Introduction to Nuclear Fuel Cycle Separations

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CRESP Short Course - Introduction to Nuclear Fuel Cycle Chemistry

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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

Hanford T-Plant 1944

20 micrograms of plutonium hydroxide 1942
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.

\[
\text{An}^{4+} + 4\text{NO}_3^- + 2\text{TBP} \leftrightarrow \text{An(NO}_3)_4 \cdot 2\text{TBP}
\]
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.

\[
\begin{align*}
\text{An}^{4+} + 4 \text{NO}_3^- + 2\text{TBP} & \rightleftharpoons \text{An(NO}_3)_4(\text{TBP})_2 \\
\text{AnO}_2^{2+} + 2\text{NO}_3^- + 2\text{TBP} & \rightleftharpoons \text{AnO}_2(\text{NO}_3)_2(\text{TBP})_2
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>Strong extraction (D&gt;&gt;0.5)</th>
<th>Weak extraction (D&lt;&lt;0.5)</th>
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<tbody>
<tr>
<td>UO(_2^{2+}) &gt; U(^{4+})</td>
<td>NpO(_2^+)</td>
</tr>
<tr>
<td>NpO(_2^{2+}) &gt; Np(^{4+})</td>
<td>Pu(^3^+)</td>
</tr>
<tr>
<td>PuO(_2^{2+}) &lt; Pu(^{4+})</td>
<td>All other species</td>
</tr>
<tr>
<td>TcO(_4^-)/UO(_2^{2+}), /Pu(^{4+}) or Zr</td>
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</tbody>
</table>

Strong extraction (D>>0.5):

- UO\(_2^{2+}\) > U\(^{4+}\)
- NpO\(_2^{2+}\) > Np\(^{4+}\)
- PuO\(_2^{2+}\) < Pu\(^{4+}\)
- TcO\(_4^-\)/UO\(_2^{2+}\), /Pu\(^{4+}\) or Zr

Weak extraction (D<<0.5):

- NpO\(_2^+\)
- Pu\(^3^+\)
- All other species
 PUREX process- Basic principles

1) Mix Phases

$$\text{UO}_2^{2+} + 2\text{NO}_3^- + 2\text{TBP} \rightleftharpoons \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$$

$$\text{Pu}^{4+} + 4\text{NO}_3^- + 2\text{TBP} \rightleftharpoons \text{Pu(NO}_3)_4 \cdot 2\text{TBP}$$

2) Allow to Settle

Aqueous Solution

Organic Solvent

TBP is added

TBP Complex
Representation of the extracted $\text{UO}_2^{2+}$ 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:

$$D_m = \frac{[M(NO_3)_x \cdot nTBP]_{org}}{[M^{x+}]_{aq}} = K_1\frac{[NO_3^-]^x_{aq} [TBP]^n_{org}}$$
Nitric acid dependency

\[ \text{UO}_2^{2+} + 2\text{NO}_3^- + 2\text{TBP} \rightleftharpoons \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP} \]

\[ \text{Pu}^{4+} + 4\text{NO}_3^- + 2\text{TBP} \rightleftharpoons \text{Pu(NO}_3)_4 \cdot 2\text{TBP} \]
• 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⁺

\[ \text{U}^{4+} + 2\text{Pu}^{4+} + 2\text{H}_2\text{O} \rightarrow \text{UO}_2^{2+} + 2\text{Pu}^{3+} + 4\text{H}^+ \]

• 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

\[ 2\text{HNO}_2 + \text{N}_2\text{H}_4 \rightleftharpoons \text{N}_2 + \text{N}_2\text{O} + 3\text{H}_2\text{O} \]
Example of Process Flowsheet Design

\[ D = \frac{[M_o]}{[M_a]} \]

\[ D = \frac{M(1)}{M(2)} \]

Acid Concentration

Dilute

Concentrated

\( D \) = Dilute Concentrated Acid Concentration
PUREX Process – unit operations

• Separations
  – Countercurrent PUREX flowsheet (1st cycle or HA cycle)
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

<table>
<thead>
<tr>
<th>ΔG (kcal per mole of chlorine)</th>
<th>Hg</th>
<th>Mo</th>
<th>W</th>
<th>Ni</th>
<th>H</th>
<th>Retained with cladding materials in the anode basket → metal waste</th>
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| Fe   | Cd | Zr    | Hg | Mo | W | Ni | H | Zn, Cr | V | Mn, Be |

- Recovered by a solid cathode as uranium product → fabrication of recycled fuel
- Recovered by liquid cadmium cathode together with uranium → fabrication of recycled fuel
- Accumulated in the molten salt → ceramic waste

External electrical potential is needed

INL Idaho National Laboratory
Schematic of Electrorefining Process to Treat Spent Fuel

\[ V_{\text{cell}} = V_a + V_c \]
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”