

Non-Aqueous Processes



Mike Goff

Idaho National Laboratory

Introduction to Nuclear Fuel Cycle Chemistry

August 5, 2009



Definition 1

“Pyrometallurgical processing techniques involve several stages: volatilisation, liquid-liquid extraction using immiscible metal-metal phases or metal-salt phases, electrorefining in molten salt, fractional crystallisation, etc. They are generally based on the use of either fused (low-melting point) salts such as chlorides or fluorides (eg $\text{LiCl}+\text{KCl}$ or $\text{LiF}+\text{CaF}_2$) or fused metals such as cadmium, bismuth or aluminium.”

From Wikipedia



Definition 1

“Pyrochemical reprocessing methods use high temperature oxidation –reduction reactions in non-aqueous media to separate the actinides, U and Pu from the fission products. These methods exploit the differences in the volatilities or thermodynamic stabilities of the compounds of actinides and fission products to achieve the separation. Pyrochemical separations can be achieved by using electrochemical methods instead of chemical equilibrations.”

From PYROCHEMICAL Reprocessing of Fast Reactor Fuels on IGCAR Website



Why Non-Aqueous Processes?

- **Potential compactness (co-location with reactor)**
- **Resistance to radiation effects (short-cooled fuel can be processed)**
- **Criticality control benefits**
- **Compatibility with advanced fuel types**
- **Capable of low purity products**



Example Non-Aqueous Processes

■ Volatilization (DUPIC, volox, AIROX, DEOX, etc.)

- Spent fuel is heated to remove volatile or gaseous fission product impurities
- Chemical form of the spent fuel may be modified to facilitate removal of fission products
- Recycle of the fuel is limited due to limited reduction of impurities



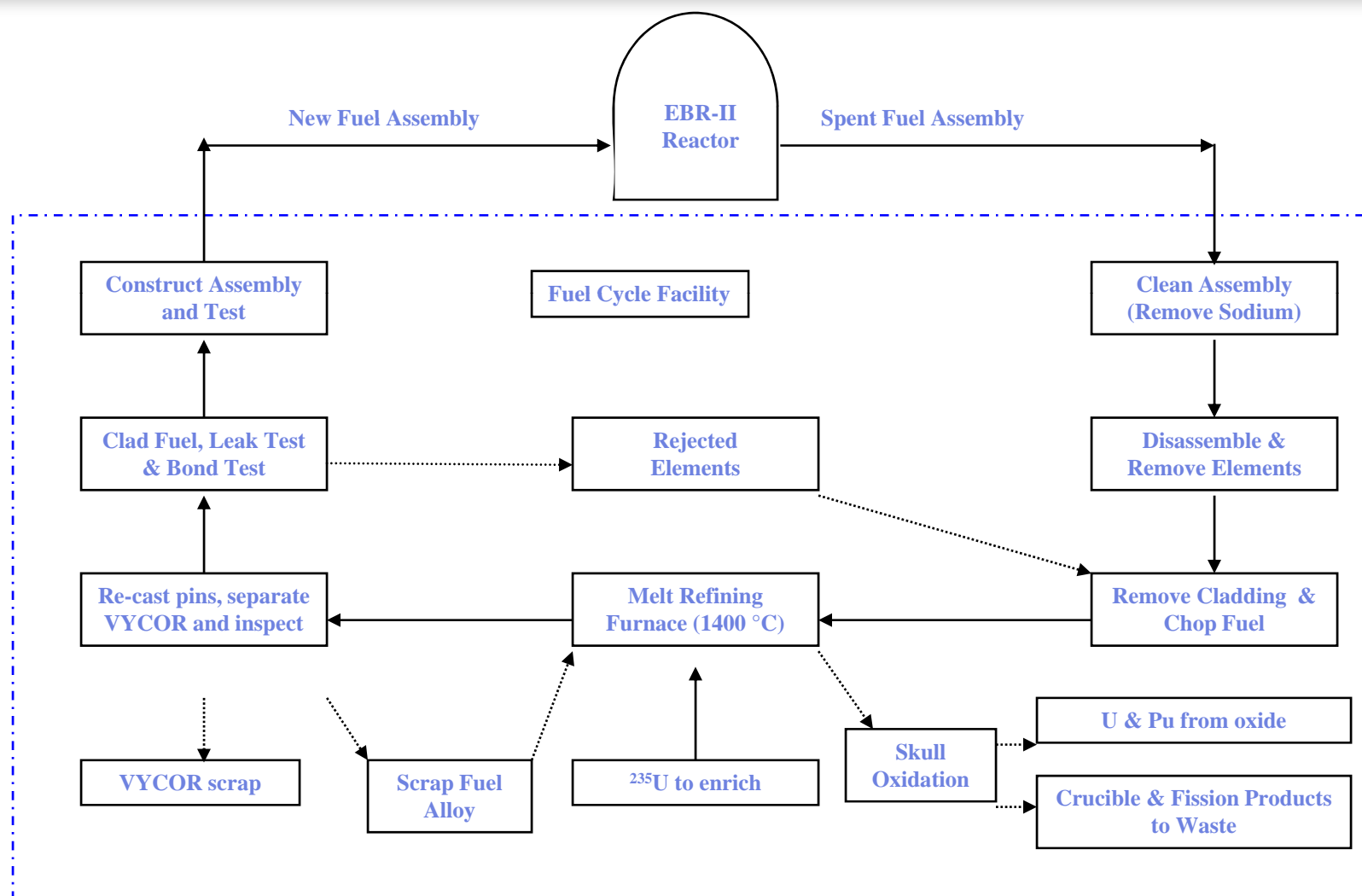
■ Halide volatility (fluoride volatility, chloride volatility)

- Fuel converted to a halide form like UF_6
- UF_6 is gaseous and separated from fission products
- Other actinides can also be converted to gaseous halides to some extent.

