



Spent Nuclear Fuel Reprocessing

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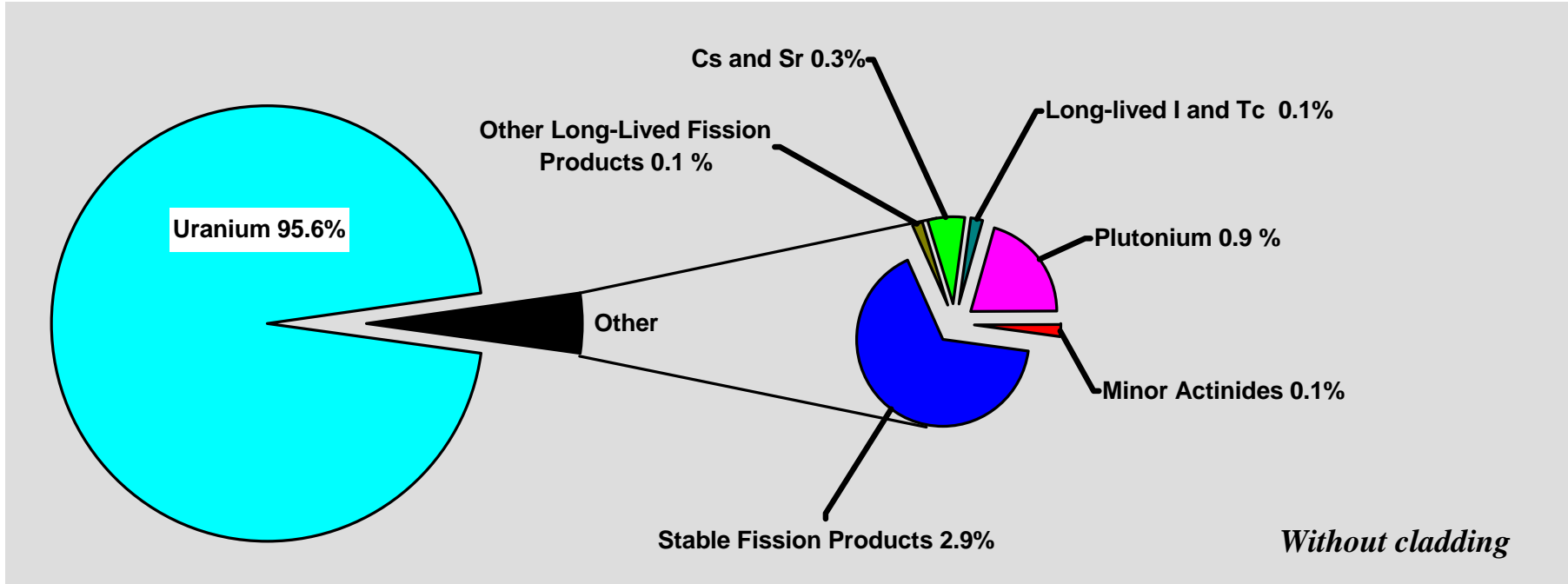
Outline

- **Spent nuclear fuel**
- **Background and history of spent nuclear fuel reprocessing**
- **PUREX process description**
- **Current reprocessing activities in the world**
- **Criticality control in PUREX plants**
- **Accidents in PUREX plants**
- **Recent process modifications to PUREX**
 - COEX/NUEX/UREX
- **Questions**





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





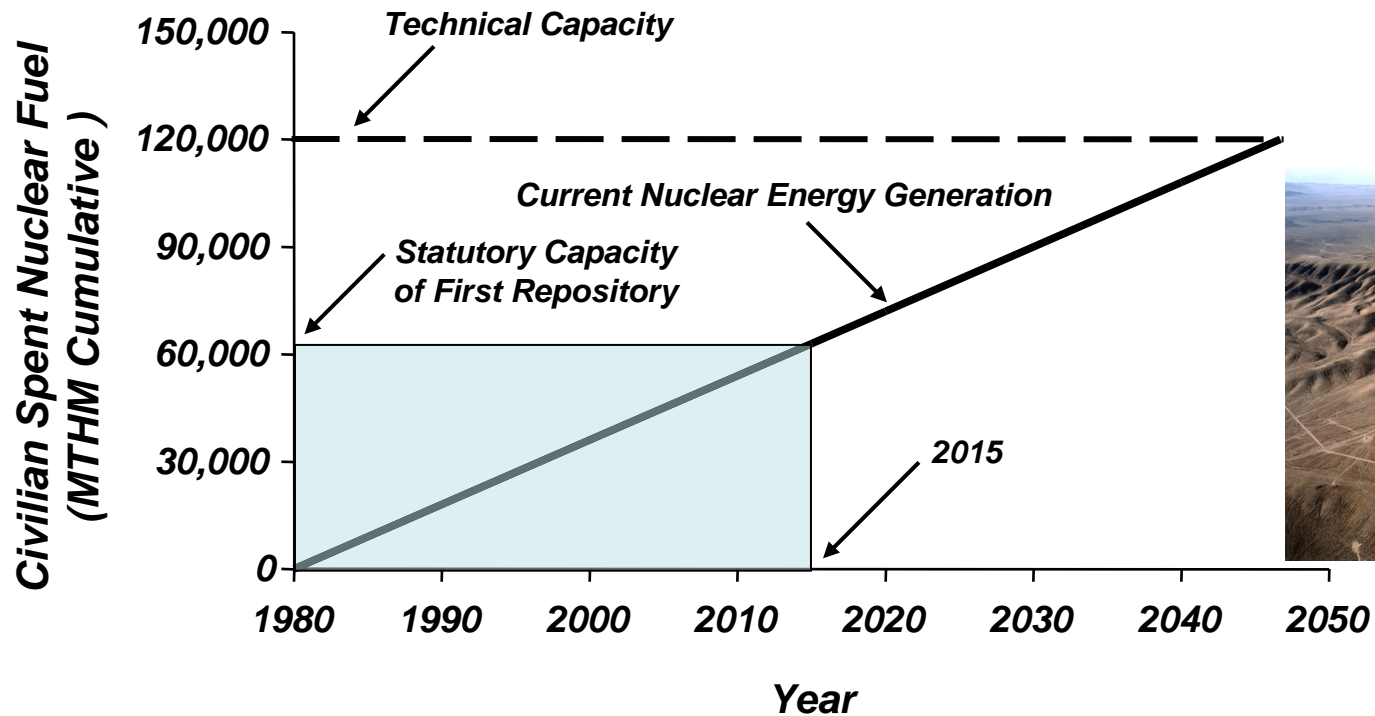
Spent Nuclear Fuel – current US situation

- Currently stored in pools or dry storage at the 60+ nuclear reactor sites in the U.S.
- Generated at approximate rate of 2100 MTHM/yr
- Slated for direct disposal into Yucca Mountain geologic repository
 - Yucca Mountain is not licensed or open at this time, spent fuel inventory will exceed legislated capacity before it is opened





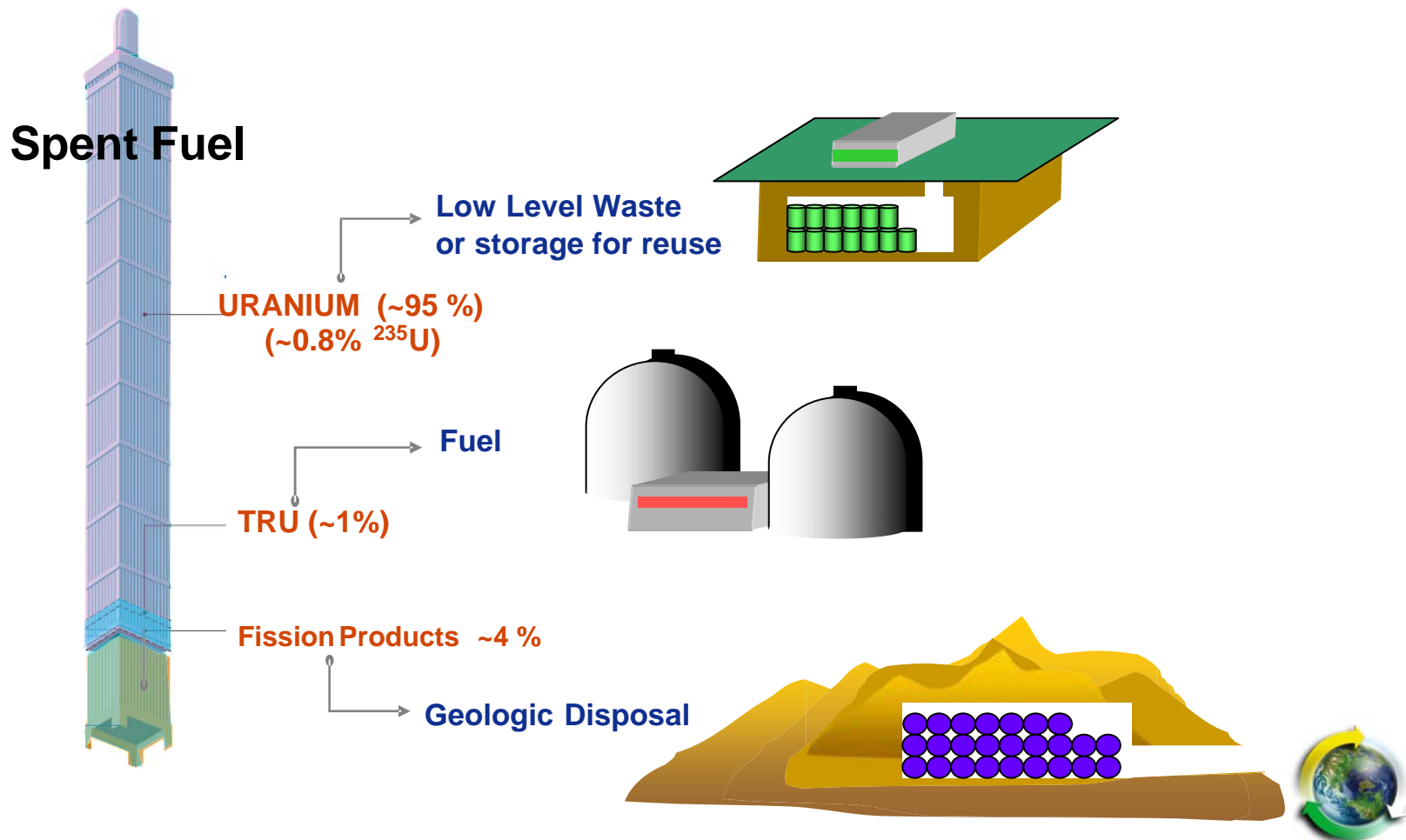
Spent nuclear fuel accumulation –direct disposal





