



Introduction to Nuclear Fuel Cycle Separations

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CRESP Short Course -Introduction to Nuclear Fuel Cycle
Chemistry

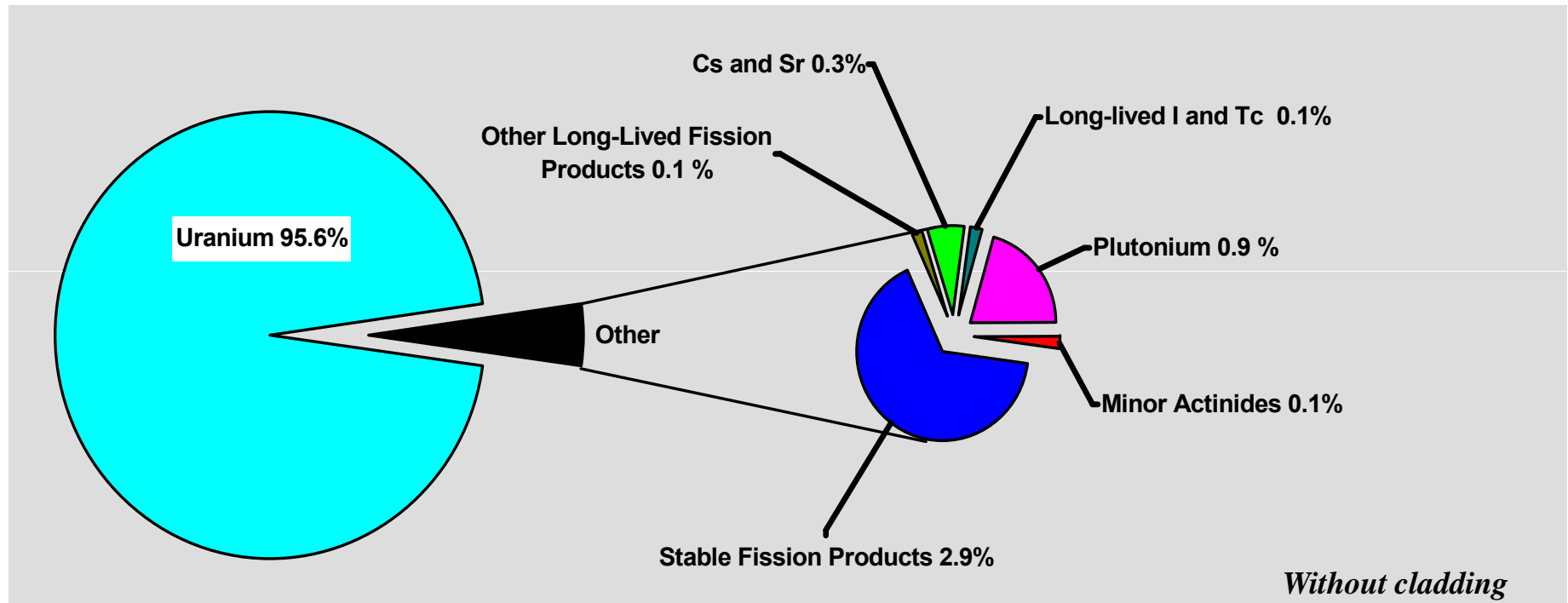
Crystal City, VA

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Why separate components of spent fuel?

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

Spent (used) Nuclear Fuel – what is it?



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

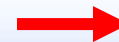
Most radiotoxicity is in long-lived fission products and the minor actinides, which can be transmuted and/or disposed in much smaller packages

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

Aqueous processing - History

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

20 micrograms of plutonium hydroxide
1942



Hanford T-Plant 1944



Bismuth Phosphate Process

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

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 highly enriched uranium recovery**



Hanford REDOX -Plant (1951)

REDOX Process

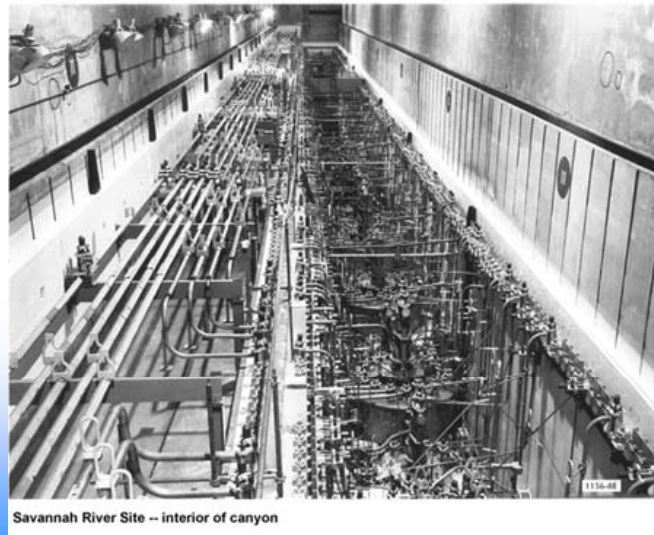
- **Hexone (methyl isobutyl ketone) used as the extractant**
 - **Immiscible with water**
 - **Used to purify uranium ore concentrates**
 - **Extracts both uranyl and plutonyl nitrates selectively from fission products**
- **Plutonium oxidized to Pu (VI) for highest recovery**
- **U (VI) and Pu (VI) 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**

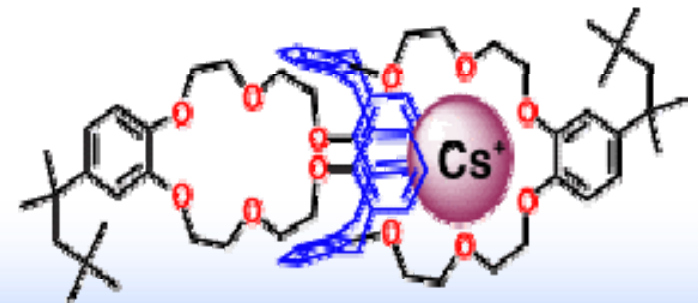
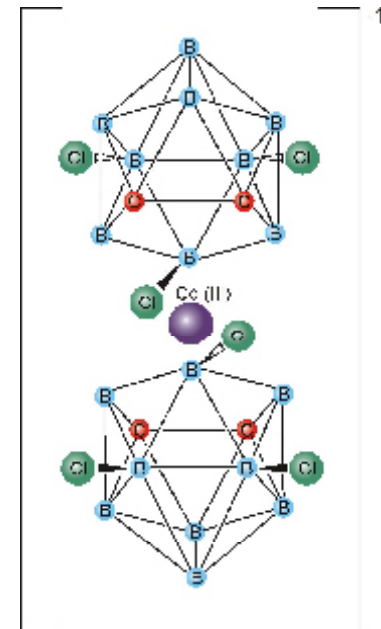
PUREX Process

- **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 1950-1952
 - Used for Pu production plant at Savannah River in 1954 (F-canyon) (H-canyon facility begin operation in 1955 and is still operational in 2008)
 - Replaced REDOX process at Hanford in 1956
 - Modified PUREX used in Idaho beginning in 1953 (first cycle)