■ Partial oxidation (melt refining, skull-reclamation, etc.)



Melt Refining Deployed in the 1960s





Molten Salt Electrolysis

- **Electrochemical technology**
- **Dry processing**
- **Pyroprocessing**
- **Pyrochemical processing**
- **Pyrometallurgical processing**
- **Electrometallurgical treatment**
- **Etc.**



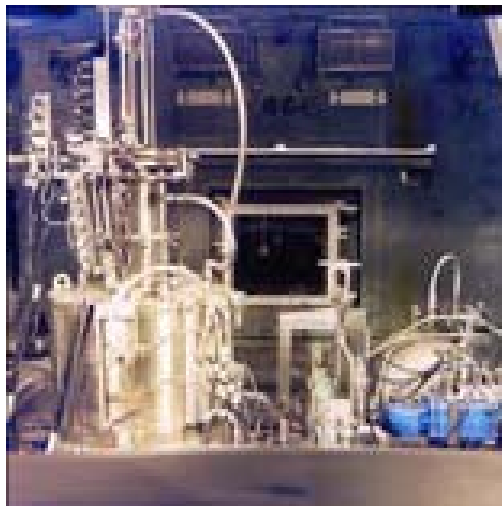
Electrochemical Technology

- Work being performed in the United States is focused on an electrochemical process involving molten salts and liquid metals.
- Work is performed primarily at Idaho National Laboratory and Argonne National Laboratory.
- This talk will focus on that technology and its development.





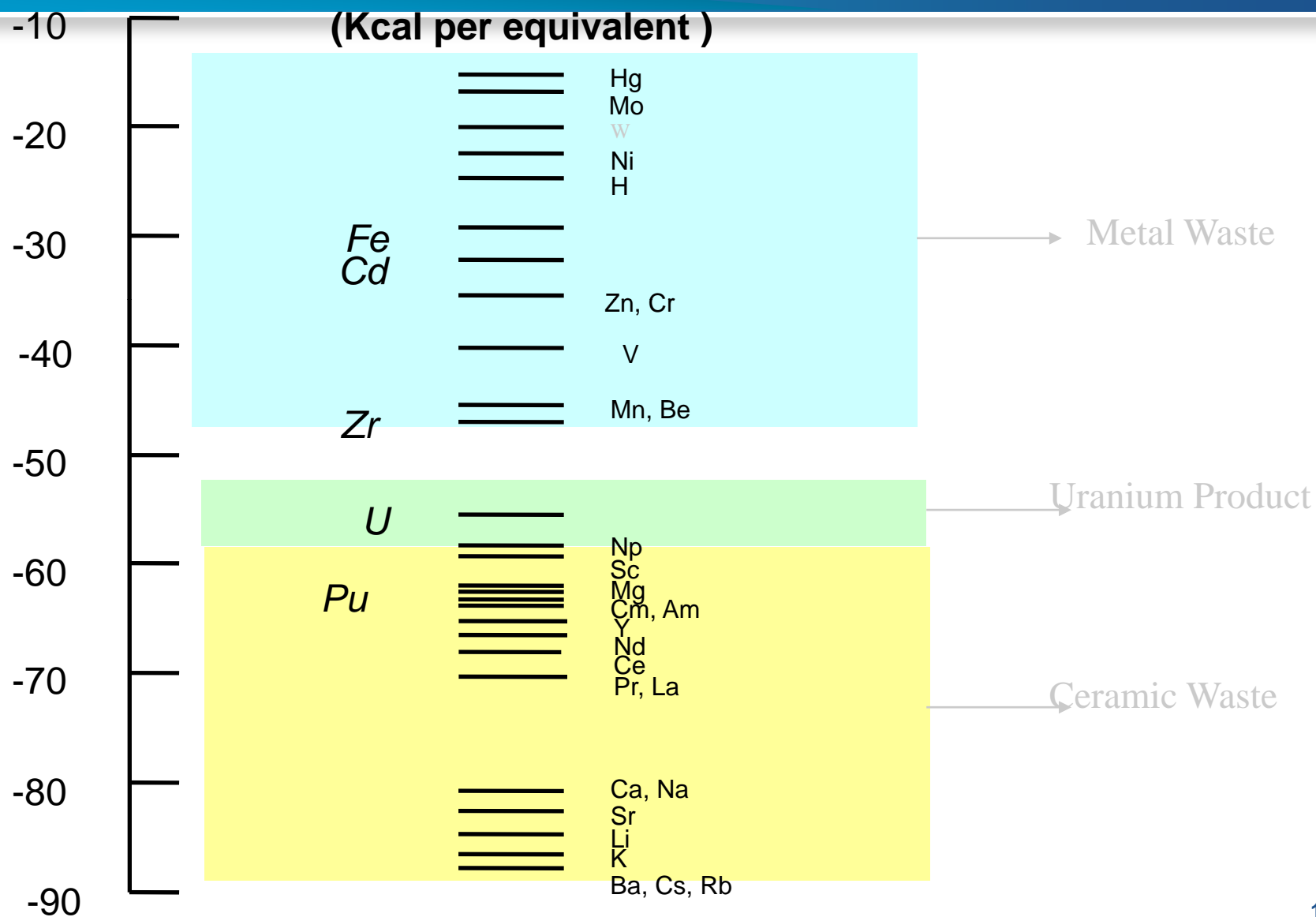
Electrochemical Processing Background



- **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.
- **Reasons technology pursued include:**
 - Capable of low purity products
 - Potential compactness (co-location with reactor)
 - Resistance to radiation effects (short-cooled fuel can be processed)
 - Criticality control benefits
 - Compatibility with advanced fuel types
- **Process was integrated with remote fuel fabrication for fast reactors.**

