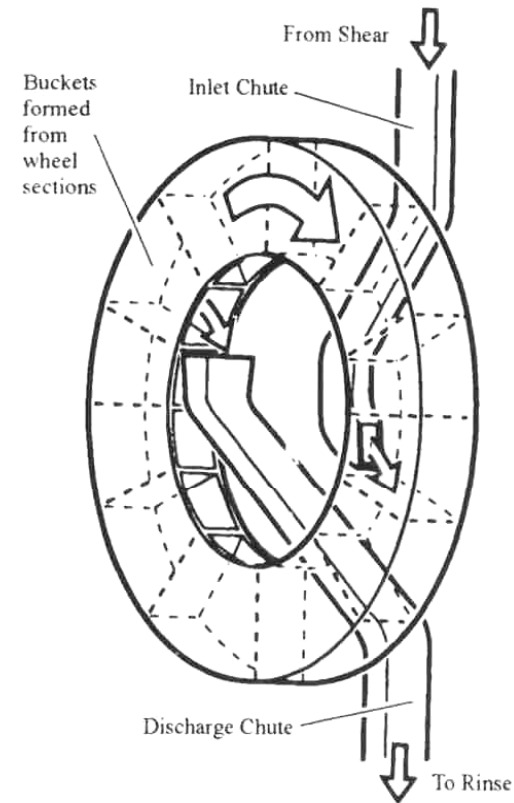
(Croff, K/NSP-121/Part 23/R2)

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:
 - $\text{U}_3\text{O}_8 + 7.35\text{HNO}_3 \rightarrow 3\text{UO}_2(\text{NO}_3)_2 + \text{NO}_2 + 0.35\text{NO} + 3.65\text{H}_2\text{O}$

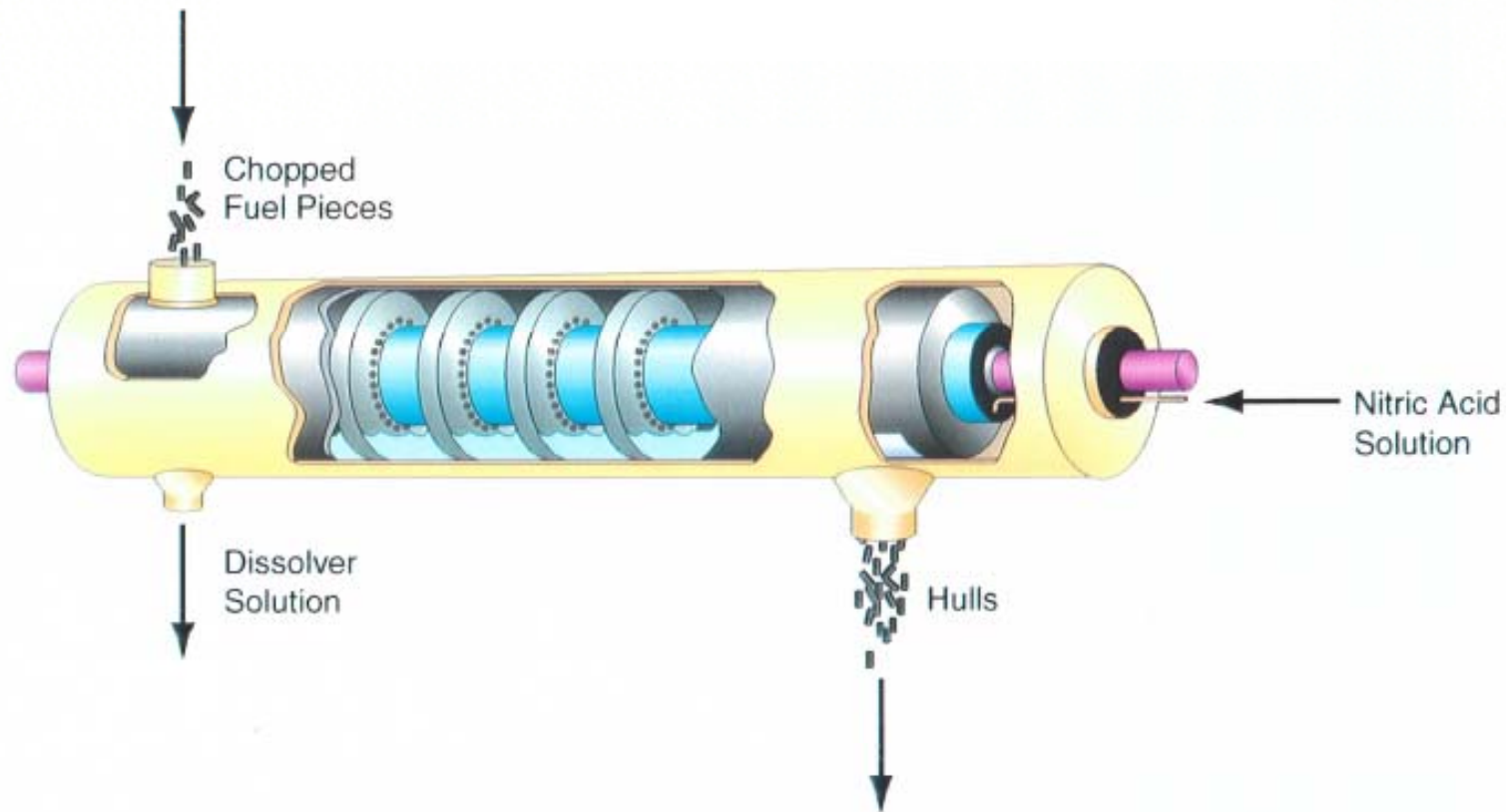
Dissolution Equipment is Designed to Aid in Mass Transfer