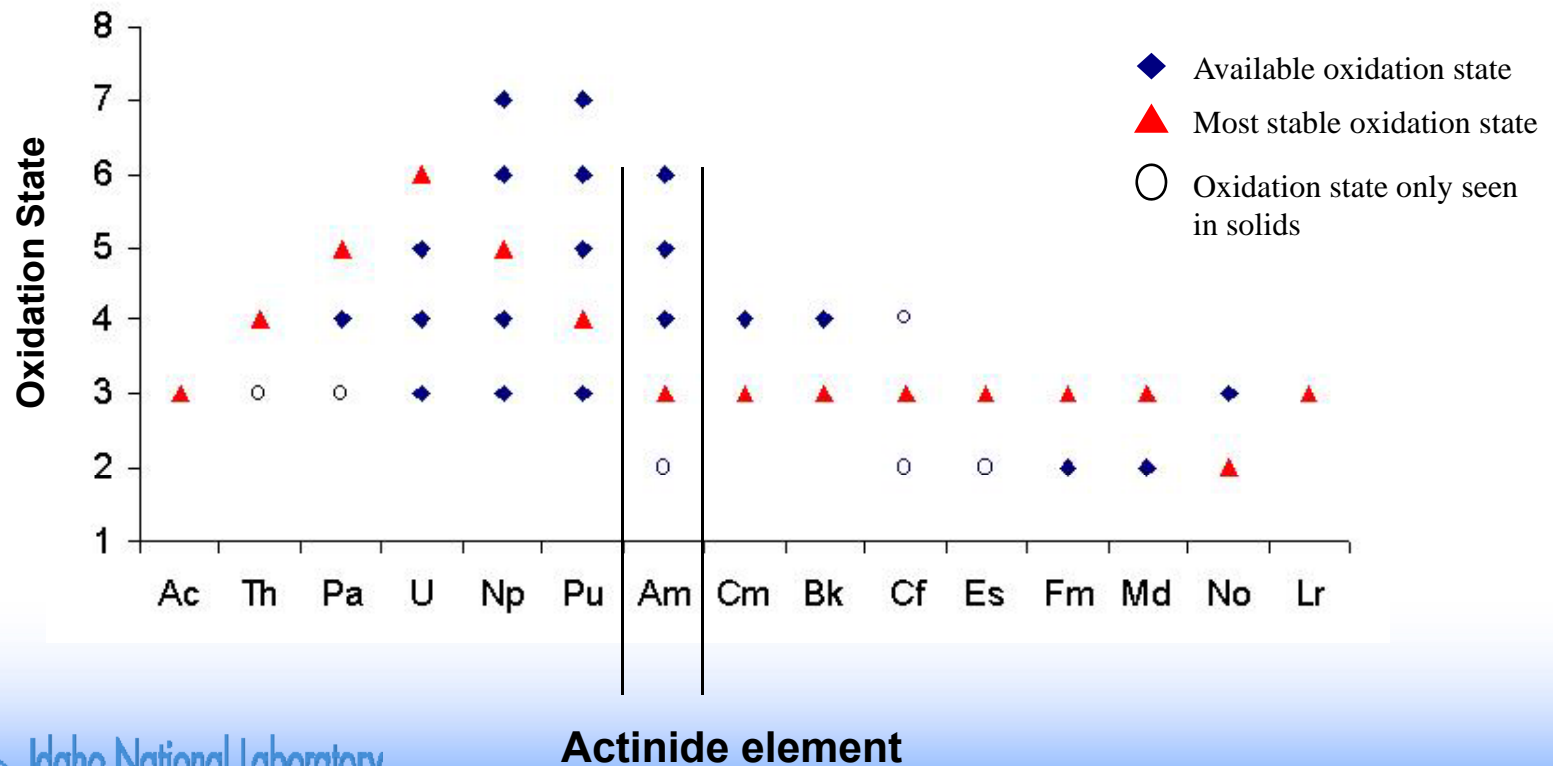
Basics of aqueous separation process chemistry

- The PUREX process will be used to describe the basics on how solvent extraction is used to separate U and Pu from dissolved fuel
 - Principles are similar for many other solvent extraction processes (e.g. separation of fission products or TRU) which use other extractants
 - Some exceptions (CCD and CSEX)