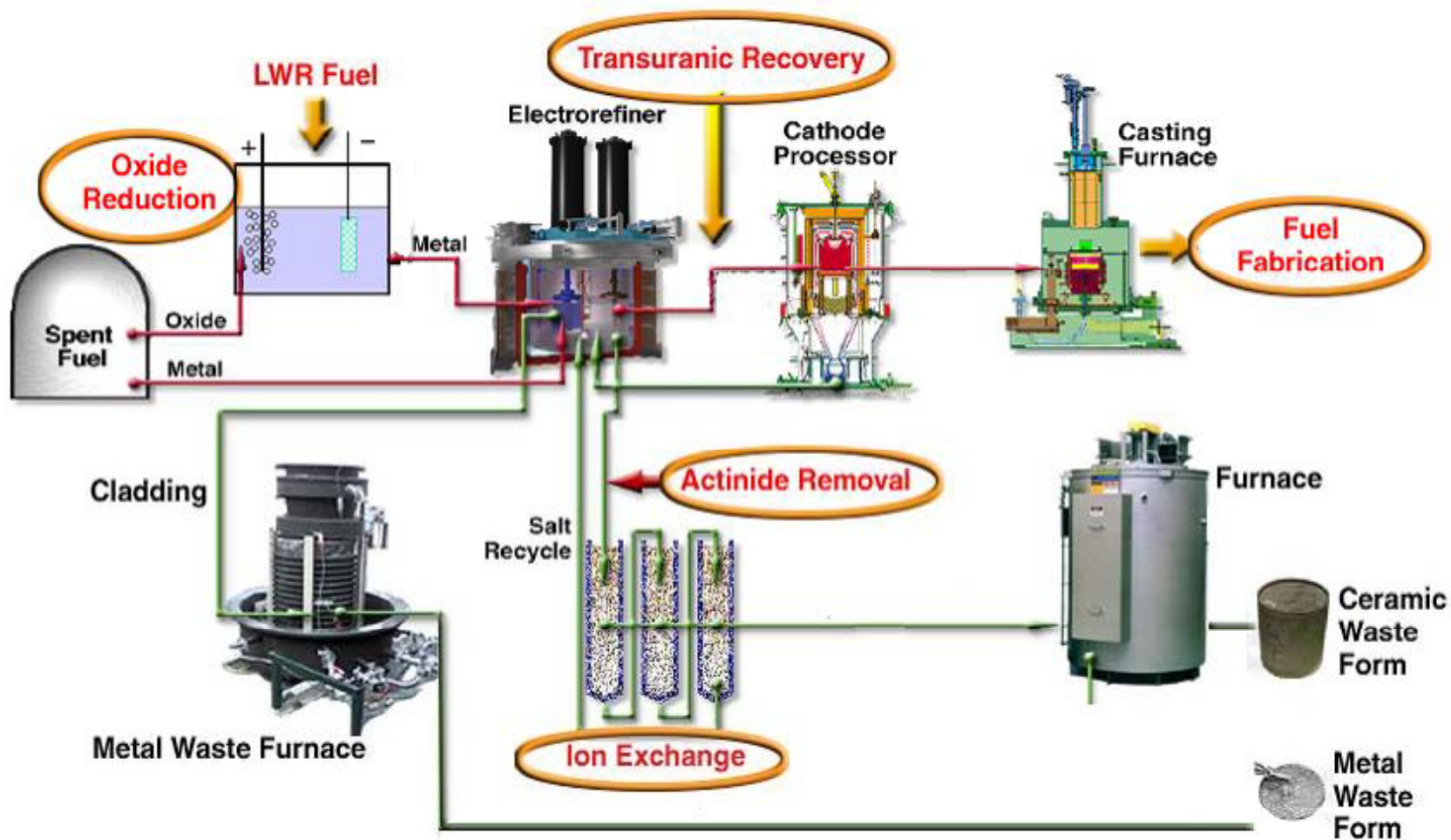


Chemical Bases for Electrochemical Processing



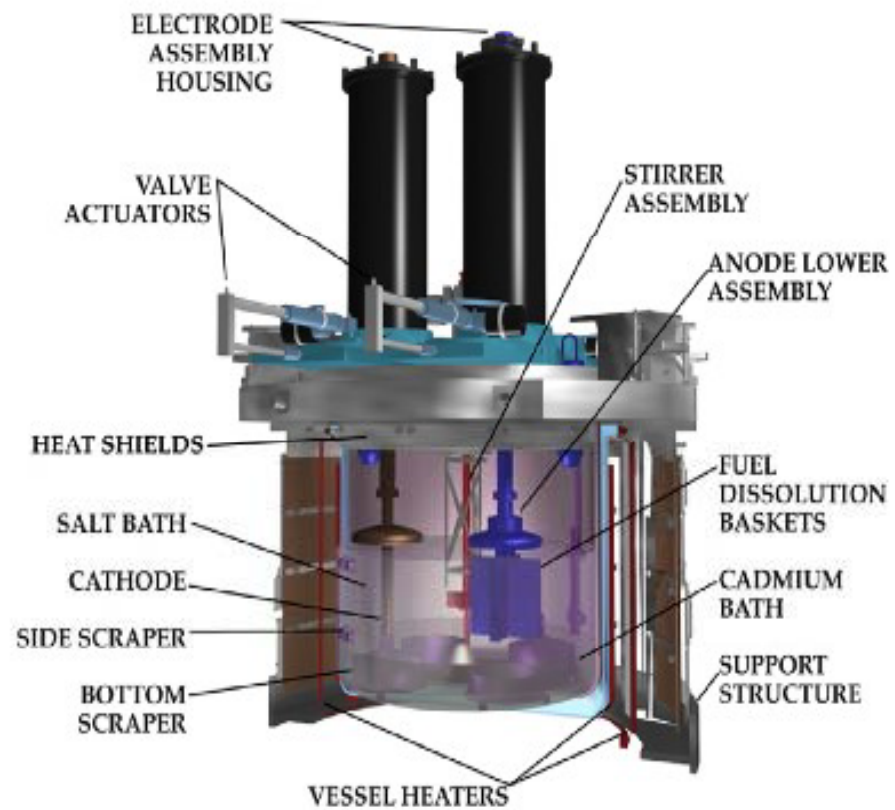


Electrochemical Process Flowsheet



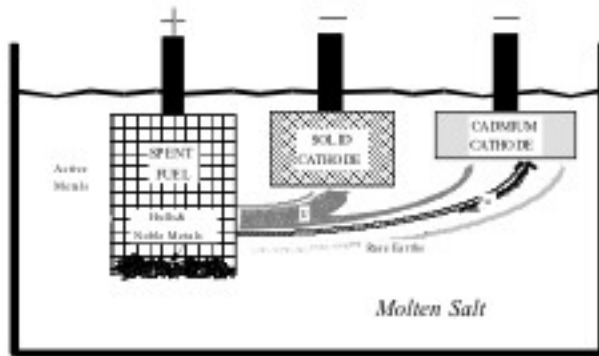


Electrorefining





Challenge to Recover All Actinides Elements

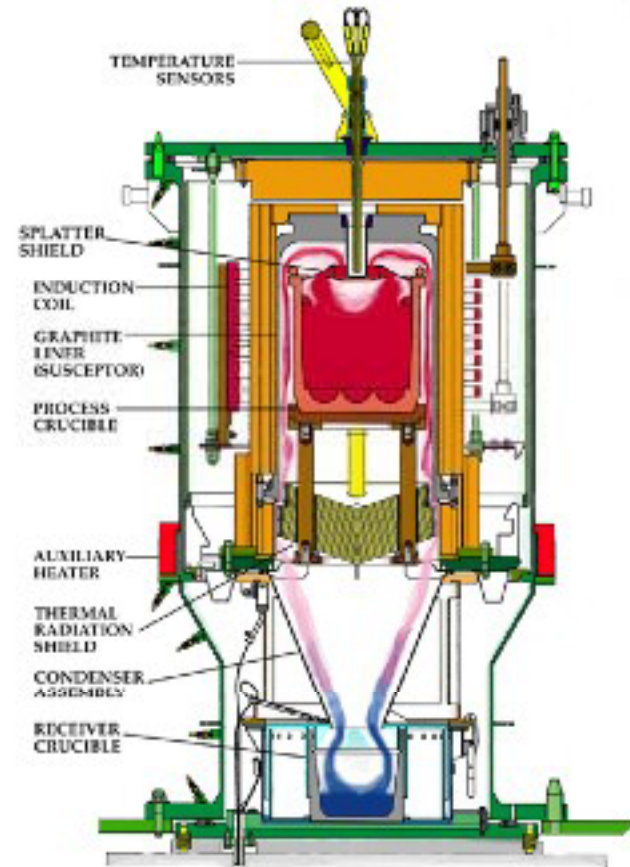


- Recovery of plutonium on a solid cathode is not feasible because the following reaction is favorable:
 - $\text{Pu} + \text{UCl}_3 \rightarrow \text{PuCl}_3 + \text{U}$ (free energy change is -21 kcal/mol)