- 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 is an Update of Traditional Dissolvers



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

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)

Focus on a 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

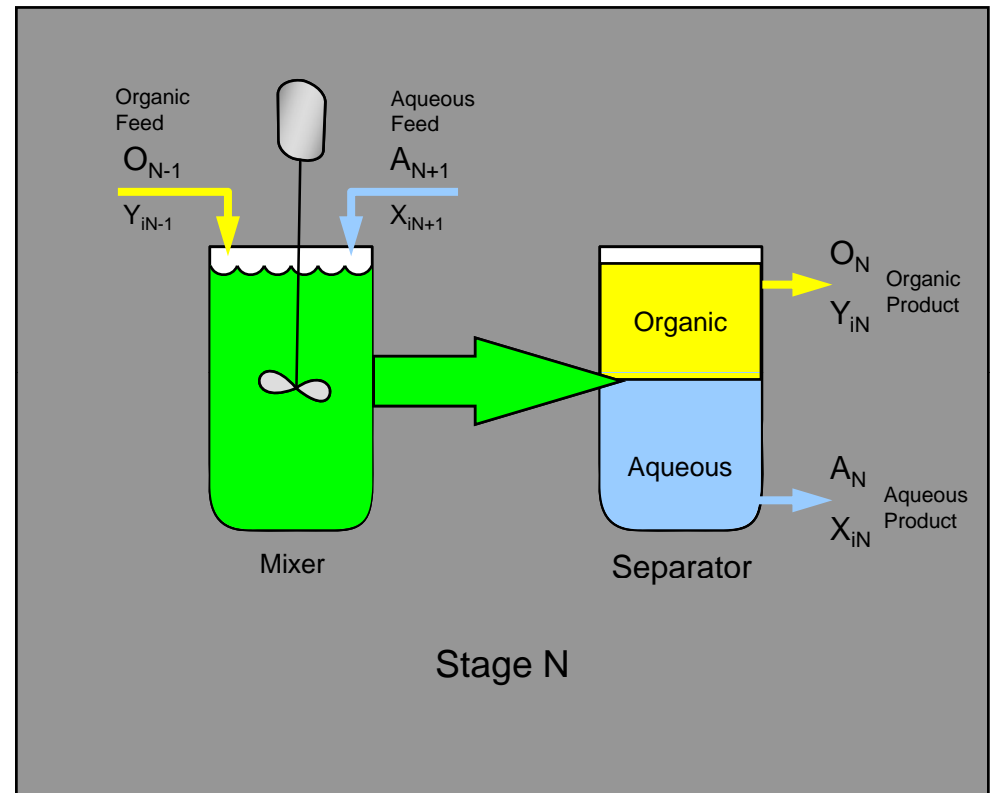
- What's extracted?