Spent Fuel Processing (recycling)

96% of the metals in Spent Fuel (excluding cladding and hardware) can be recovered, with only a small fraction sent to the geologic repository





Spent fuel recycling

■ Benefits

- Natural resource conservation
- Reduction of waste heat load and radiotoxicity
- Reduced dependence on foreign oil, LNG, and coal

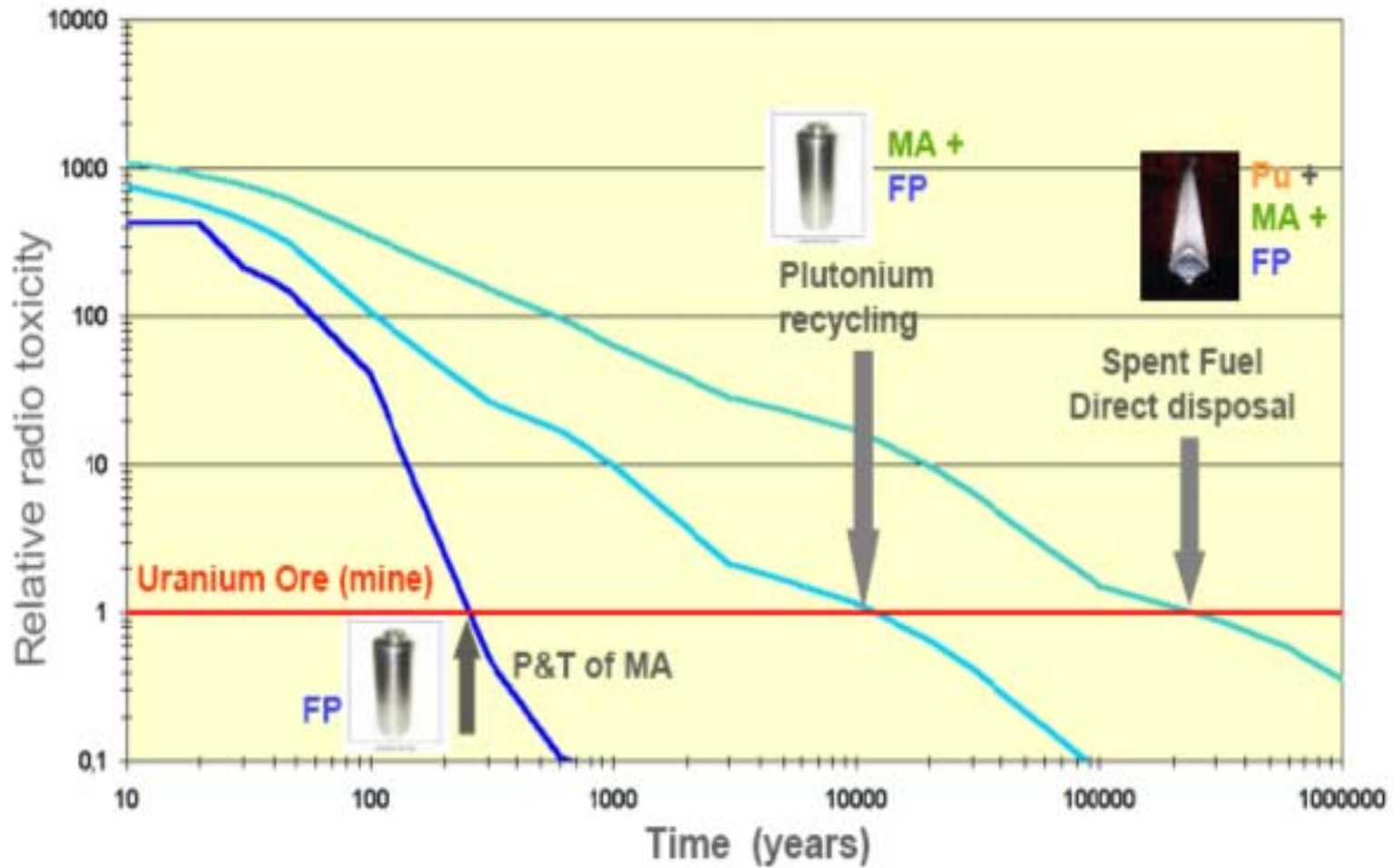
■ Challenges

- Cost
- Impact to the environment
- Proliferation and safety concerns
- Public acceptance





Spent fuel – radiotoxicity





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





Bismuth Phosphate Process

- **Dissolution of irradiated fuel or targets in nitric acid**
- **Pu valance 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**





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)





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 Nat. Lab 1948-49**
- **REDOX plant built in Hanford in 1951**
- **Used at Idaho for U-235 recovery**



Hanford REDOX -Plant (1951)





REDOX Process

- **Hexone (methyl isobutyl ketone) used as the extractant**
 - Immiscible with water
 - Used to purify uranium ore concentrates
 - Extracts both uranyl and plutonyl nitrates selectively from fission products
- **Plutonium oxidized to Pu (VI) for highest recovery**
- **U (VI) and Pu (VI) co-extracted, then Pu is reduced to Pu (III) by ferrous sulfamate and scrubbed from the solvent**
- **Hexone is highly flammable and volatile**
- **Large amounts of nonvolatile salt reagents added to process increased waste volume**





BUTEX Process

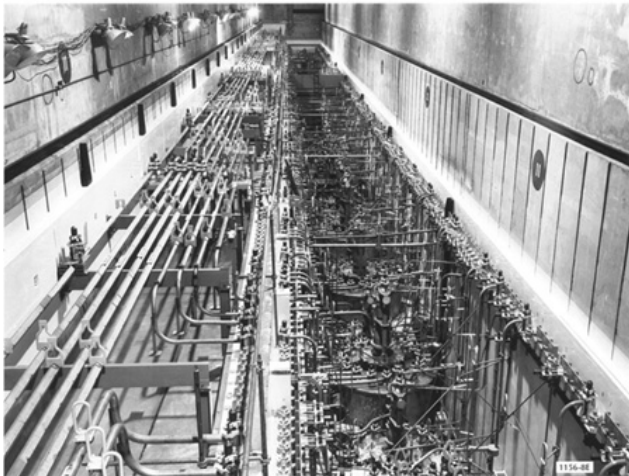
- **Developed in late 1940's by British scientists at Chalk River Laboratory**
- **Utilized dibutyl carbitol as solvent**
 - Lower vapor pressure than hexone
- **Nitric acid was used as salting agent**
 - Replaced need to use aluminum nitrate as in REDOX process
 - *Lower waste volumes*
- **Industrial 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 1950-52
 - Used for Pu production plant at Savannah River in 1954 (H-canyon facility still operational in 2008)
 - Replaced REDOX process at Hanford in 1956
 - Modified PUREX used in Idaho beginning in 1953 (first cycle)