- Theoretically the ratio of $[\text{PuCl}_3]$ to $[\text{UCl}_3]$ needs to be approximately 10^6 in order to deposit plutonium metal.
- Plutonium and uranium can be co-deposited in liquid cadmium because the activity coefficient for plutonium is very small ($\sim 10^{-4}$).
 - The ratio of $[\text{PuCl}_3]$ to $[\text{UCl}_3]$ needs to be only 2-3 in order to deposit plutonium in cadmium with other actinides and some fission products.



Cathode Processing

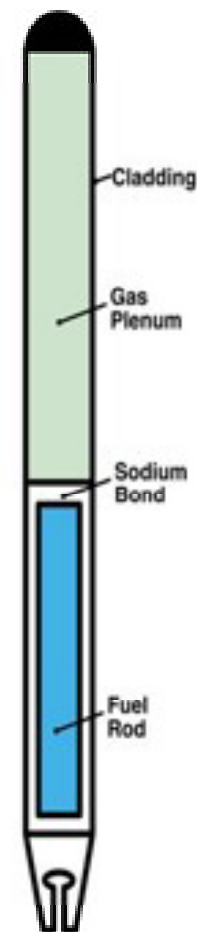
- Salt must be separated from recovered actinides.
- Salt is distilled and recycled back to electrorefiners.