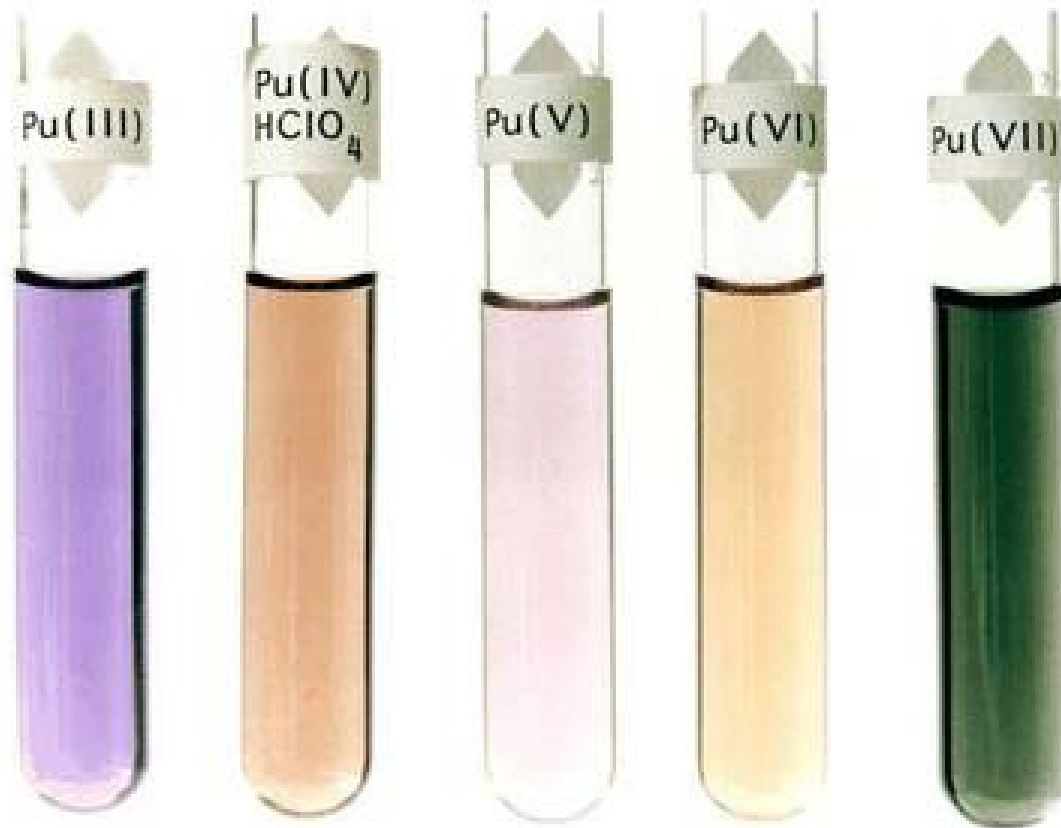
PUREX process chemistry

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



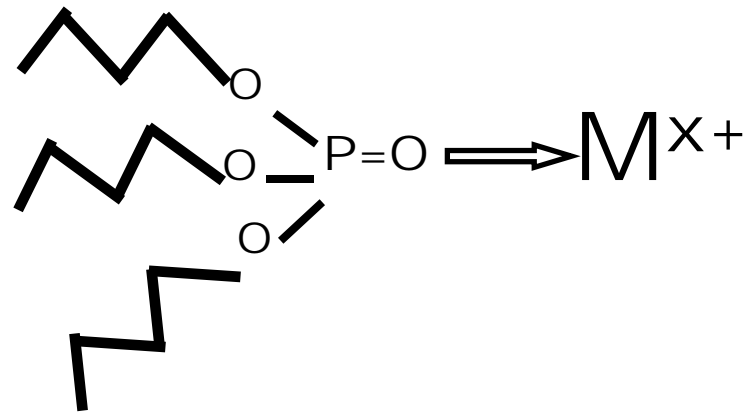
PUREX process chemistry

The multiple oxidation states of plutonium



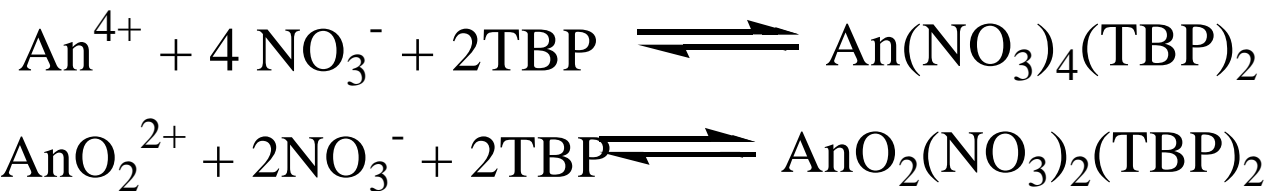
PUREX process chemistry

- The PUREX solvent is typically 30 vol% TBP in a hydrocarbon diluent (dodecane or kerosene)
- The extracting power of TBP is derived mainly from its phosphoryl oxygen atom coordinating to metal ions:
- TBP is classed as a neutral extractant *i.e.* it will only extract electroneutral complexes into the organic phase e.g.



PUREX process chemistry

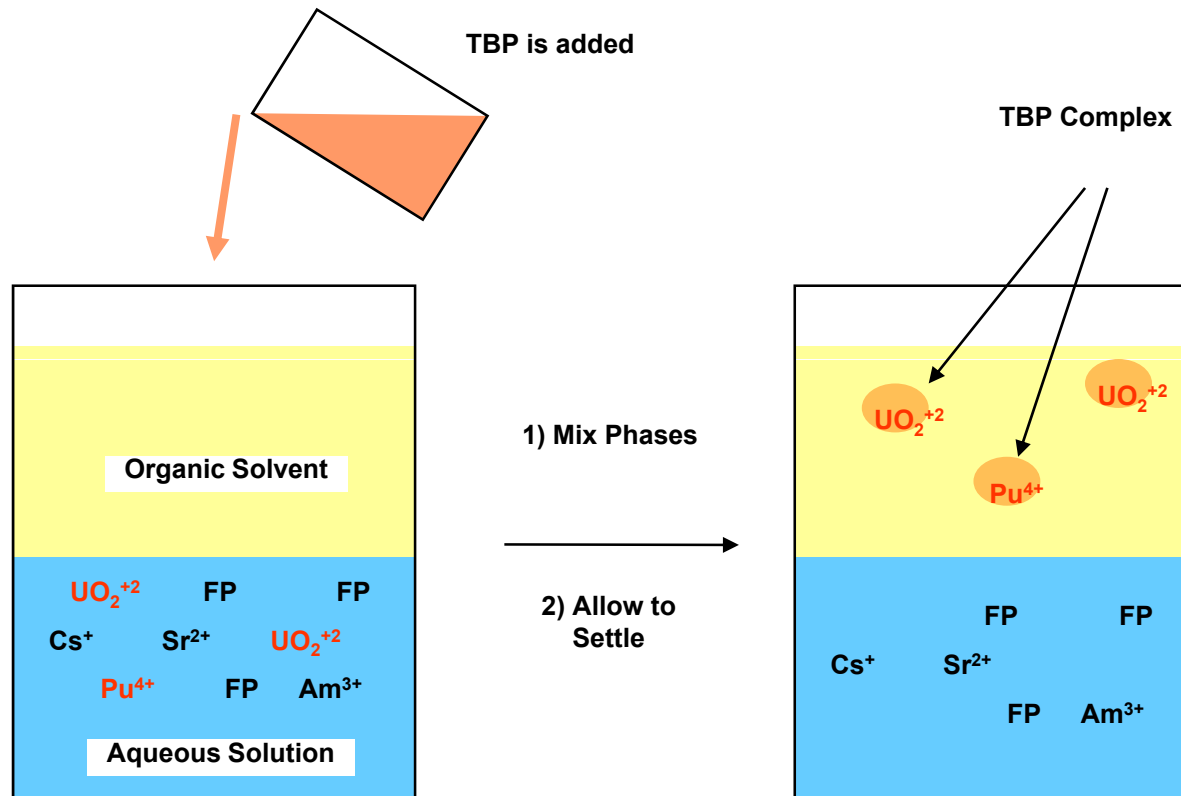
- As a general rule only metal ions in the +4 and +6 oxidation states are extracted, this means that all other species present are rejected



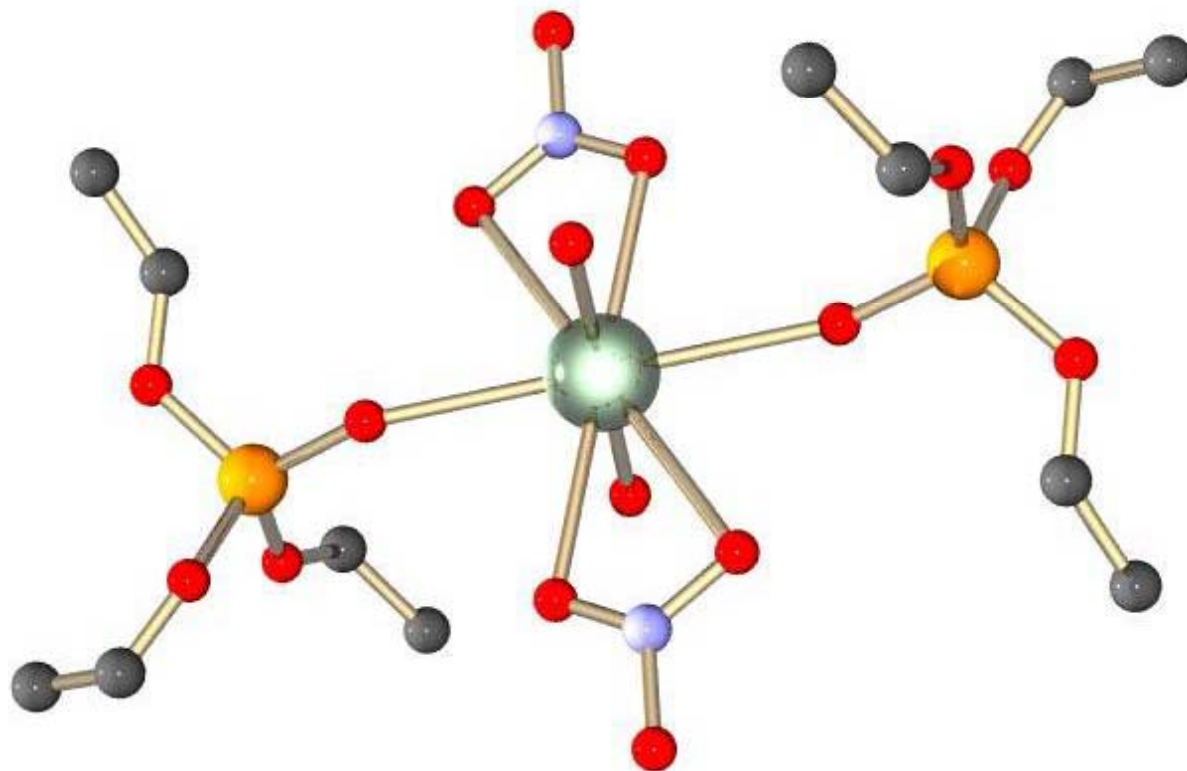
- This leads to an effective separation of U and Pu away from nearly all other species in dissolved nuclear fuel