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

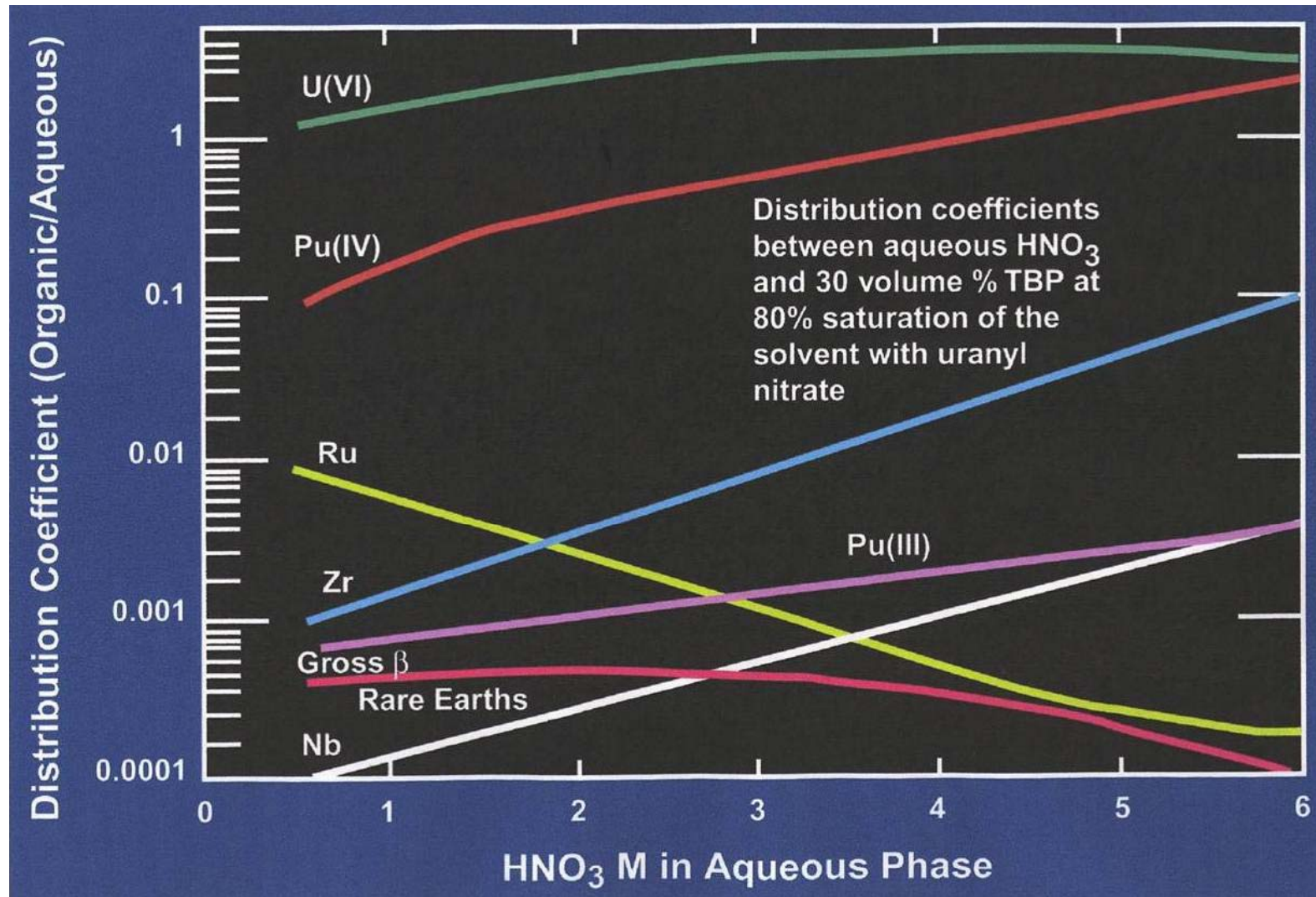
$$y_n = D(x_{n+1}) / (OD/A + 1)$$

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



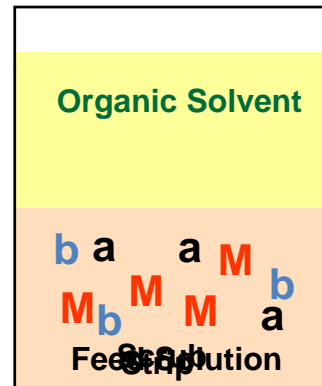
(Croff, K/NSP-121/Part 23/R2)