Electrochemical Treatment of EBR-II Spent Fuel

- **EBR-II used a sodium-bonded metallic fuel.**
 - Reactive materials (sodium and uranium metal)
 - Highly enriched uranium in driver fuel (53-78% U-235)
 - Approximately 1% plutonium in blanket fuel
- **Technology was formally demonstrated with spent fuel between 1996 and 1999.**
- **Demonstration was reviewed for the National Research Council.**
 - *Finding: The Committee finds that ANL has met all of the criteria developed for judging the success of its electrometallurgical demonstration project.*

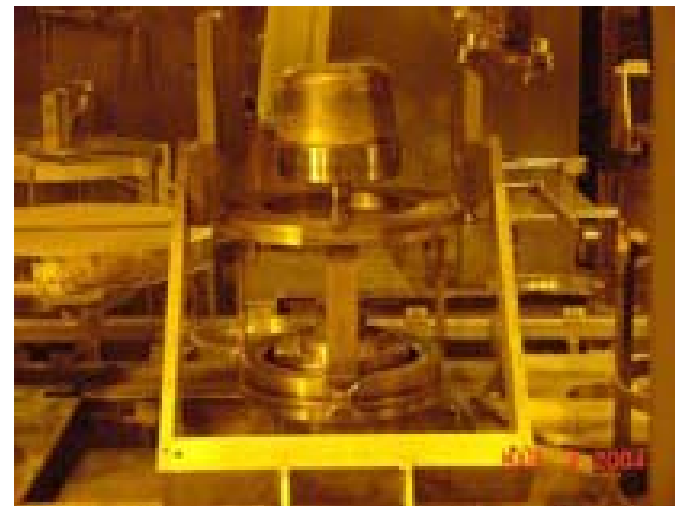


***Schematic Drawing of
EBR-II Fuel Element***



Mission of Electrochemical Processing

- **Until 1994, focus was on demonstration of closed fuel cycle with a fast reactor.**
 - Recycle of fast reactor fuel
 - Limited work on production of fast reactor feed material from LWRs
- **In 1994, activities were redirected to treatment for disposal.**
 - Engineering-scale experience was gained with spent fuel.
- **With the formation of the Advanced Fuel Cycle Initiative (AFCI) in 2002, recycle focus was renewed and stressed.**

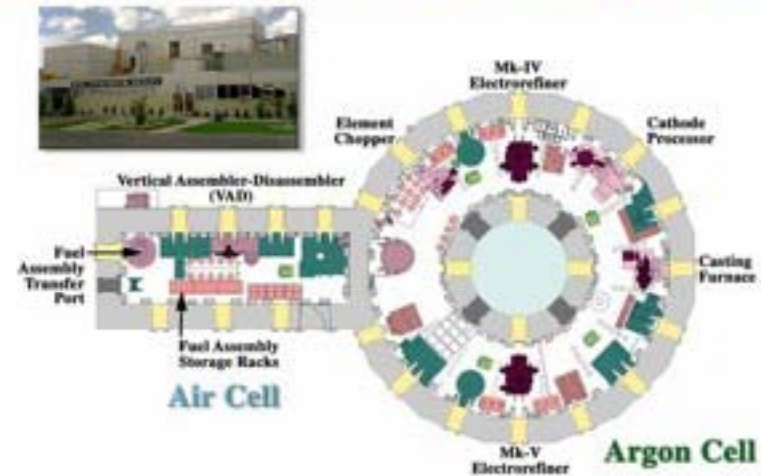




Electrochemical Processing Facilities

- The Fuel Conditioning Facility (FCF) is a one-of-a-kind electrochemical processing facility.
- FCF is used for treatment of fuel and demonstration of electrochemical process operations.
- Work includes development, qualification, and production of high-level waste.
- High-level waste work is performed in the Hot Fuel Examination Facility (HFEF).