| Strong extraction ($D \gg 0.5$) | Weak extraction ($D \ll 0.5$) |
|---|---|
| $\text{UO}_2^{2+} > \text{U}^{4+}$ $\text{NpO}_2^{2+} > \text{Np}^{4+}$ $\text{PuO}_2^{2+} < \text{Pu}^{4+}$ $\text{TcO}_4^- / \text{UO}_2^{2+}, / \text{Pu}^{4+}$ or Zr | NpO_2^+ Pu^{3+} All other species |

PUREX process- Basic principles



Representation of the extracted UO_2^{2+} complex with TBP

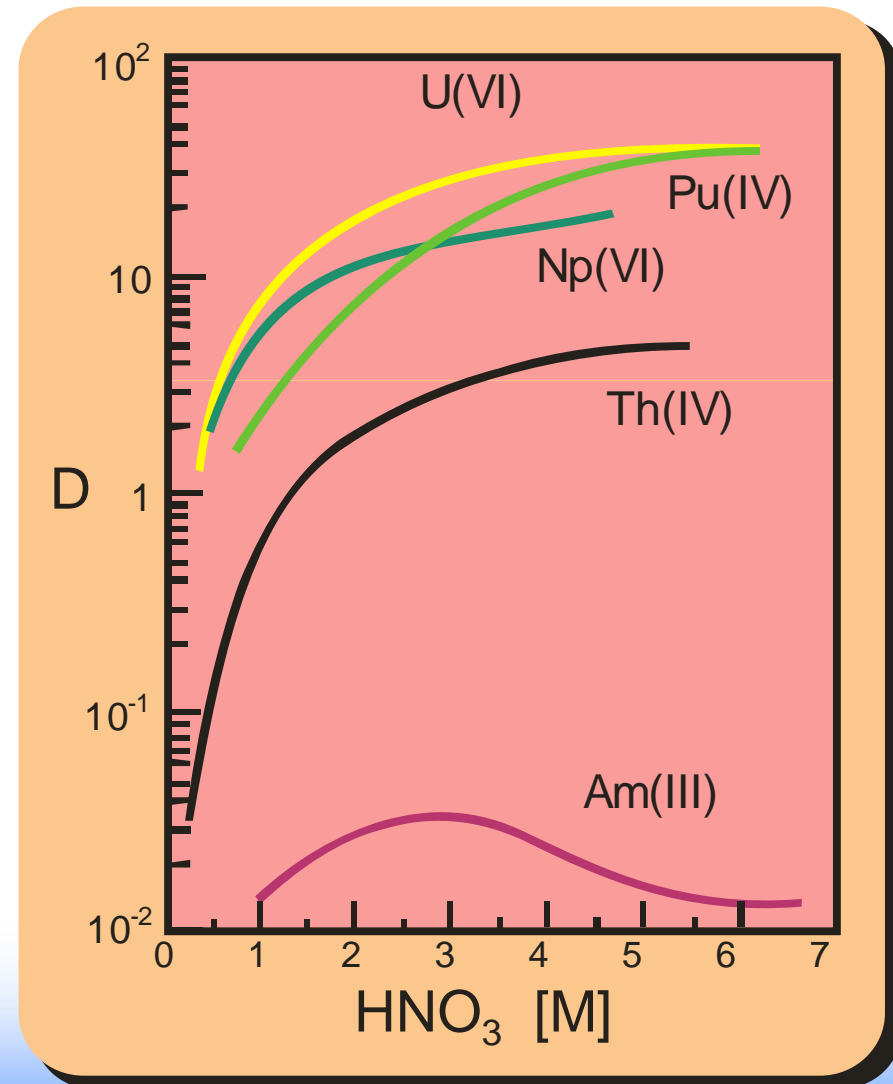


PUREX process – Basic Principals

- The amount of metal extracted is quantified by the analytical concentration of M in the organic phase to its analytical concentration in the aqueous phase at equilibrium. This is more commonly known as the distribution coefficient:

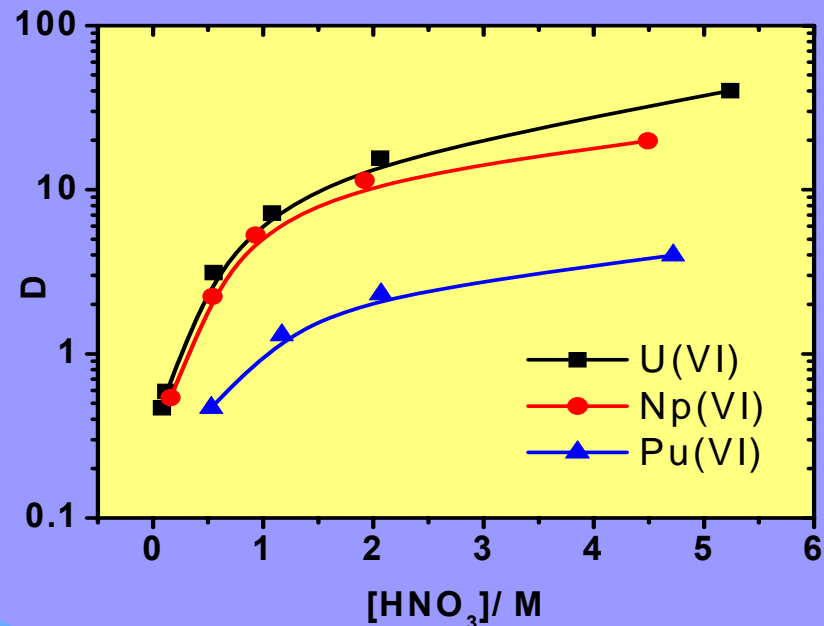
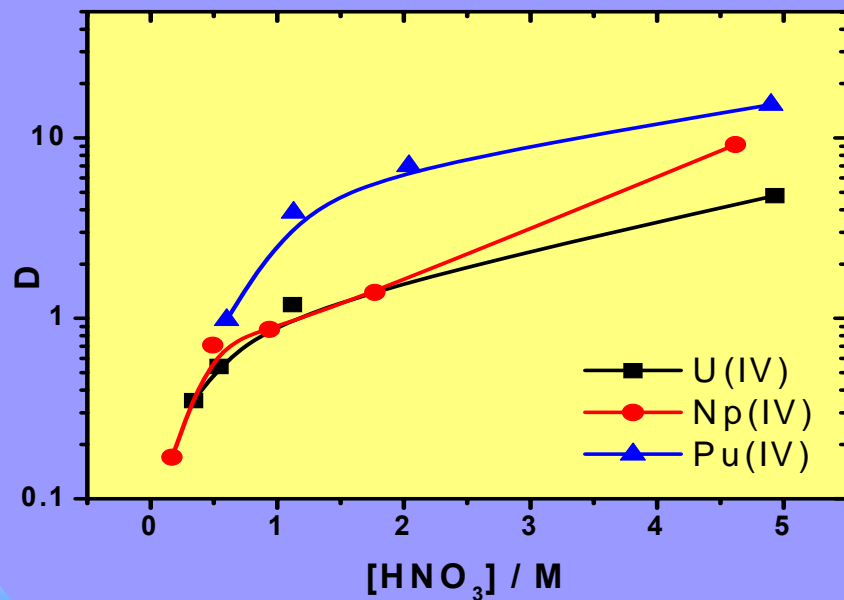
$$D_m = \frac{[M(NO_3)_x \bullet nTBP]_{org}}{[M^{x+}]_{aq}} = K_1 [NO_3^-]_{aq}^x [TBP]_{org}^n$$