Basic Principles of Multistage Solvent Extraction

Extraction

Scrubbing

Stripping

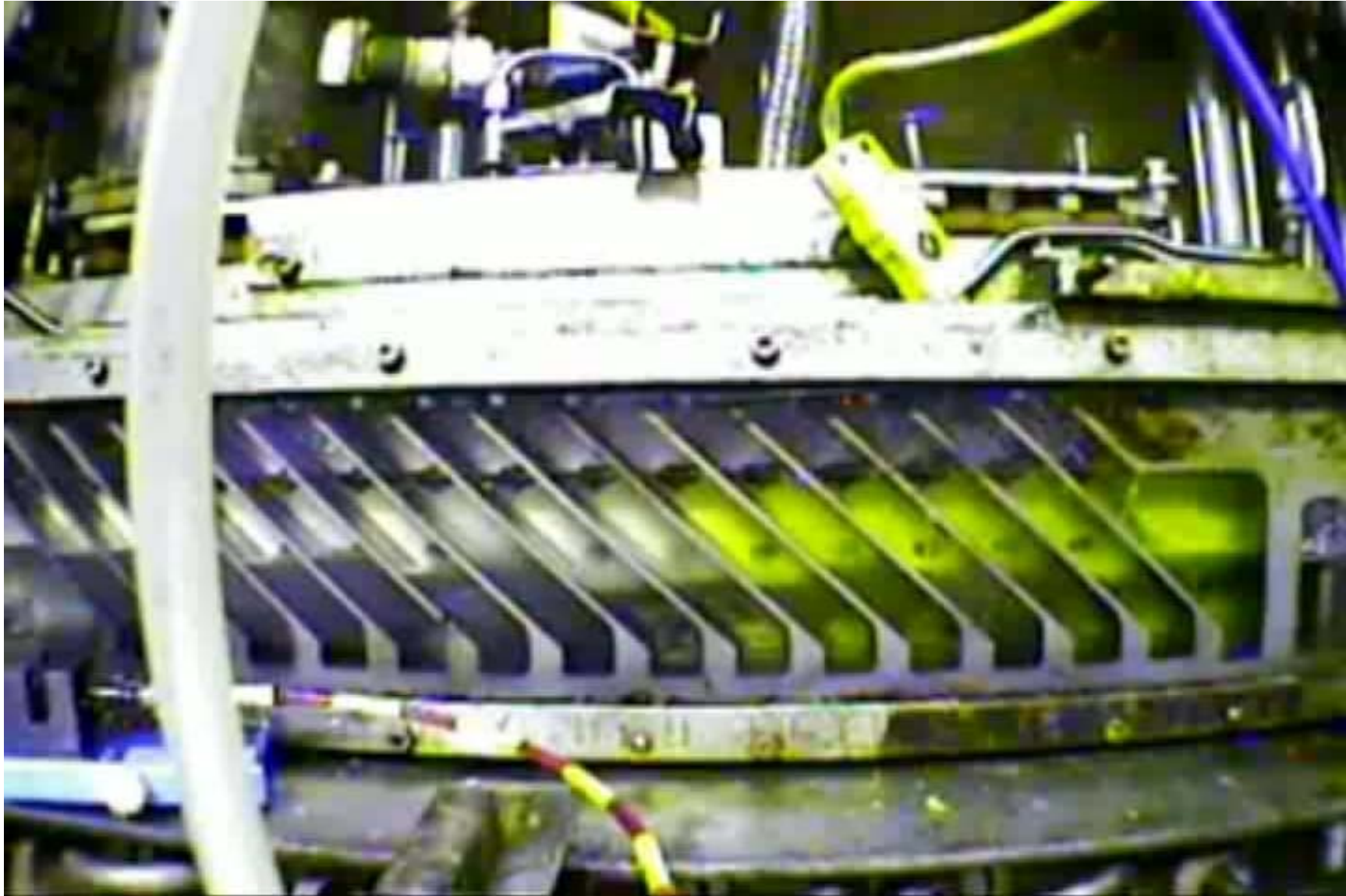


Separates metal to be recovered

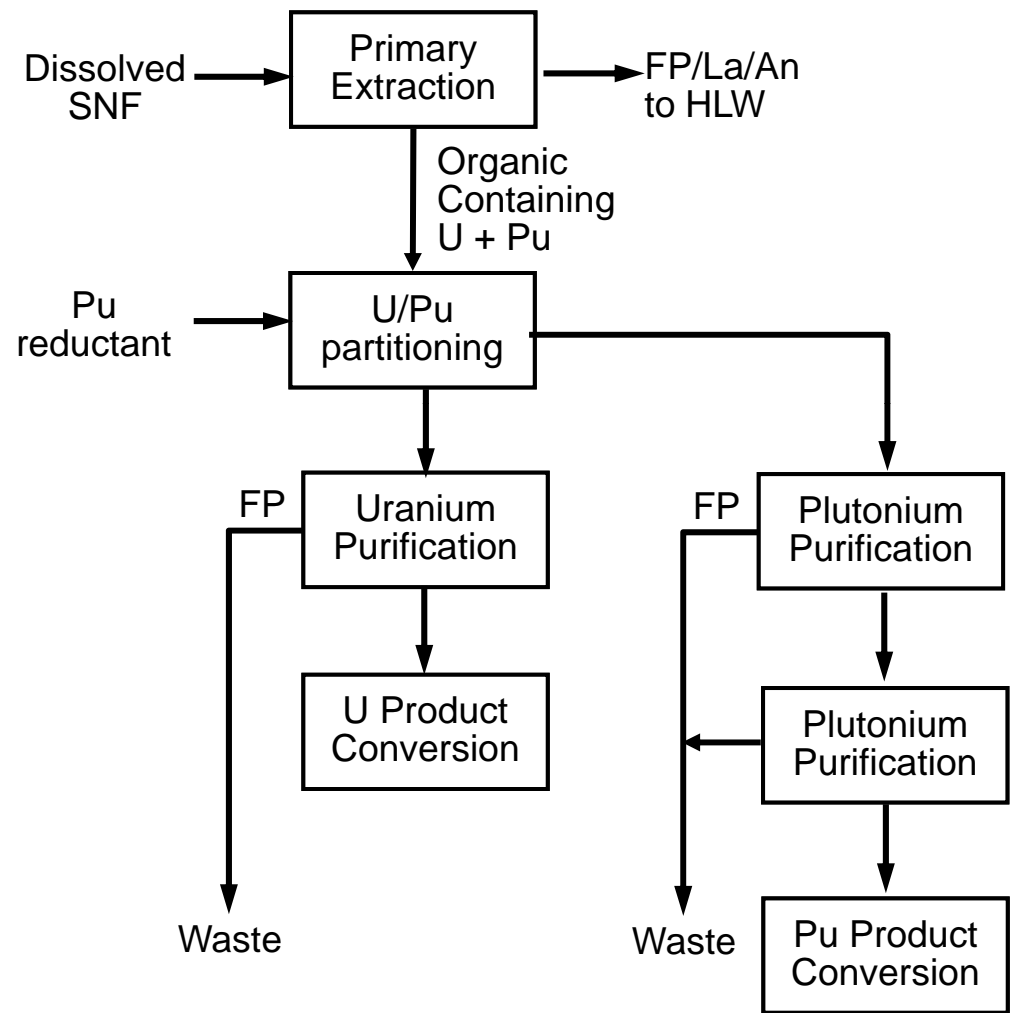