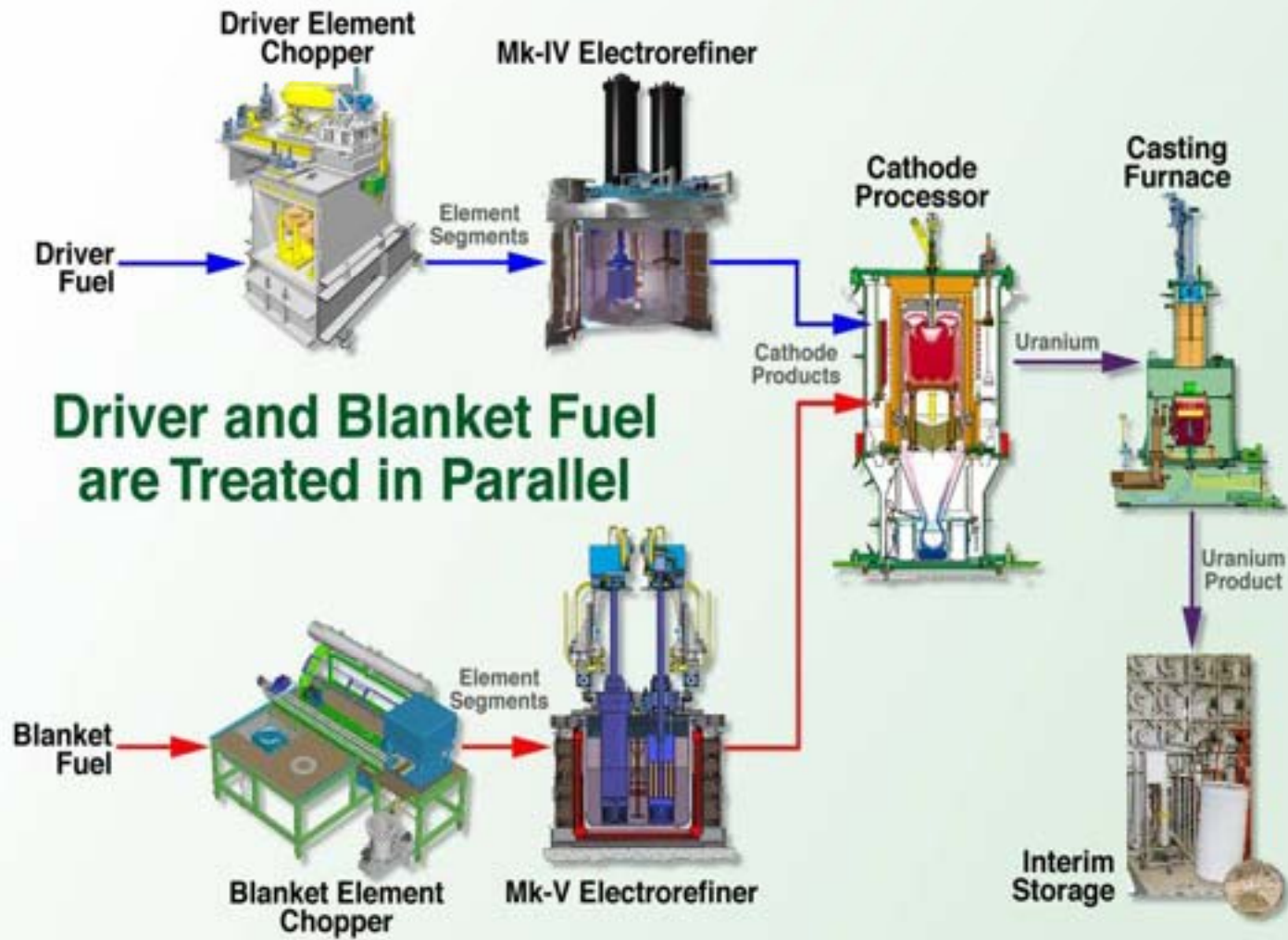
Fuel Conditioning Facility for Spent Nuclear Fuel Treatment



Hot Fuel Examination Facility



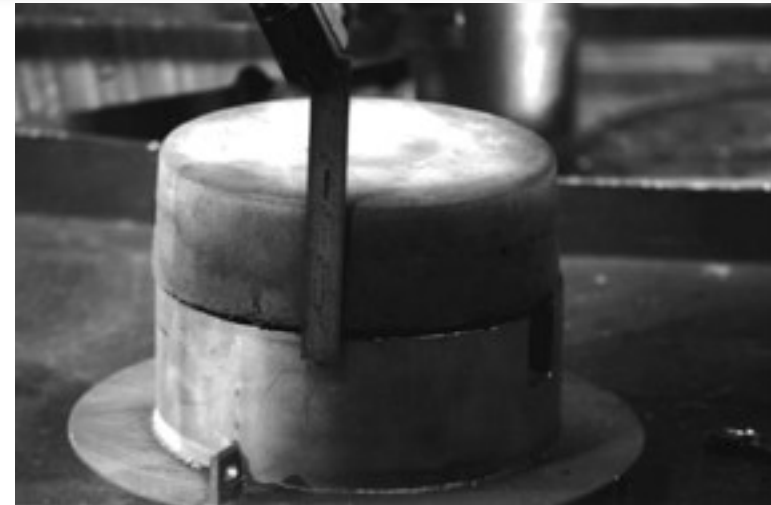
Processing Lines in FCF





Electrochemical Treatment of Spent Fuel

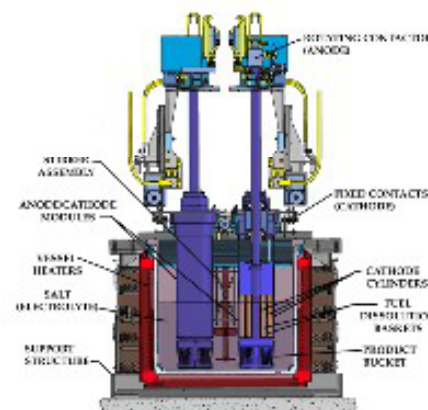
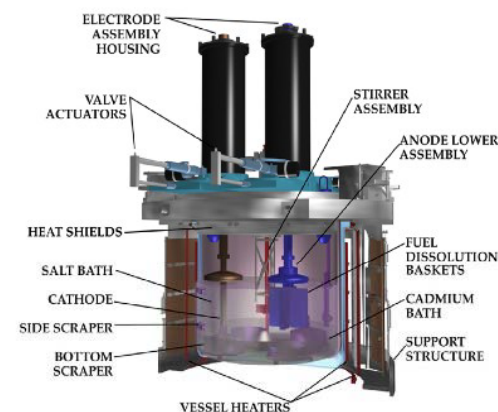
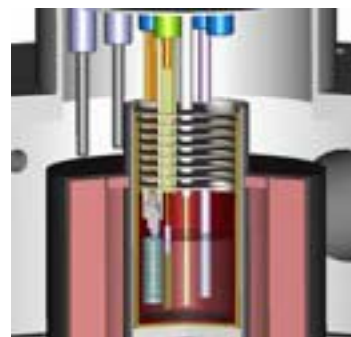
- **Electrochemical processing has been performed on the engineering-scale with irradiated fuel since 1996.**
- **Approximately 3.5 MTHM of fuel, including highly enriched uranium fuels, have been treated.**
- **Installed process equipment could support throughputs between 3 and 5 MTHM per year.**
-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