Nitric acid dependency



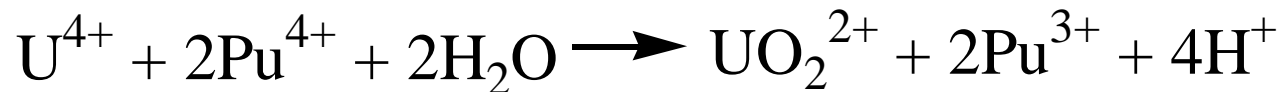
PUREX Process – Basic Principals

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



PUREX Process – Basic Principals

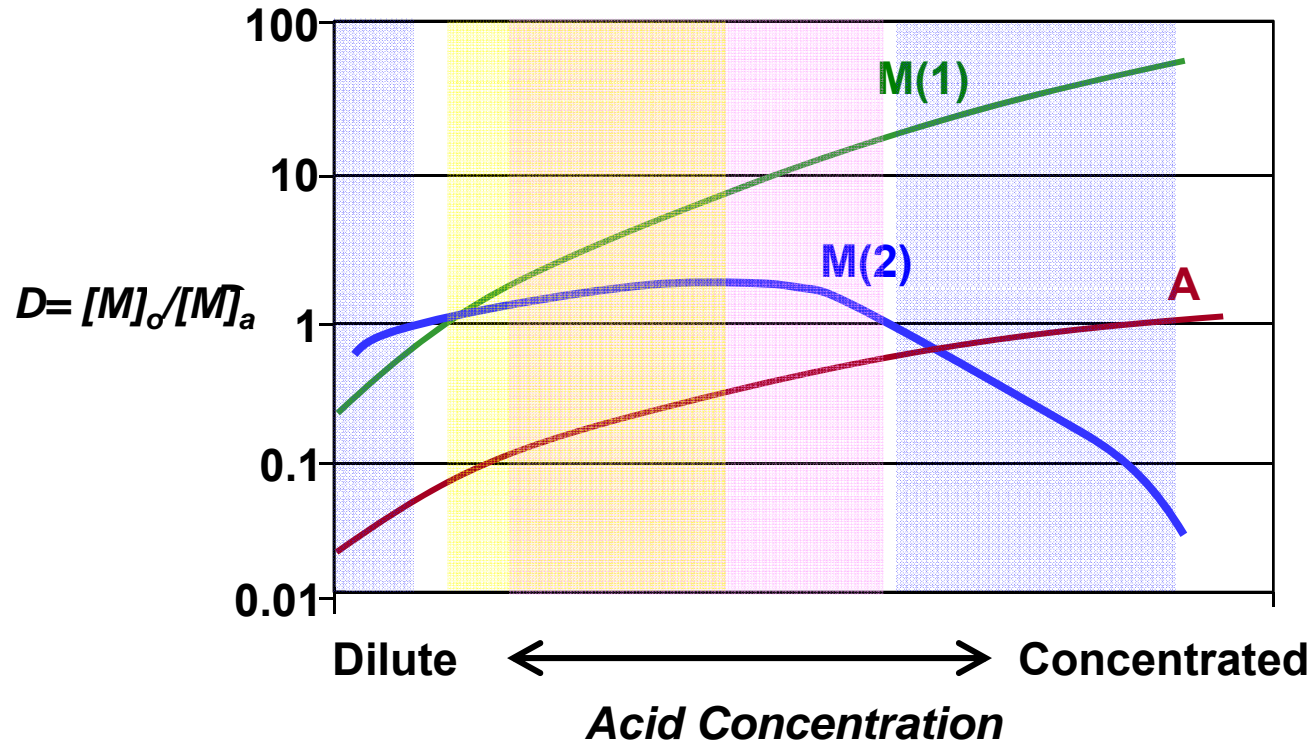
- To remove Pu from the organic phase Pu⁴⁺ is reduced to inextractable Pu³⁺ using a reducing agent, usually Fe²⁺ or U⁴⁺