Removes impurities from metal

Recovers product in solution

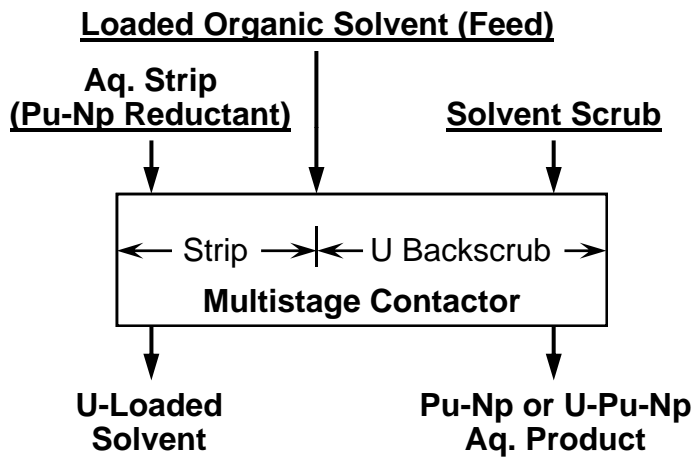
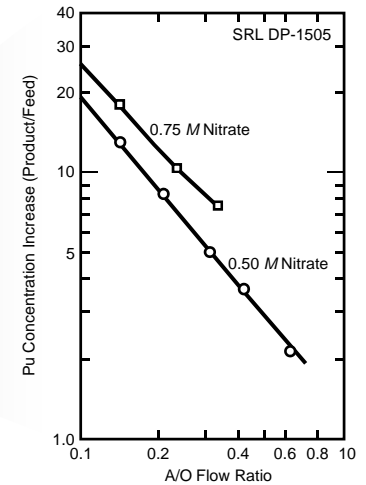
Solvent Extraction Equipment in Operation