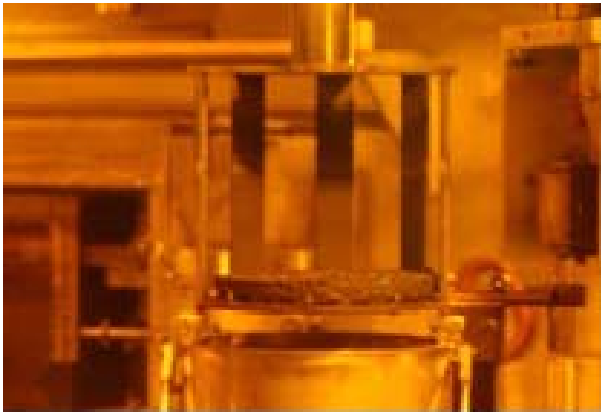
Hot Cell Electrorefiner Scale-up

- Throughout development of electrochemical processing, electrorefining has been scaled significantly for hot cell application.
- First hot cell electrorefiner has a current capacity of 3.5 amps.
- Mark IV electrorefiner has a current capacity of 200 amps.
- Mark V electrorefiner has a current capacity of 2400 amps.
- Technology has been scaled in cell by three orders of magnitude.





Electrochemical Processing Accomplishments



Recovered Transuranic Ingot

- **Group transuranic recovery tests have been successfully performed at laboratory and engineering-scales.**
 - Recoveries of more than 1 kg of transuranics have been obtained.
 - Purity requirements for fast reactor fuel have been demonstrated at both scales.



Uranium Deposit from Electrefining

- **Engineering-scale electrorefining operations continue to demonstration high dissolution of actinides (99.7%).**



Electrochemical Processing Accomplishments



Zirconium-rich cathode



HfN-Coated Nb Crucible (6 liter)

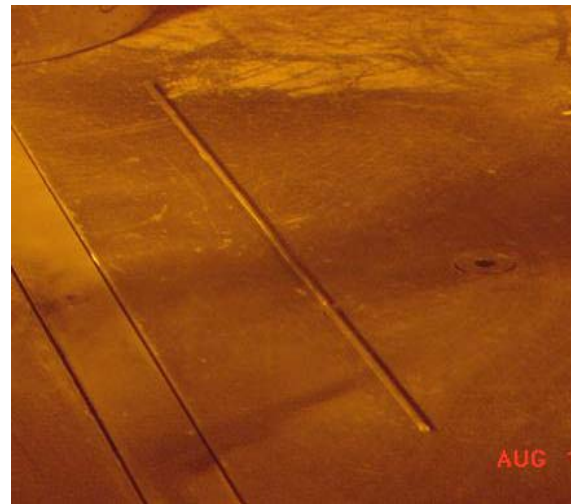
- **Electrochemical recovery of zirconium has been demonstrated.**
- **Improved crucible materials for high temperature processing have been successfully tested at engineering-scale.**
 - Crucibles are reusable, which supports increased throughput.
 - Very little dross forms in new crucibles.



Metallic Fuels



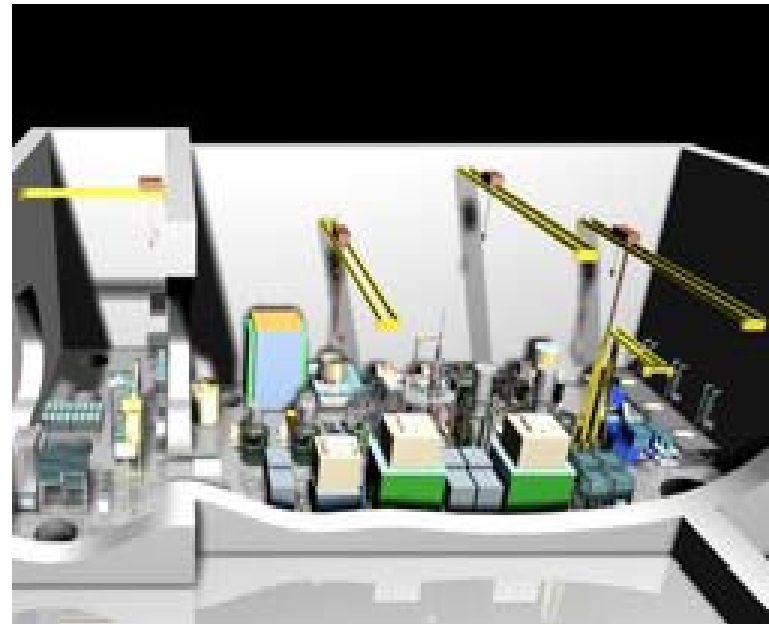
- Process development work has focused on metallic fuels.
- Metallic fuels are amenable to remote fabrication.
- Metallic fuels are capable of high burnups.