Savannah River Site -- interior of canyon

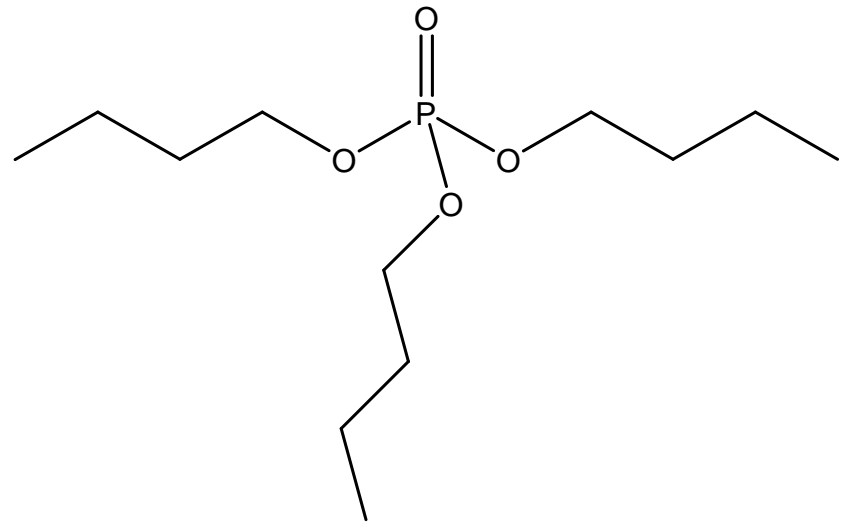




PUREX Process

■ 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 US

■ 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 reprocessing history Non-US (all PUREX)

■ 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 (~1200 MT/yr)

■ Japan

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





Reprocessing history in Russia

■ Mayak

- Plant B operated from 1949 to 1960
 - *Acetate precipitation followed by precipitation from fluoride solutions*
 - *High level wastes discharge to Techa river, then Lake Karachai*
- Plant BB operated from 1957 to 1987
 - *Similar acetate precipitation process, but repeated twice*
- Plant RT-1 (PUREX Process)
 - *Operation began in 1976*
 - *400 MTHM/yr capacity*
 - *Multiple lines to process commercial, HEU and naval fuels*





PUREX Process – history Russia

■ Krasnoyarsk -26

- Processing of Pu production reactor fuel began in 1964 using PUREX process
- Construction of new RT-2 plant began in 1972 (1000-1500 MTHM/yr capacity)
 - *Plant construction never completed*

■ Tomsk -7

- Processing of Pu production reactor fuel began in sometime after 1955 using PUREX process





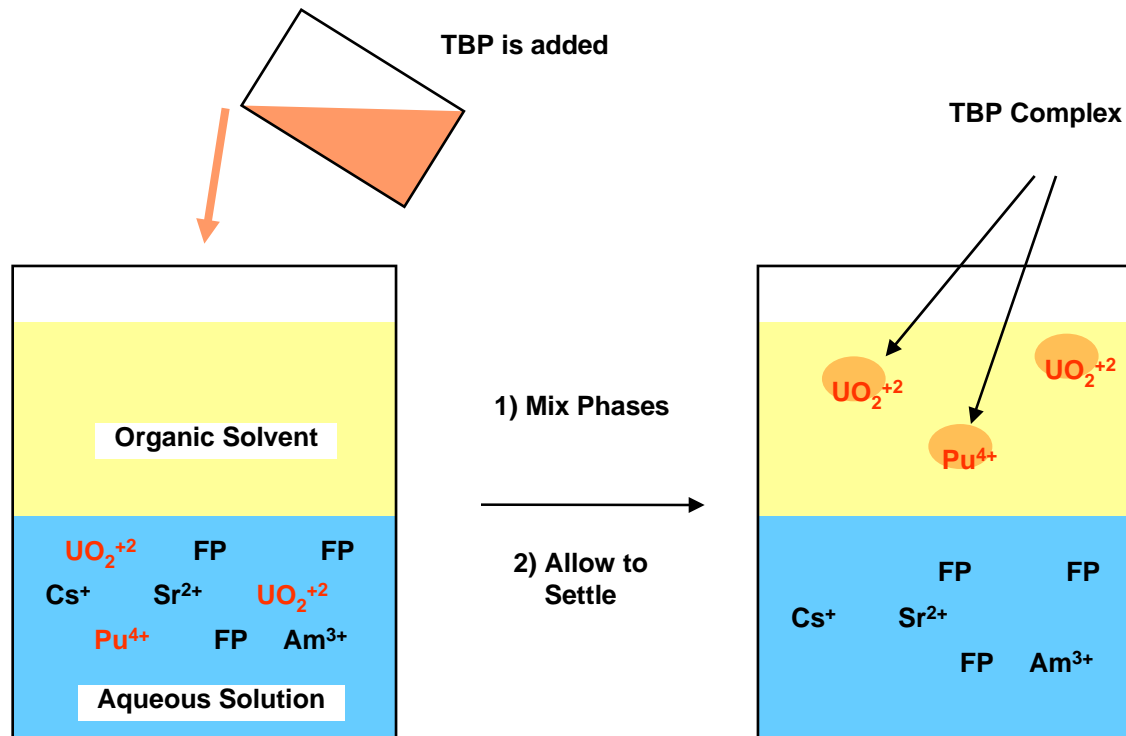
PUREX Process- Basic principles

- **Tri-butyl phosphate forms soluble complexes with uranyl nitrate and plutonium nitrate (neutral species of U(VI) and Pu(IV))**
- **Spent fuel is dissolved in nitric acid and is then mixed with a solution of TBP in a hydrocarbon diluent (immiscible with aqueous phase)**
- **At higher nitric acid concentrations (>0.5 M) the plutonium and uranium partition to the organic (solvent) phase while most of the metals and fission products stay in the aqueous phase**
- **Once separated from the fission products, the solvent can be mixed with another aqueous solution of low acidity (<0.01 M) and the uranium and plutonium will partition back to the aqueous phase.**
- **To separate plutonium from uranium, a reductant is added to the aqueous stream, reducing Pu(IV) to Pu(III), which is not soluble in the organic solvent and partitions to the aqueous phase while U(VI) remains in the solvent**





PUREX Process- Basic principles



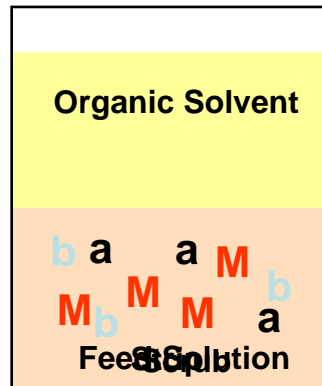


PUREX Process- Basic principles

Extraction

Scrubbing

Stripping



Separates metal to be recovered

Removes impurities from metal

Recovers product in solution





PUREX Process- Basic Principles

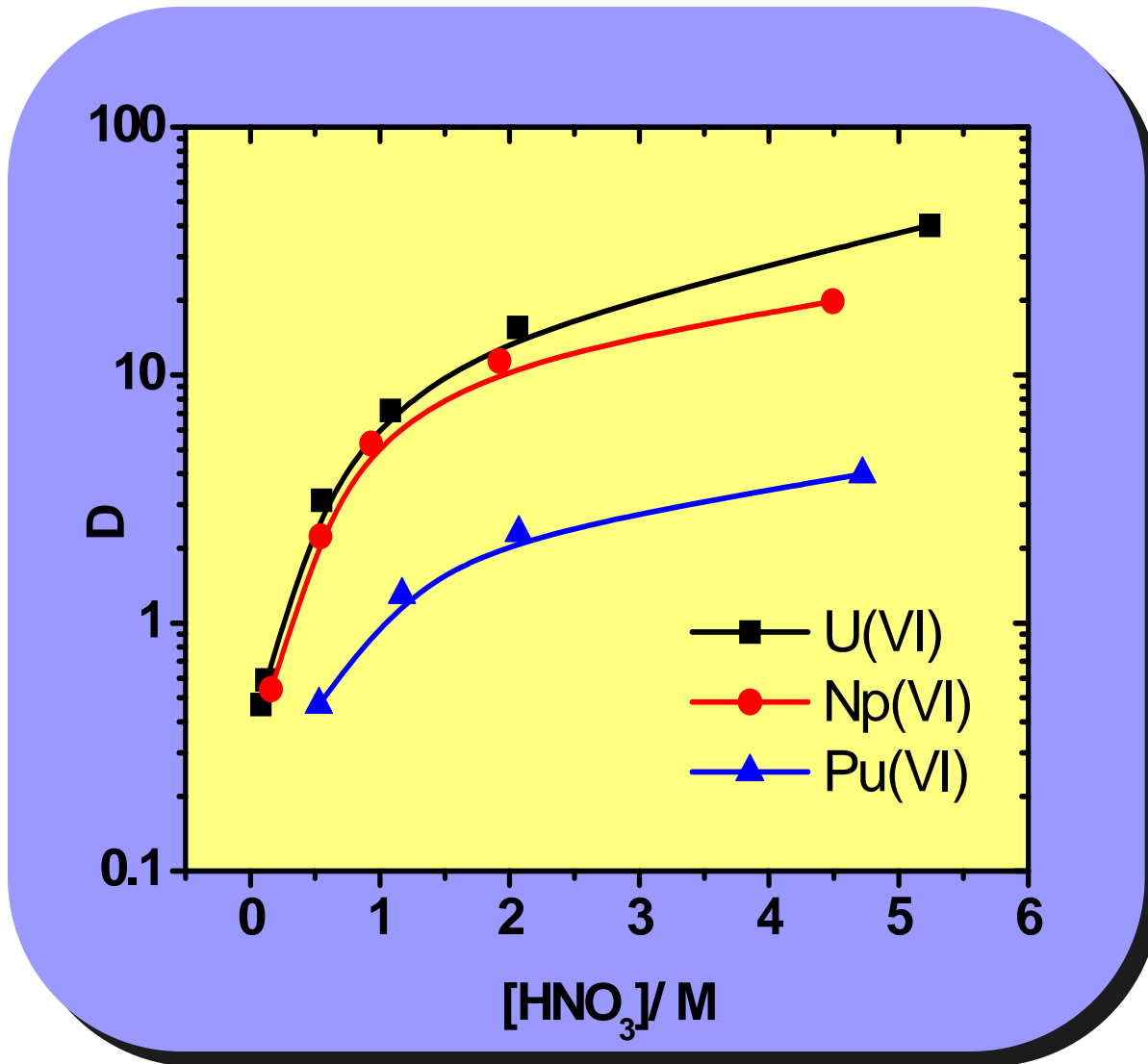
- **TBP is an effective extractant, but is too dense and viscous to use pure**
 - Hydrocarbon diluent used to improve physical characteristics
 - Typically 30 vol% TBP is used in the PUREX process
 - Diluents typically dodecane or kerosene (straight or branch chain hydrocarbons ranging from C-10 to C-14)