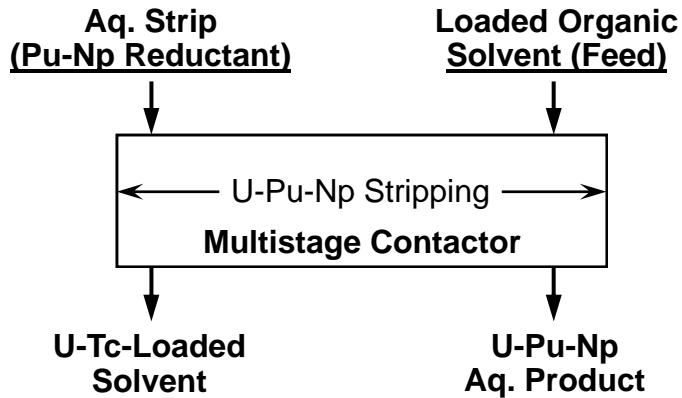
The Basic PUREX Process Flowsheet



There is an Option for Partial Partitioning of Uranium



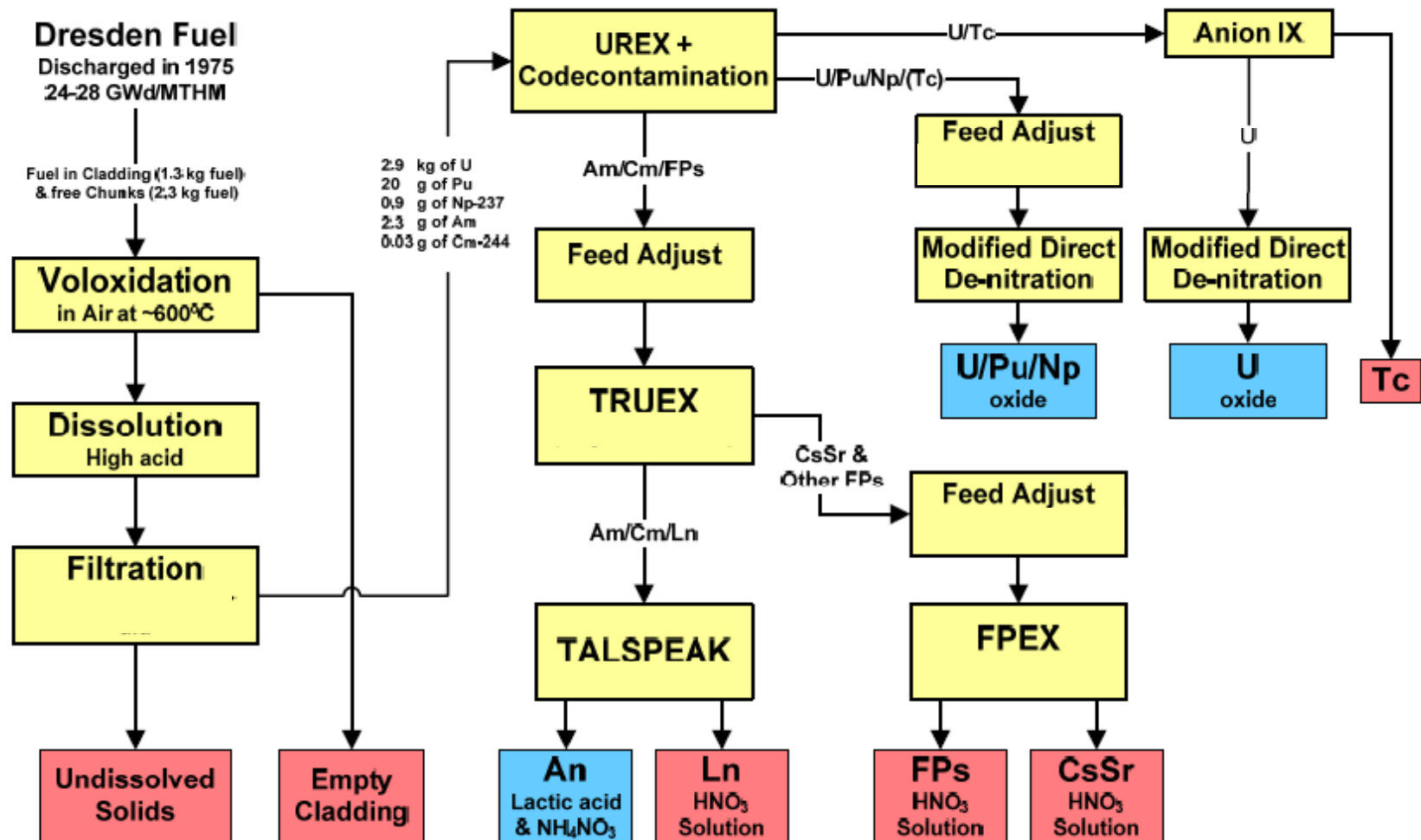
**PUREX-Type
Partitioning Contactor Bank**
(Complete or partial partitioning is possible)