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



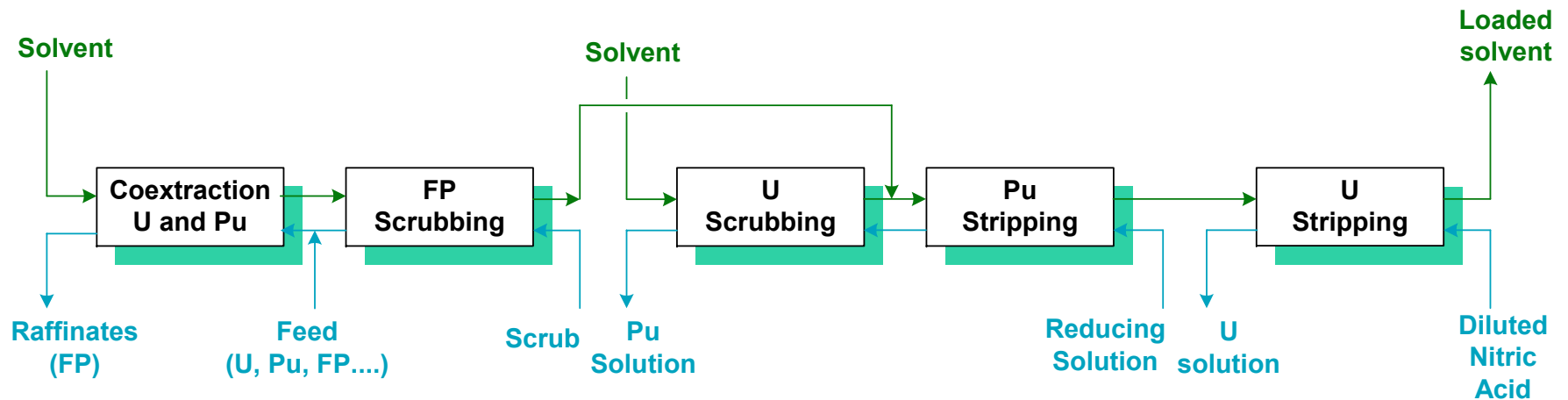
Example of Process Flowsheet Design



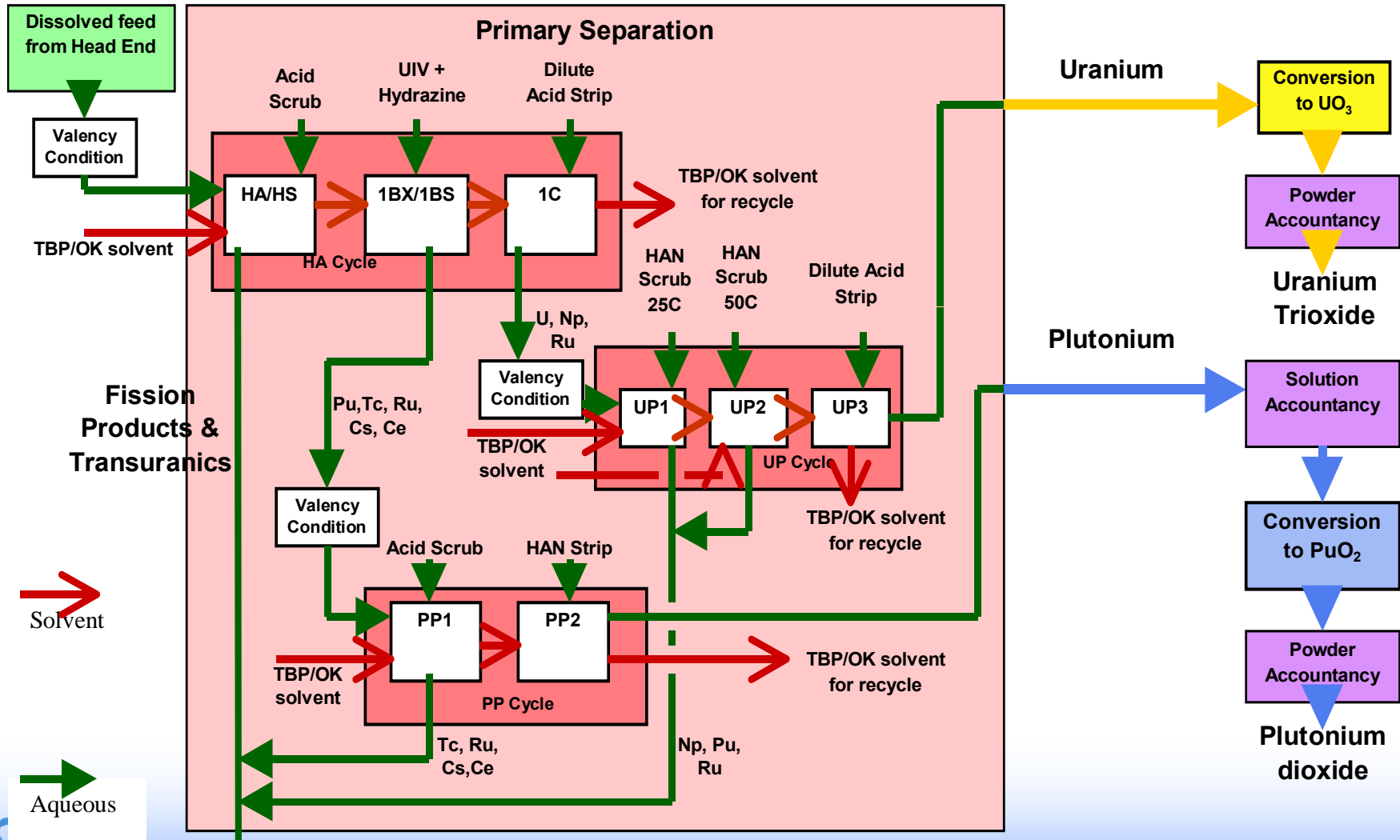
PUREX Process – unit operations

- **Separations**

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



THORP Reprocessing Flowsheet



Commercial spent fuel reprocessing in the US (PUREX process)

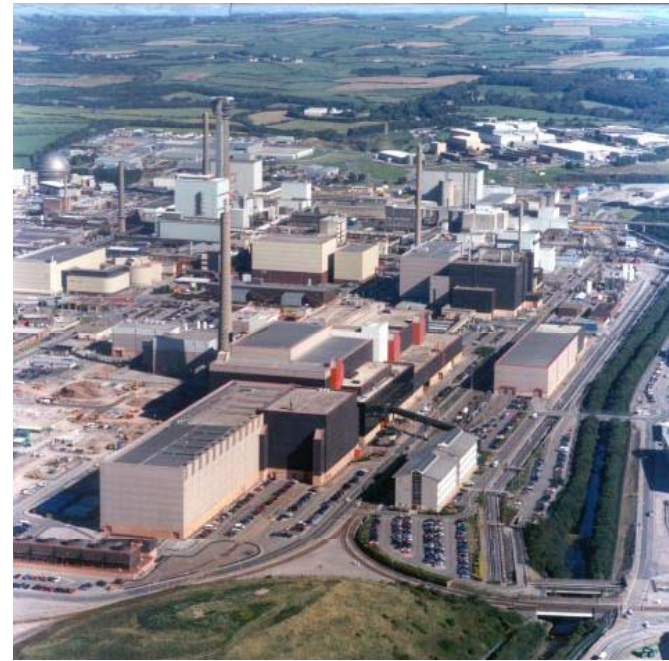
- **West Valley, NY**
 - *First plant in US to reprocess commercial SNF*
 - *Operated from 1966 until 1972*
 - *Capacity of 250-300 MTHM/yr*
 - *Shutdown due to high retrofit costs associated with changing safety and environmental regulations and construction of larger Barnwell facility*
- **Morris,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

Commercial-scale application of the PUREX process abroad

- **France**
 - Magnox plant in Marcoule began operation in 1958 (~400 MT/yr)
 - Magnox plant in La Hague began operation in 1967 (~400 MT/yr)
 - LWR oxide plant (UP2) began in La Hague in 1976 (800 MT/yr)
 - LWR oxide plant (UP3) began in La Hague in 1990 (800 MT/yr)
- **United Kingdom**
 - Windscale plant for Magnox fuel began in 1964 (1200-1500 MT/yr)
 - THORP LWR oxide plant began in 1994 (1000-1200 MT/yr)
- **Japan**
 - Tokai-Mura plant began in 1975 (~200 MT/yr)
 - Rokkasho plant currently undergoing hot commissioning (800 MT/yr)
- **Russia**
 - Plant RT-1
 - Began operation in 1976, 400 MT capacity
 - Variety of headend processes for LWR, naval fuel, fast reactor fuel

PUREX Process – Current Commercial Operating Facilities

THORP, UK



La Hague, France



Rokkasho, Japan



PUREX Process – advantages and disadvantages

- **Advantages**

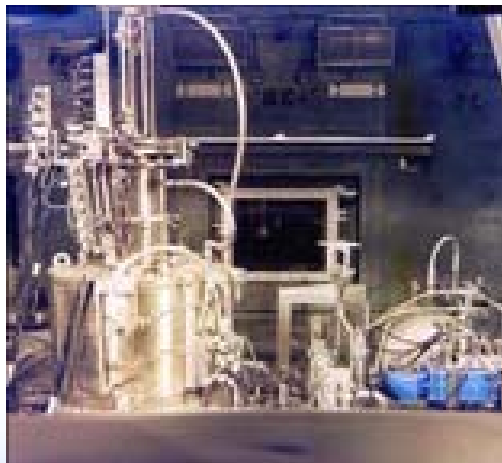
- Continuous operation/ High throughput
- High purity and selectivity possible – can be tuned by flowsheet
- Recycle solvent, minimizing waste