- **Salting effect**
 - Uranium and plutonium extraction is a function of nitrate concentration (called salting effect)



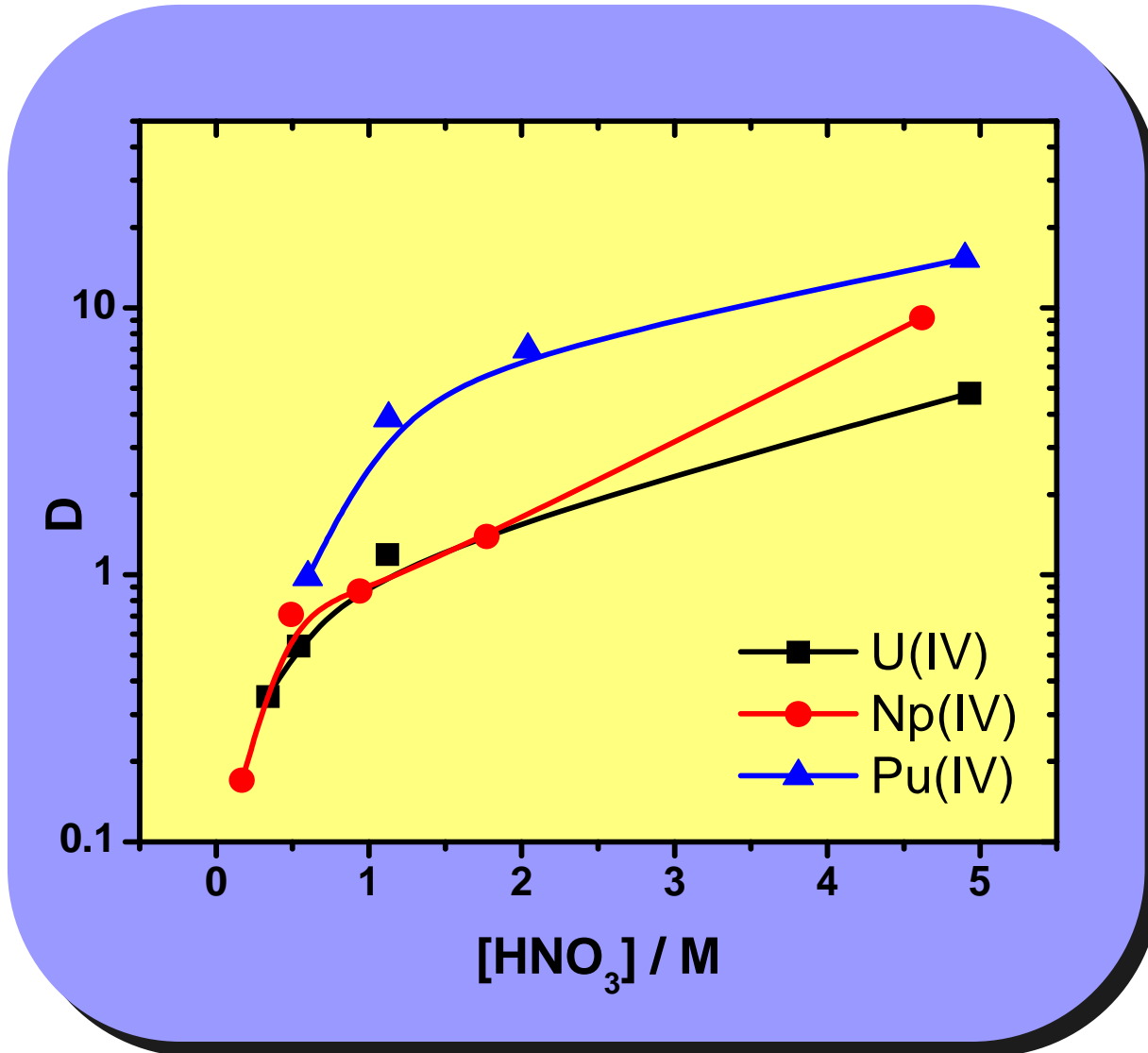


PUREX Process – Nitric acid dependence





PUREX Process – Nitric acid dependence





PUREX Process – Advantages and Disadvantages

■ Advantages of liquid-liquid extraction

- Continuous operation/ High throughput
- Countercurrent operation/ High purity and selectivity
- Recycle solvent, minimizing waste

■ Disadvantages of liquid-liquid extraction

- Solvent degradation due to hydrolysis and radiolysis
- Degradation products interfere with process chemistry
 - *Dibutyl and monobutyl phosphates*
 - Efficiently extract Pu, but cannot strip Pu from DBP or MBP
- Requires substantial tankage and reagents





PUREX Process – Process unit operations

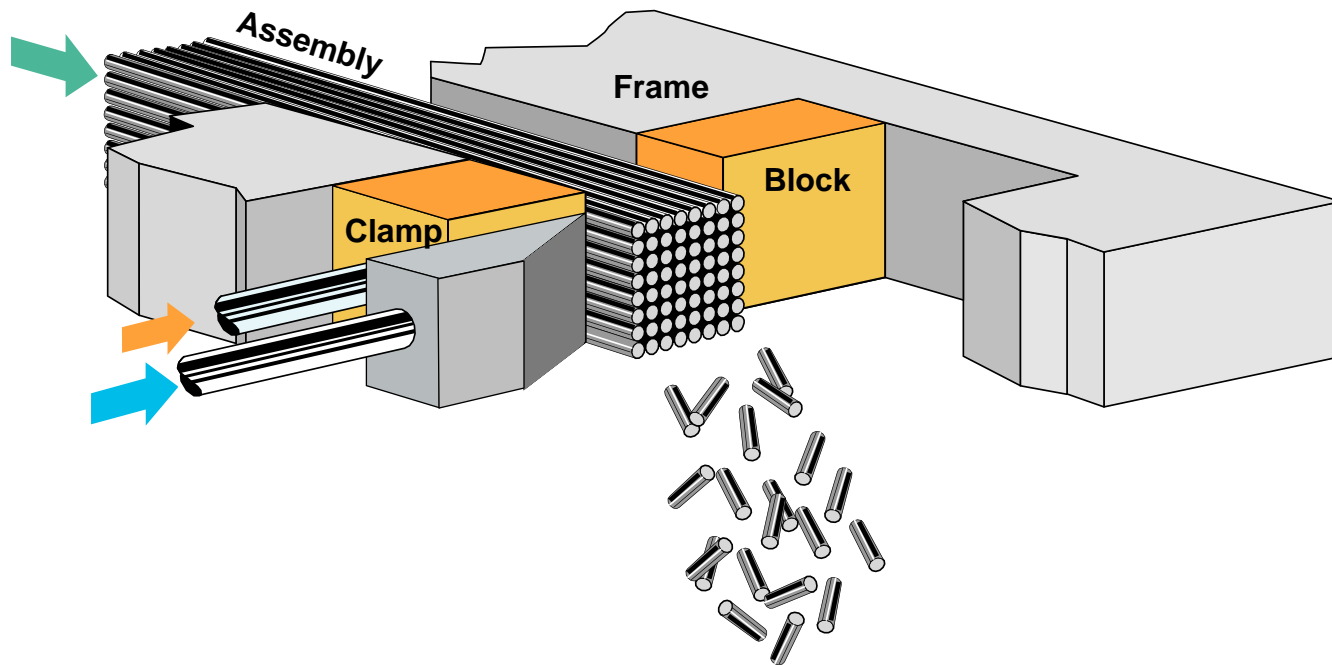
- Fuel decladding
- Dissolution/ feed clarification
- Separations
- Product conversion
- Waste treatment