**UREX+ Codecon Flowsheet
Partial Partitioning Contactor Bank**

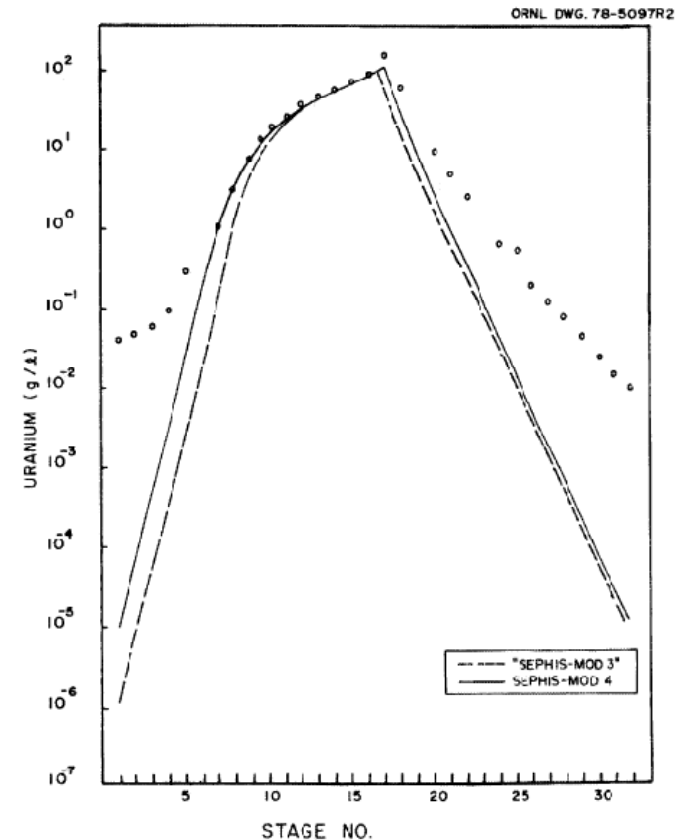
- Hydroxylamine nitrate (HAN) is used as combination Pu-Np reductant – aqueous salting agent
- Excess HAN in U-Pu-Np product readily decomposed by NOx to gases and water
- No holding reductant (hydrazine) is required

Recent Demonstration Flowsheet for the AFCI Program



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.



Basics of Ion Exchange

- 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)

Product Conversion is Necessary to Move from Aqueous to Solids

- 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)

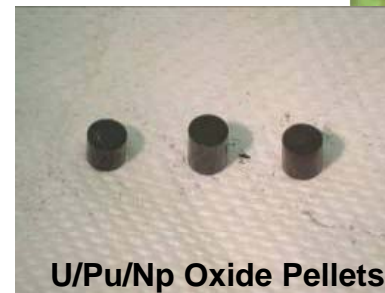
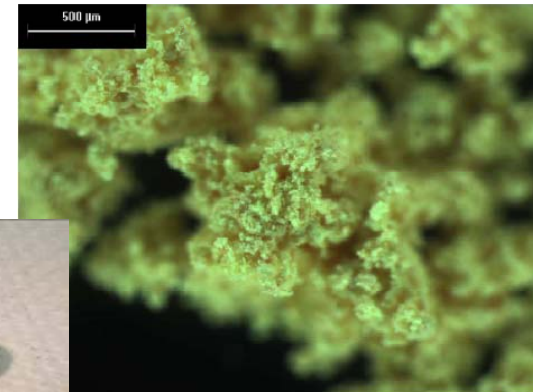
Product Denitration is an Option for Conversion

- 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)



Recycle / Recovery Systems are Necessary for Waste Minimization

- 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”

Basics of Distillation

- 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

Applications of Distillation / Evaporation

- Acid recycle
 - Nitric acid recovery from off-gas and waste processing
 - Dissolution in 800MT/yr plant requires ~ 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 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

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

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.