- **Disadvantages**

- Solvent degradation due to hydrolysis and radiolysis
- Dilute process, requires substantial tankage and reagents
- Historical handling of high-level waste
- Stockpiles of plutonium oxide

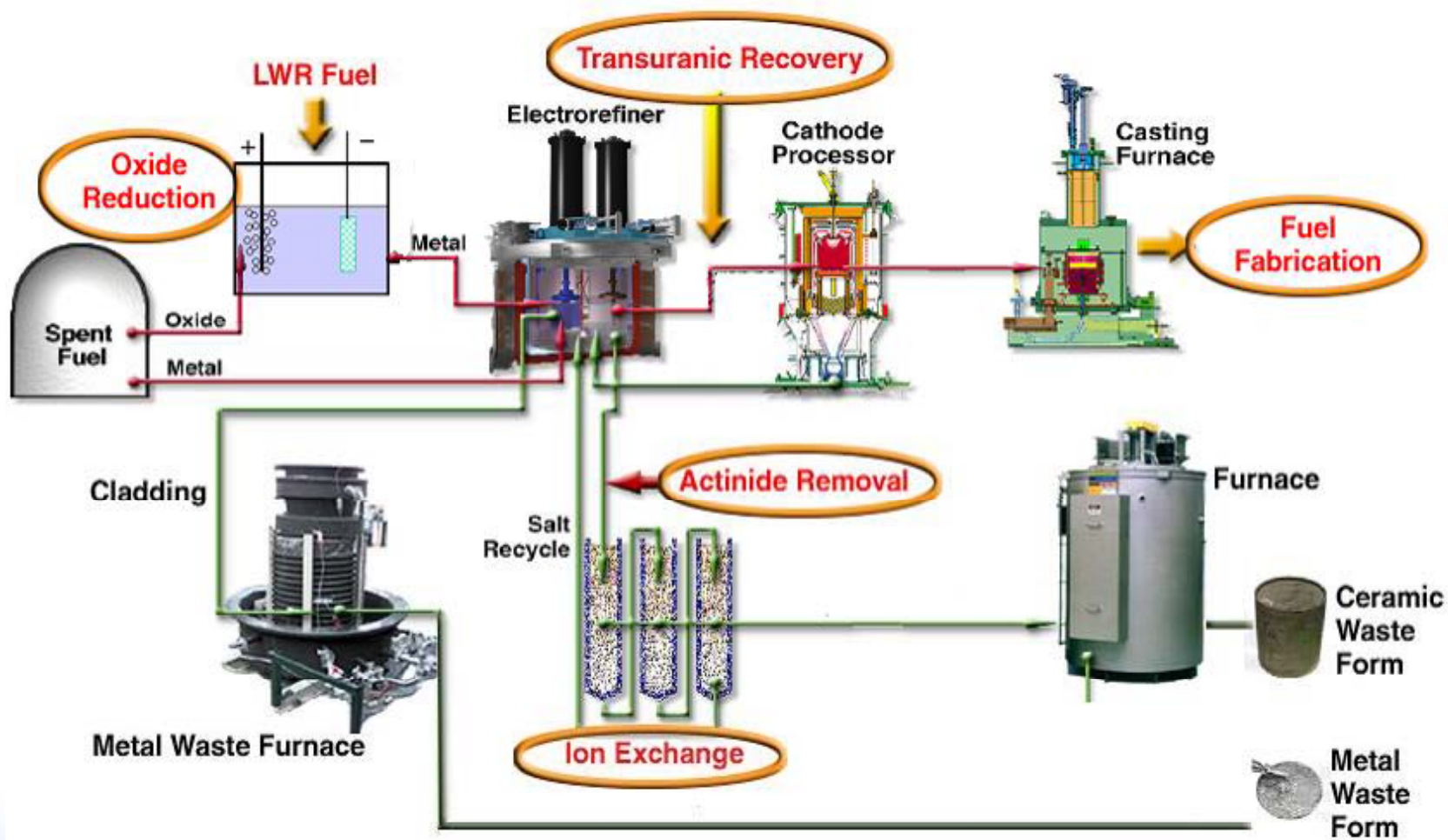


Electrochemical Processing Background



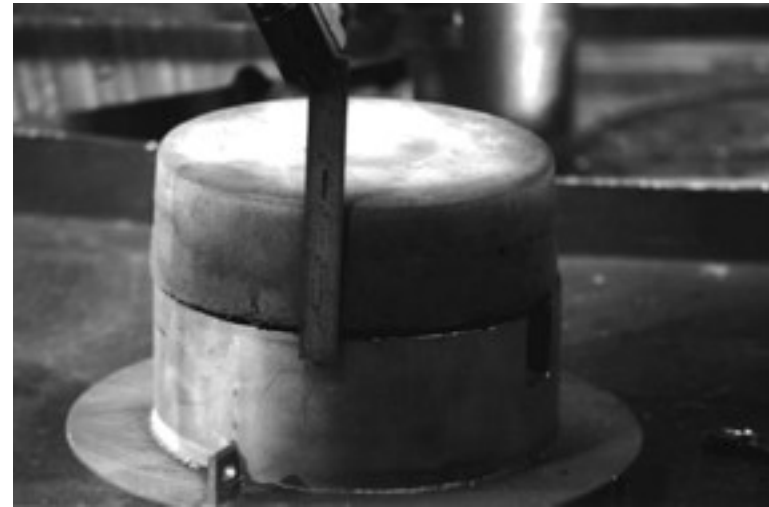
- Present generation of technology for recycling or treating spent fuel started in the 1980s
- Electrochemical processes were developed for the fast reactor fuel cycle
 - *The fast reactor fuel does not require a high degree of decontamination*
 - *Potential compactness (co-location with reactor)*
 -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

Example of an electrochemical flowsheet (LWR or FR fuel to FR fuel)