PUREX Process – Process unit operations

■ Fuel Decladding

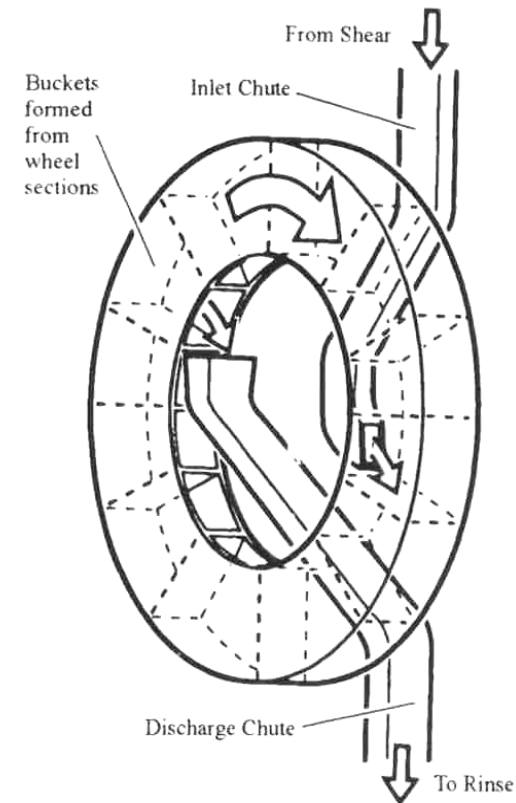




PUREX Process – Process unit operations

■ Dissolution/ feed clarification

- 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





PUREX Process – Process unit operations

■ Separations

- Continuous, countercurrent extraction operations are performed in mixer settlers, pulse columns or centrifugal contactors
- First cycle separates uranium and plutonium together from fission products
- U and Pu are then separated and sent to separate purification cycles

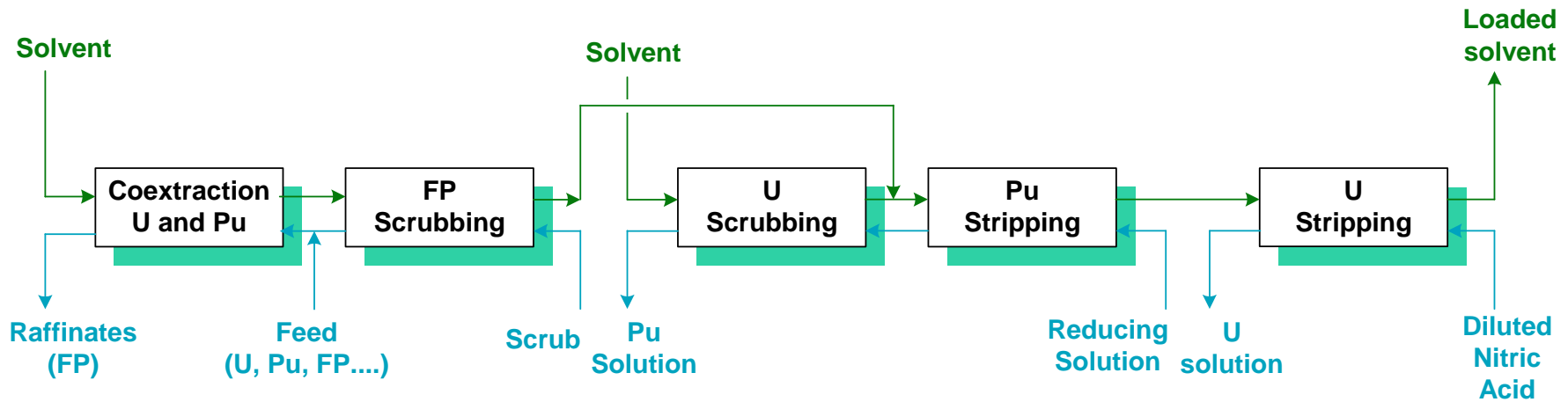




PUREX Process – Process unit operations

■ Separations

- Countercurrent PUREX flowsheet

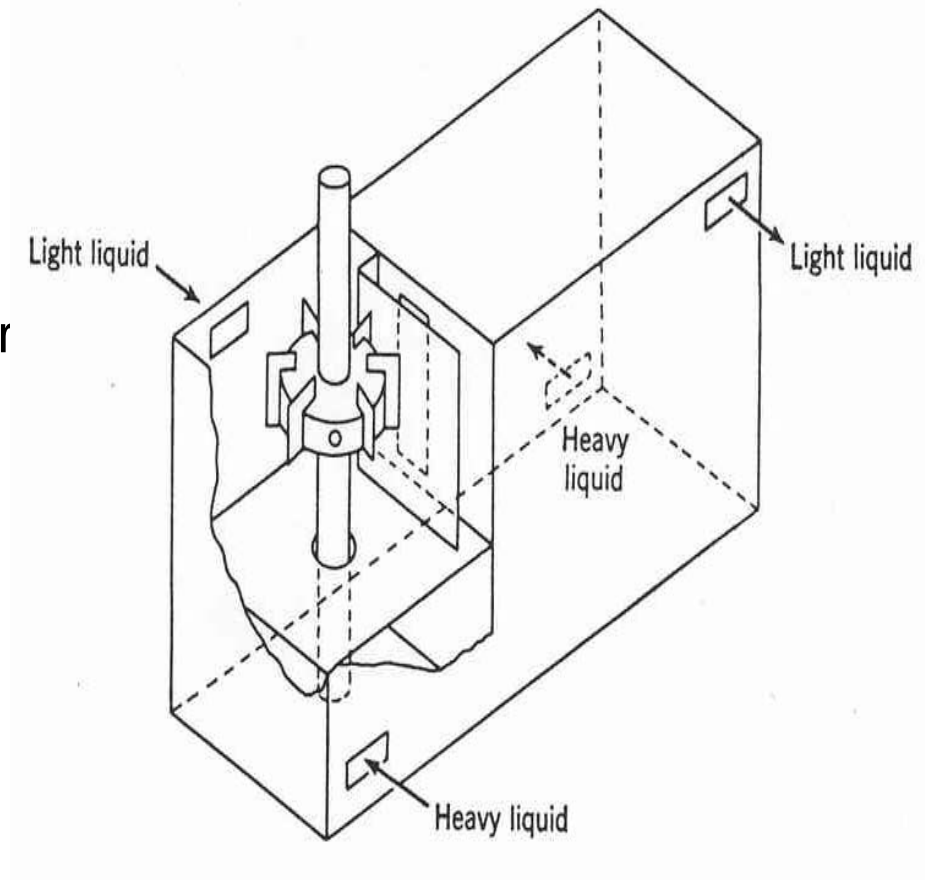




PUREX Process – Process unit operations

■ Mixer Settlers

- Discrete stage units (with efficiencies < 1)
- Low capital cost
- Requires large amount of floor space (but low headroom)
- Large solvent inventory
- Long residence times