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

10 CFR 20	Air (Ci/m ³) at site boundary	Water (Ci/m ³)
Tritium	1.0×10^{-7}	1.0×10^{-3}
Carbon-14 (as CO ₂)	3.0×10^{-5}	---
Krypton-85	7.0×10^{-7}	N/A
Iodine-129	4.0×10^{-11}	2.0×10^{-7}

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

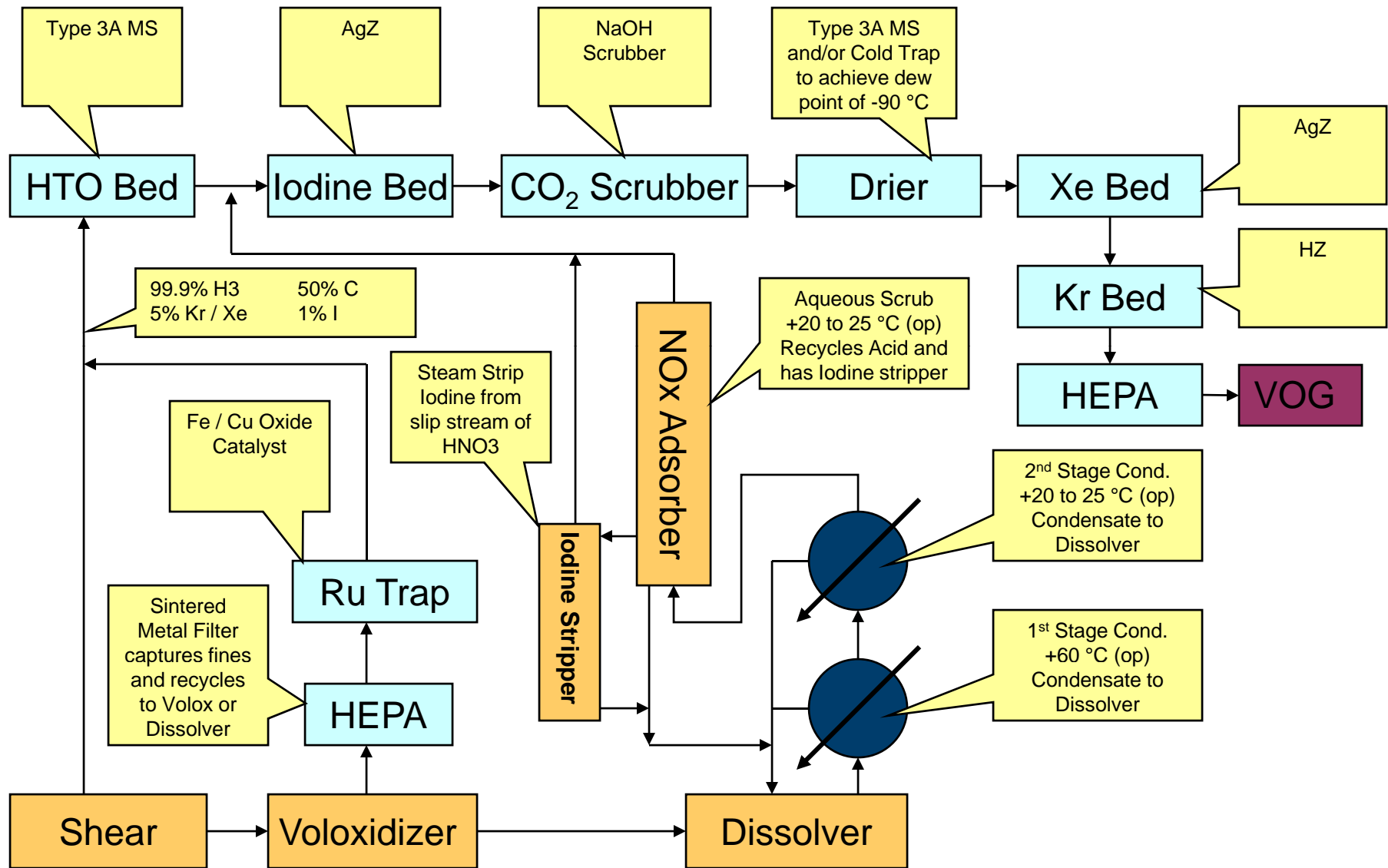
Regulatory Drivers: 40 CFR 190

- (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
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

Notional Combined VoxOG / DOG System



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