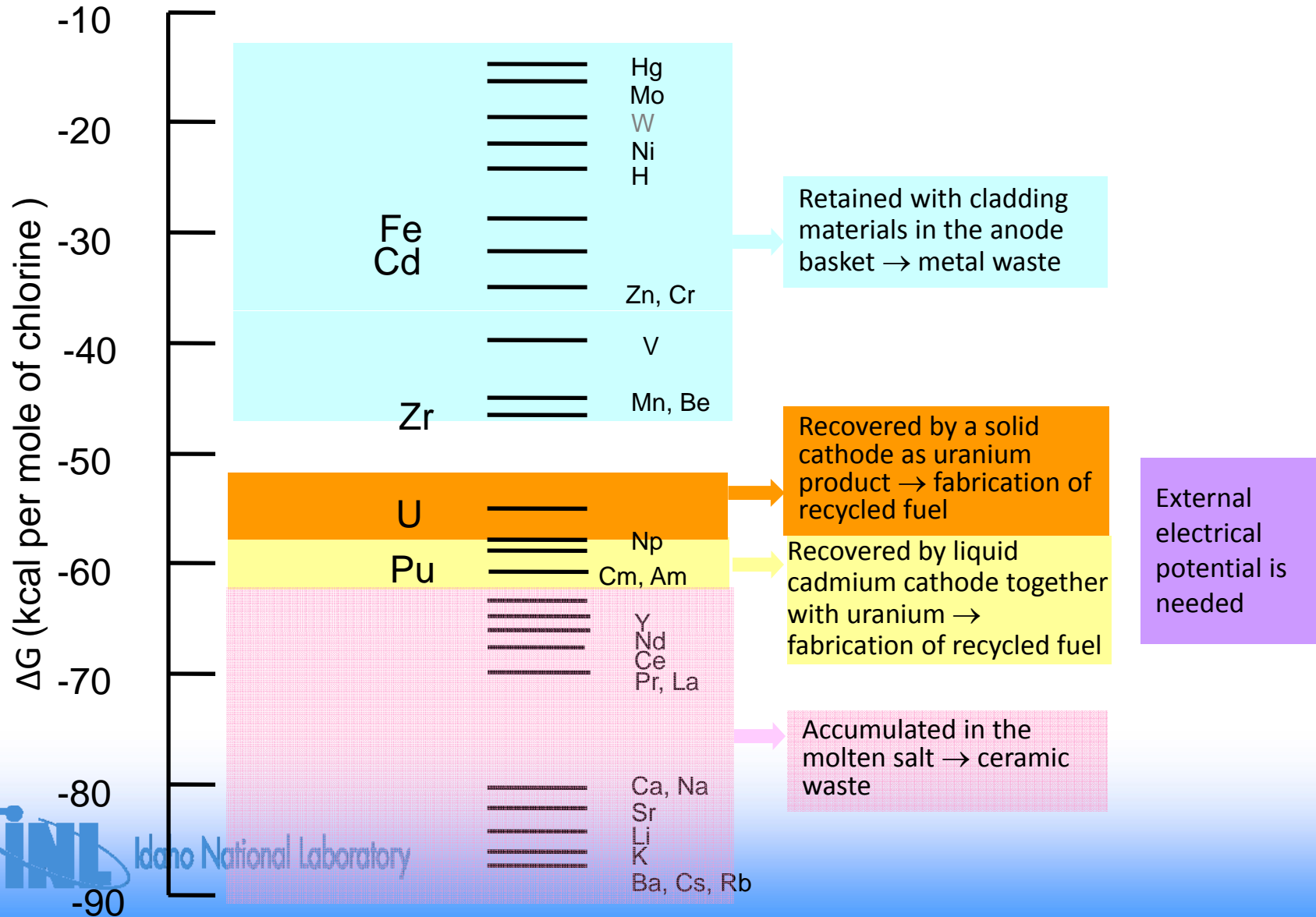


Electrochemical Treatment of Spent Fuel

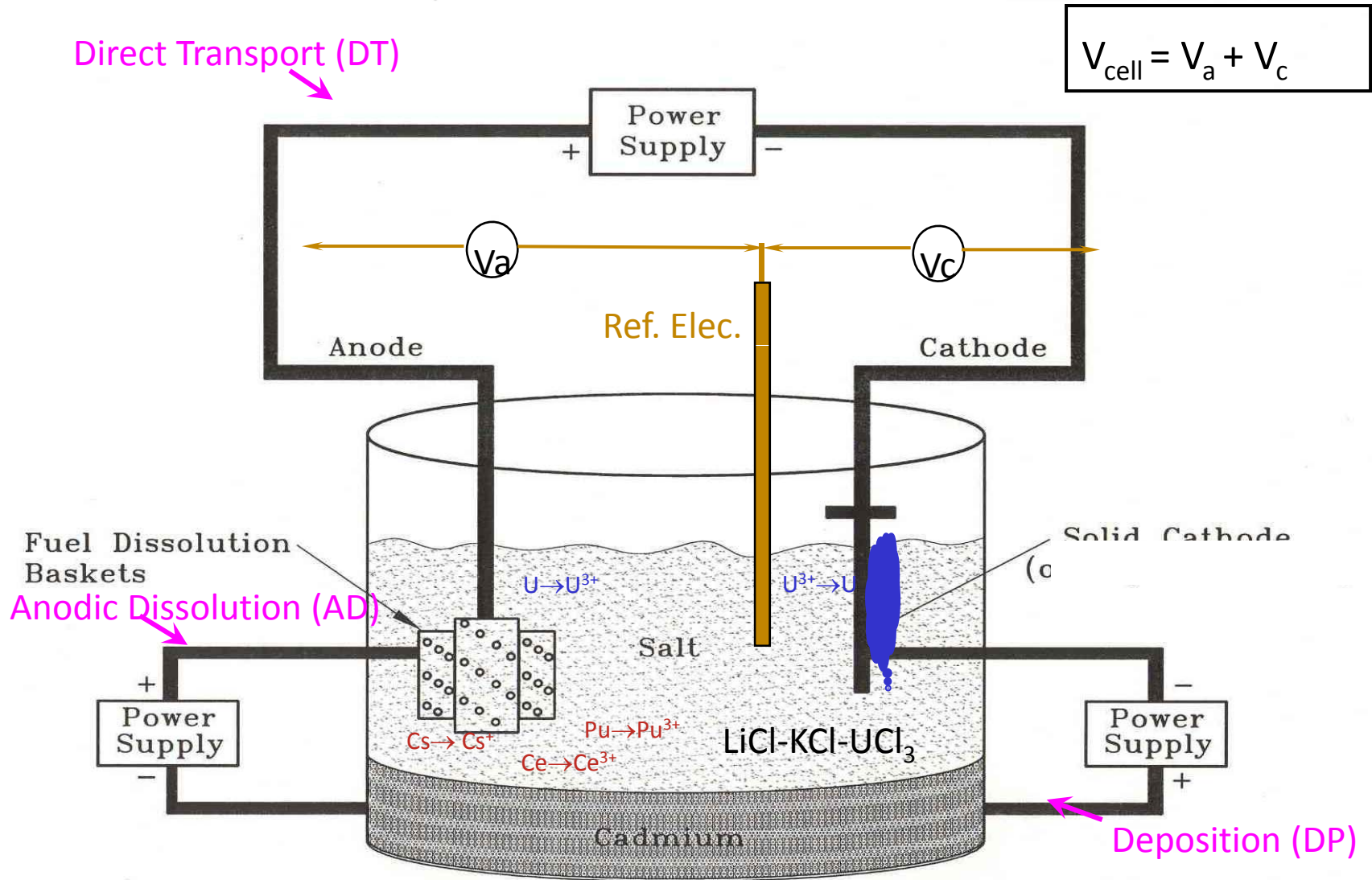
- *Electrochemical processing has been performed on the engineering-scale with irradiated fuel since 1996*
- *Approximately 3.5 MTHM of fuel, including highly enriched uranium fuels, have been treated*
- *Installed process equipment could support throughputs between 3 and 5 MTHM per year*
- *Advancements in the technology are a major focus of GNEP*



Spent Fuel Constituents are Partitioned According to Free Energy of Formation of Chlorides at 500°C



Schematic of Electrorefining Process to Treat Spent Fuel



AFCI Electrochemical processing R&D focus

- *Electrorefining*
 - *Fundamental electrochemistry and thermodynamics*
 - *Advanced TRU recovery*
- *Cathode processing for U/TRU recovery*
- *Salt treatment for recycle*
- *Process monitoring and control*
- *Process modeling and simulation*

What about proliferation?

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

Where are we today?

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

Where are going?

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