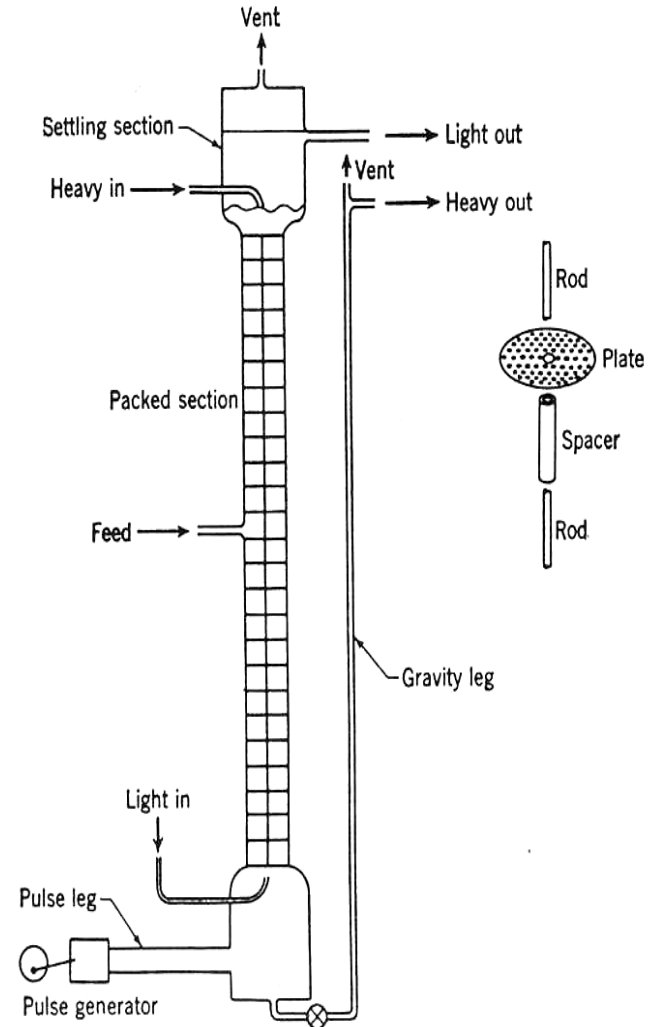




PUREX Process – Process unit operations

■ Pulse Extraction Column

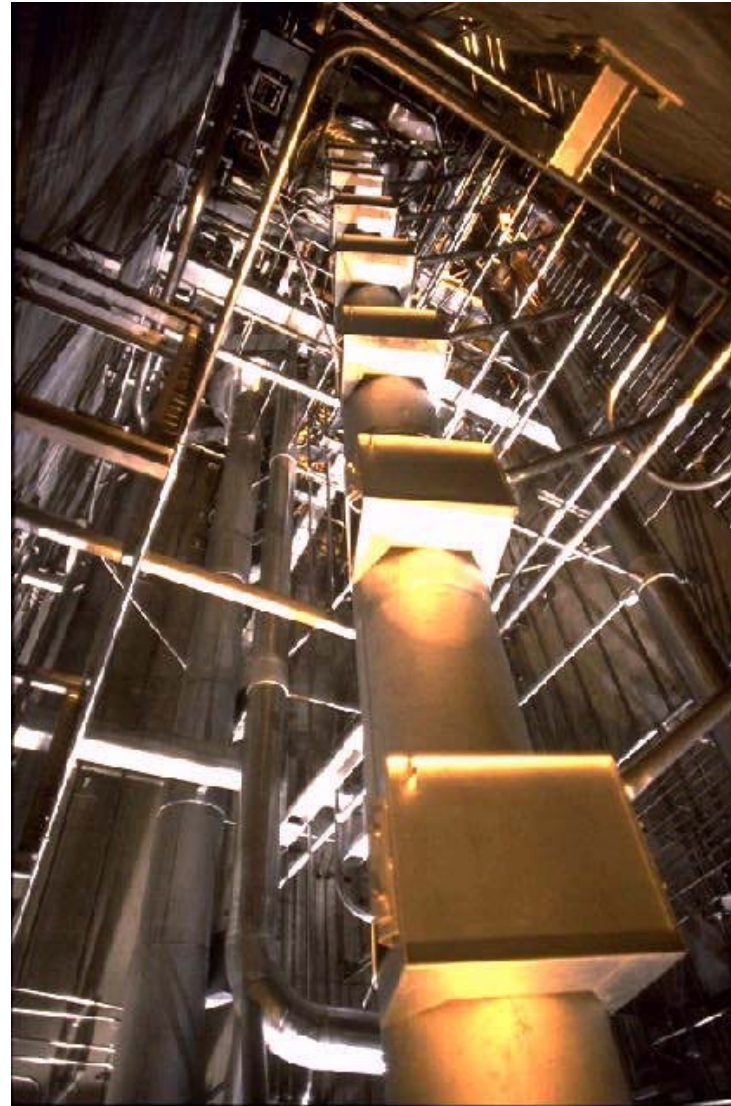
- Several feet of column needed for one theoretical stage
- Low capital cost
- Requires large amount of head space (40-50'), but little floor space
- Moderate solvent inventory
- Long residence times





PUREX Process – Process unit operations

- Pulse column at La Hague UP3 plant



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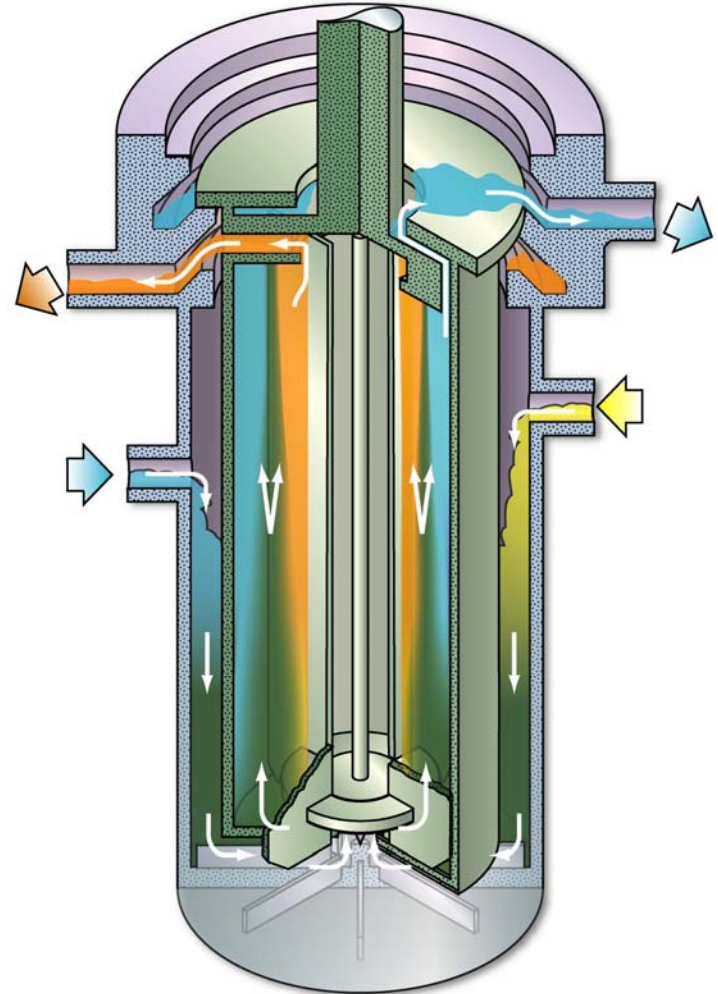




PUREX Process – Process unit operations

■ Centrifugal Contactors

- Each unit near one theoretical stage
- Higher capital cost
- Requires little headroom or floor space, but requires remote maintenance capability
- Small solvent inventory
- Short residence times





PUREX Process – Process unit operations

■ Product Conversion

- Uranyl nitrate is converted to UO_3 by denitration at elevated temperature
 - *Produces NO_x off-gas*
- Plutonium nitrate is precipitated by oxalate or peroxide and calcined to PuO_2





PUREX Process – Process wastes

LIQUIDS

- HLW (RAFFINATE FROM FIRST CYCLE – TANK WASTE)
- LAW (SOLVENT SCRUB; EVAPORATORS)

GASES

- ^{85}Kr (DISSOLVER OFF-GAS; UNTREATED IN THE PAST)
- ^{129}I (DISSOLVER OFF-GAS; REMOVED FROM EARLIEST DAYS)
- ^{14}C (AS CO_2) (DISSOLVER OFF-GAS; UNTREATED IN THE PAST)
- ^3H (MOSTLY AS TRITIATED WATER VAPOR)

SOLIDS

- HLW (CONTAMINATED EQUIPMENT; CLADDING HULLS?)
- LAW (MISCELLANEOUS WASTES FROM OPERATIONS)





PUREX Process – Process unit operations

■ High Level Waste Treatment

- High level waste is the remaining liquid after U and Pu have been removed (contain fission products and transuranium actinides)
- Wastes from weapons production at Hanford and Savannah River were neutralized using NaOH and stored in carbon steel underground tanks
 - *Hanford* - 177 ~ one million gallon tanks
 - *Savannah River* – 51 ~ 750,000 gallon tanks
- Multi-billion dollar waste treatment plants are in operation (Savannah River) or under construction (Hanford) to treat these wastes by converting the highly radioactive liquids into glass
- France, Russia and the UK convert their high-level waste into glass





PUREX Process – Current Commercial Operating Facilities

THORP, UK



La Hague, France



Rokkasho, Japan





Commercial PUREX operations

■ La Hague, Rokkasho and THORP

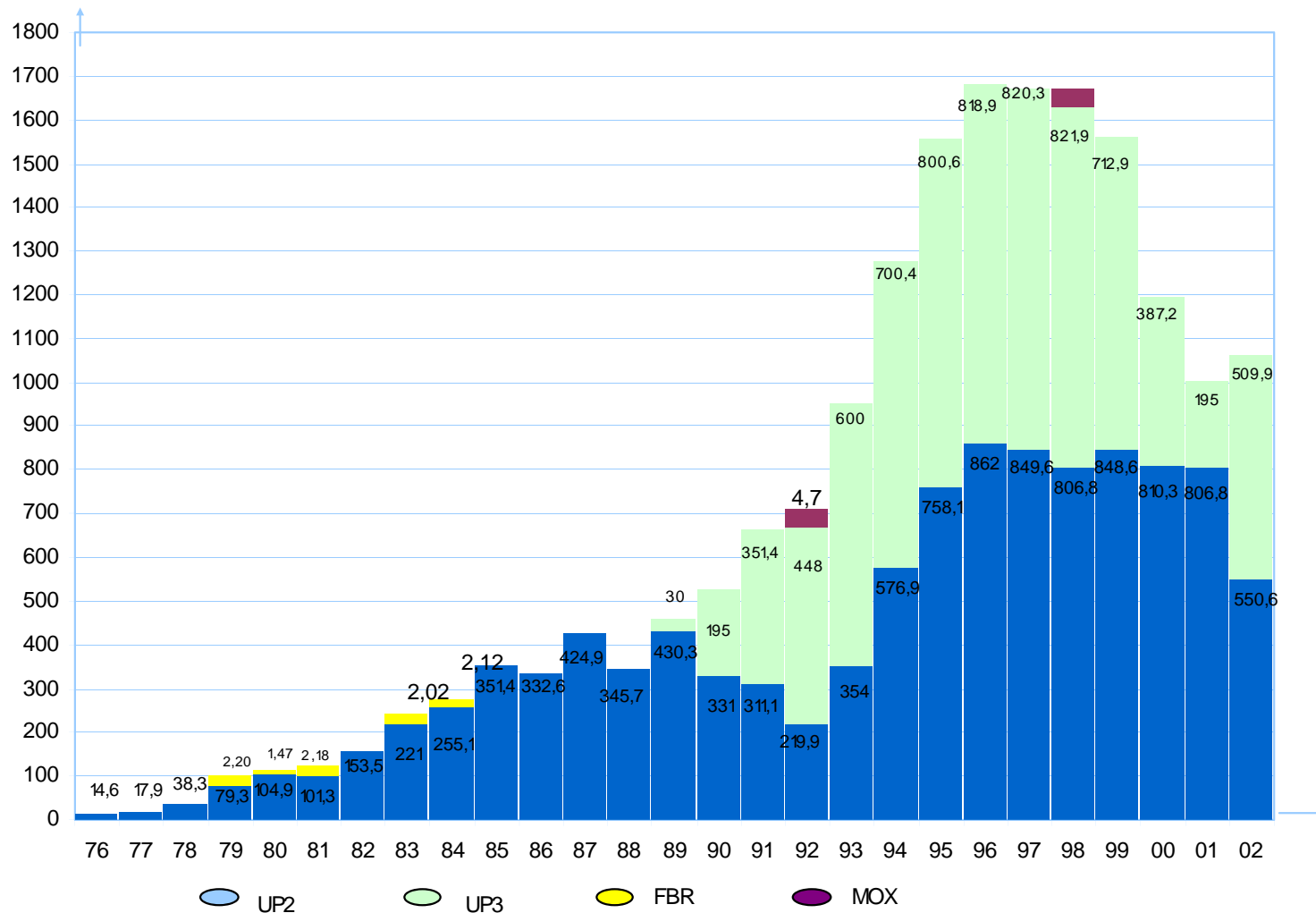
- Utilize pulse columns for first cycle extraction
- Mixer settlers and centrifugal contactors in purification cycles
- All are located near the ocean, discharge iodine to the ocean

- La Hague UP2 and UP3 plants - 800 MTHM/yr each
- Rokkasho – based on UP3 design- 800 MTHM/yr
- THORP – 1200 MTHM/yr design capacity, actual capacity less than 1000 MTHM/yr



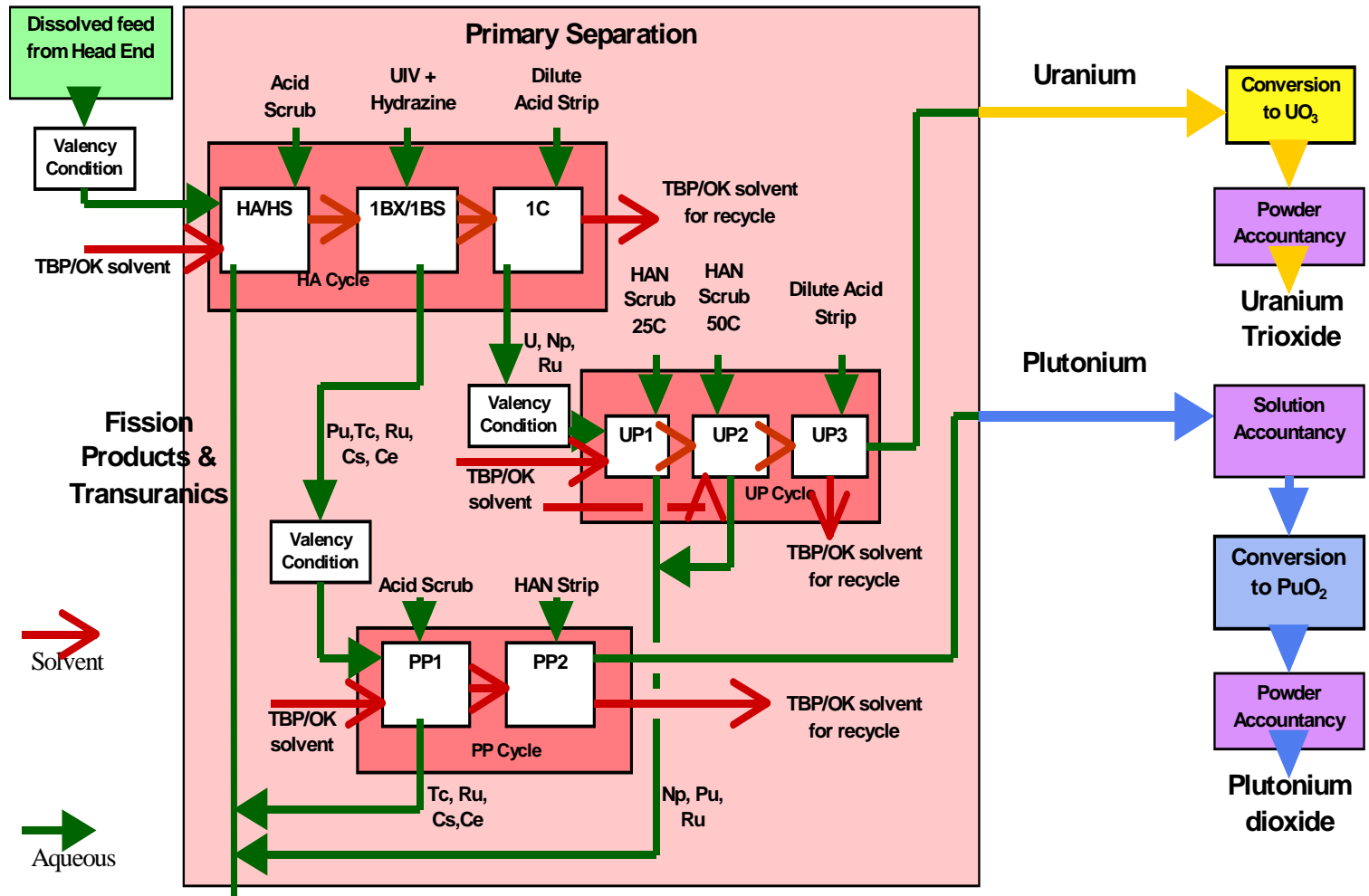


Commercial PUREX operations – La Hague UP2/UP3





THORP Reprocessing Flowsheet





Criticality Control in the PUREX Process

■ Factors that affect criticality safety

- Fissile nuclide (^{235}U , ^{233}U or ^{239}Pu)
- Fraction of fertile nuclide diluting fissile nuclide (^{238}U , ^{232}Th or ^{240}Pu)
- Mass of fissile nuclide
- Geometry
- Volume
- Concentration of fissile nuclide
- Neutron moderators
- Neutron reflectors
- Neutron absorbers





Criticality Control in the PUREX Process

- **The preferred method of criticality control are engineered controls, such as limiting geometry to be criticality safe under any credible conditions**
 - This often leads to conservative assumptions for credible conditions and adds to cost and complexity of the process
 - Limits equipment size and process throughput
- **Administrative controls have greater operational complexity (procedures, standards, etc), but offer greater design flexibility and throughput**
 - Typically, administrative controls require a double parameter failure for a criticality to occur (no one single control failure would cause a criticality)





Criticality Control in the PUREX Process

■ Single-parameter subcritical limits for uniform aqueous solutions

Parameter	²³⁵ U	²³³ U	²³⁹ Pu
Mass of fissile material, g	760	550	510
Solution cylindrical diameter, cm	13.9	11.5	15.7
Solution slab thickness, cm	4.6	3.0	5.8
Solution volume, L	5.8	3.5	7.7
Concentration of fissile nuclide, g/L	11.5	10.8	7.0
Areal density of fissile nuclide, g/cm ²	0.4	0.35	0.25
Uranium enrichment wt% ²³⁵ U	1.0 %		





Criticality accidents in reprocessing plants

■ Mayak 1953

- Procedural errors led to an unrecognized accumulation of 842 g of plutonium (as Pu nitrate solutions) in one vessel, which became critical and brought the vessel contents to boiling. The operators transferred contents of another vessel to the first, ending the reaction

■ Mayak 1957

- The accident occurred in a glovebox assembly within which uranium solution was precipitated into vessels. An unexpectedly large amount of uranium precipitate accumulated in a filter receiving vessel. The operator at the glovebox observed the filter vessel bulge prior to ejection of gas and some solution and precipitate from the vessel within the glovebox.

■ Mayak 1958

- Following the criticality accident at the same facility in 1957, an apparatus had been constructed to test criticality phenomena in fissile solutions. A 400-liter tank on a platform was used for measurements involving solutions; after each experiment, the tank was drained into individual 6-liter containers of favorable geometry. On this occasion, the tank contained uranyl nitrate solution (90% U-235) and was being drained for another experiment. After filling several 6-liter containers, operators decided to circumvent the standard procedure to save time. Three operators unbolted the tank and lifted it to pour directly into containers. The presence of the operators provided sufficient neutron reflection to cause a criticality excursion, producing a flash of light and ejecting solution as high as the ceiling, 5 meters above the tank.





Criticality accidents in reprocessing plants

■ Oak Ridge 1958

- A leak in a tank containing uranyl nitrate solution (93% U-235) was discovered on 15 June. The leak was not properly logged. The following day other tanks were being drained into a 55-gallon drum; uranium solution from the leaking tank also entered the drum. The operator nearest the drum noticed yellow-brown fumes rising from the drum's contents; he retreated before seeing a blue flash as the criticality excursion occurred. Excursion power output rose for at least 3 minutes, then ended after 20 minutes

■ Idaho 1959

- Air sparging cylinders containing highly enriched uranyl nitrate solution initiated a siphon that transferred 200 L of solution to a 5000 gallon tank containing about 600 liters of water. The resulting criticality lasted about 20 minutes





Criticality accidents in reprocessing plants

■ Idaho 1961

- 40 L of 200 g/L uranyl nitrate solution was forced up from a 5 in diameter section of an evaporator into a 24 in diameter disengagement cylinder, well above normal solution level. Operators were attempting to clear a plugged line with air, which entered the evaporator, forcing the solution upward

■ Hanford 1962

- Plutonium solution was spilled onto the floor of a solvent extraction hood. Improper operation of valves allowed a mixture of plutonium solutions in a tank that became supercritical. The excursion continued at low power levels for 37.5 hours, during which a remotely controlled robot was used to check conditions and operate valves. Criticality was probably terminated by precipitation of plutonium in the tank to a non-critical state





Criticality accidents in reprocessing plants

■ Mayak 1968

- Solutions of plutonium were being transferred from a large tank into a stainless steel vessel using a glass bottle. While a worker was pouring a second load from the glass bottle into the vessel, a criticality excursion occurred.

■ Idaho 1978

- A leaking valve allowed water to dilute the scrub solution used in the first cycle extraction process. This leak was undetected because of a failed alarm system. Because of the dilution, highly enriched uranium was stripped from the organic solvent (normally would remain in solvent). Over the course of a month, the concentration of uranium increased in the large diameter bottom of the scrub column, resulting in a criticality.





Criticality accidents in reprocessing plants

■ Tokai-mura 1999

- Three operators were engaged in processes combining uranium oxide with nitric acid to produce a uranium-containing solution for shipment. The uranium involved was 18.8% U-235. The procedure used deviated from that licensed to the facility. In particular the uranium solution was being placed in a precipitation tank for dispensing into shipment containers, not the more narrow vessel (geometrically favorable to minimizing criticality risks) prescribed by license. While two workers were adding a seventh batch of uranium solution to the tank, a criticality excursion occurred.





Major industrial accidents in reprocessing plants

■ Red Oil

- 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 DNFSB report “Tech 33” Nov. 2003





Controls to avoid Red Oil accidents

■ How do we avoid red oil in reprocessing facilities?

- 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





Other major accidents in reprocessing facilities

■ Mayak 1957

- Liquid high-level waste was stored in underground tanks. The high level waste, coming from the B plant, contained sodium nitrate and acetate salts, from the acetate precipitation process. Cooling system in one of the tanks failed, and the temperature in the tank rose to 350 °C. The tank contents evaporated to dryness, causing a massive explosion (estimated to be equivalent to 75 tons of TNT). Over 20 MCi of radioactivity were released to the environment.

■ Tokai-mura 1997

- A fire occurred in the bitumen waste facility of the demonstration reprocessing plant at Tokai-mura. Bitumen is used to solidify intermediate-level activity liquid radioactive waste. The fire apparently occurred after errors made in monitoring a chemical reaction. The fire was not completely extinguished and about ten hours later, after chemicals had accumulated, an explosion occurred which ruptured the confinement of the facility.





Other major accidents in reprocessing facilities

■ Hanford 1997

- Hydroxylamine nitrate and nitric acid were stored in a tank and allowed to evaporate to dryness. The resulting explosion destroyed the tank and blew a hole in the roof of the building. Hydroxylamine is a reagent used to reduce plutonium valance from (IV) to (III).

■ THORP 2005

- A pipe failure resulted in about 83,000 L of highly radioactive dissolver solution leaking into the stainless-steel lined feed clarification of the THORP facility. This solution contained about 20 MT of uranium and plutonium. The leak went undetected for months before being discovered. No injuries or exposure to radiation. The plant is still shutdown in 2008.





Recent modifications to the PUREX Process

- Industrial reprocessing firms have a high degree of confidence in the PUREX process, however, the PUREX process has been the subject of criticism for the past 30 years related to the separation of a pure plutonium stream
- Recall that the PUREX process co-extracts both uranium and plutonium, *then* partitions them into separate streams
- Modifications to the PUREX process have recently been proposed and developed that leave a small fraction of the uranium with the plutonium, producing a mixed product for production of mixed oxide (MOX) fuel
- These modified processes have been called COEX™, NUEX or UREX+ 3 and are all based on modified PUREX chemistry
- Calling these processes “co-extraction” to differentiate them from PUREX is misleading because the PUREX process also co-extracts uranium and plutonium





Recent modifications to the PUREX Process

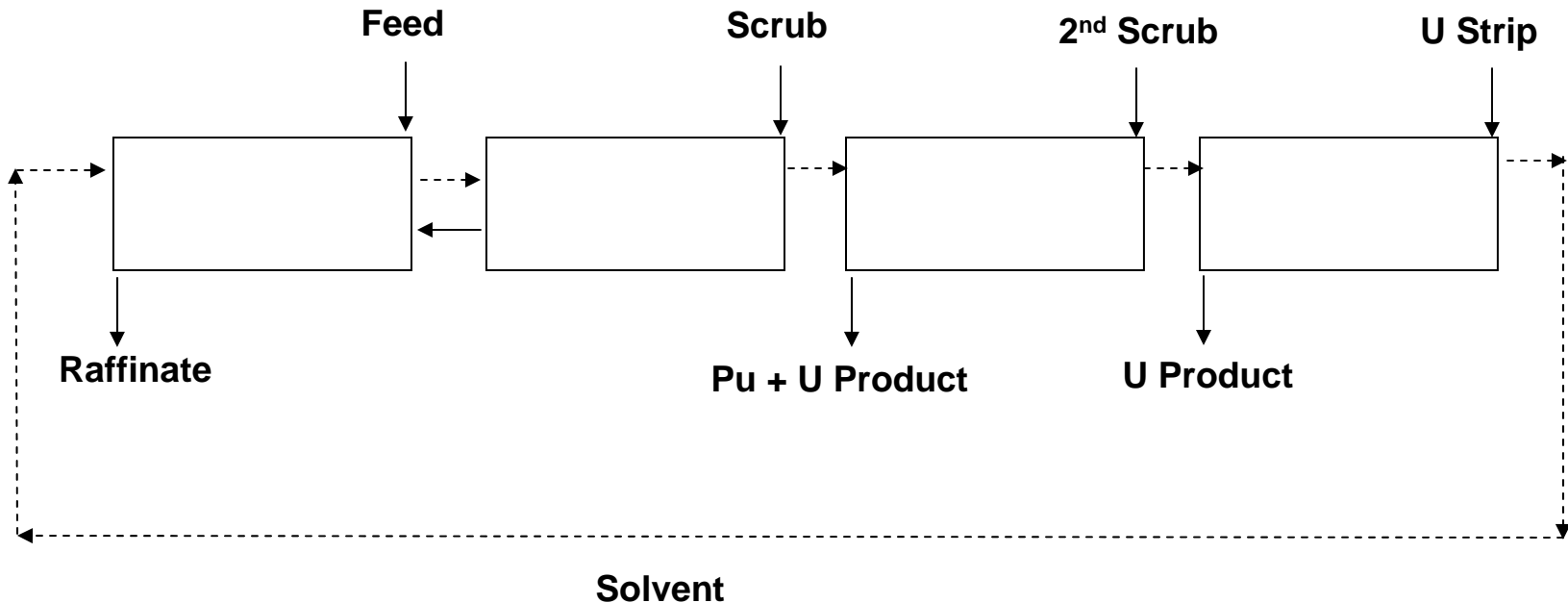
- Each specific process has its own proprietary methods of stripping plutonium from the solvent, with a fraction of uranium
- In the PUREX process, the nitric acid concentration in the second scrub is kept higher than ~ 0.5 M to keep the uranium in the organic solvent, while the plutonium is reduced to the trivalent state and partitions to the aqueous phase.
- In the modified process, the acid concentration in the second scrub stream is maintained at a controlled value (typically lower than 0.5 M) to allow a small amount ($\sim 1\%$) of the uranium to partition to the aqueous stream along with the plutonium (III)
- After the plutonium and small fraction of uranium are removed in the second scrub stream, uranium is stripped from the solvent by using dilute (0.01 M) nitric acid





Recent modifications to the PUREX Process

Simplified flowsheet for U and U/Pu products





Summary

- **Spent nuclear fuel reprocessing is a mature technology, having over 50 years of industrial experience with the PUREX process**
- **Nuclear energy must solve the waste disposal issue soon for it to grow. This solution could include building more repositories, reprocessing fuel and/or a combination of both**
- **History has shown that there must be a strong emphasis on safety, including criticality safety, safeguards and industrial safety**
- **New “evolutionary” processes employ minor adjustments to PUREX process chemistry to keep from producing pure plutonium and facilitate more near-term implementation**