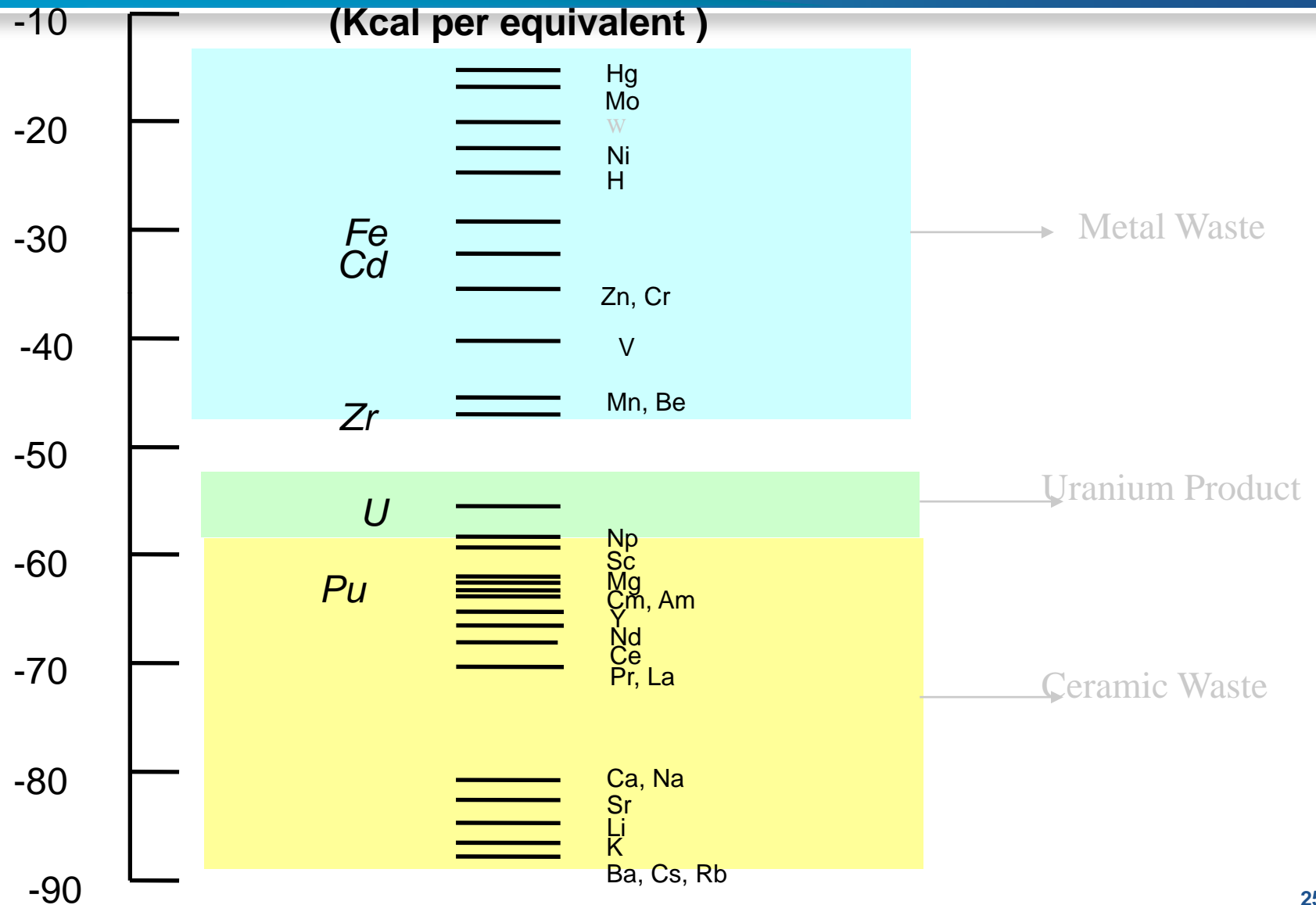
Electrolytic Reduction Process Scale-Up

- Pre-conceptual layouts of an engineering-scale electrolytic reduction vessel (20 to 40 kg oxide fuel batch size) based on a planar electrode configuration have been generated.
- A pre-conceptual design of a facility to treat spent oxide fuel has been prepared to help focus research on critical activities.





Chemical Bases for Electrochemical Processing

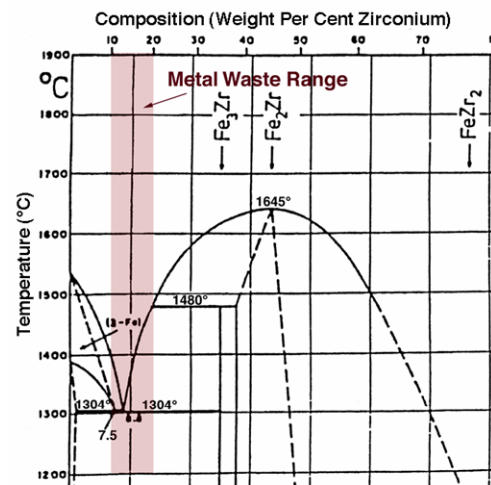
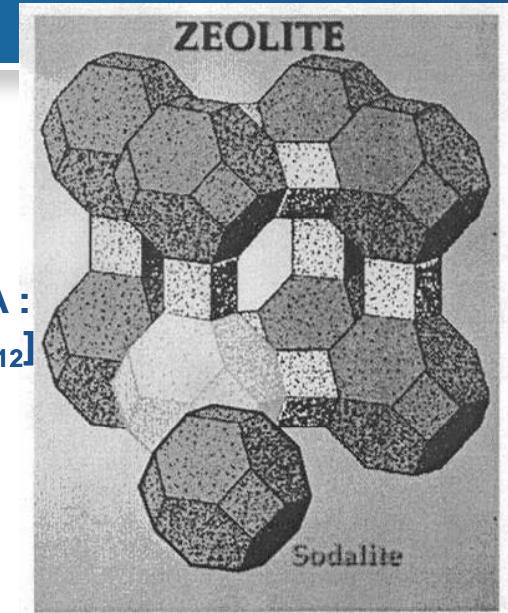




High-Level Wastes from Electrochemical Processing

- Two high-level wastes are produced from electrochemical processing.
- A zeolite-based ceramic waste stabilizes fission products that form chlorides.
- A stainless-steel-15% zirconium metal waste stabilizes the cladding hulls and more noble fission products.

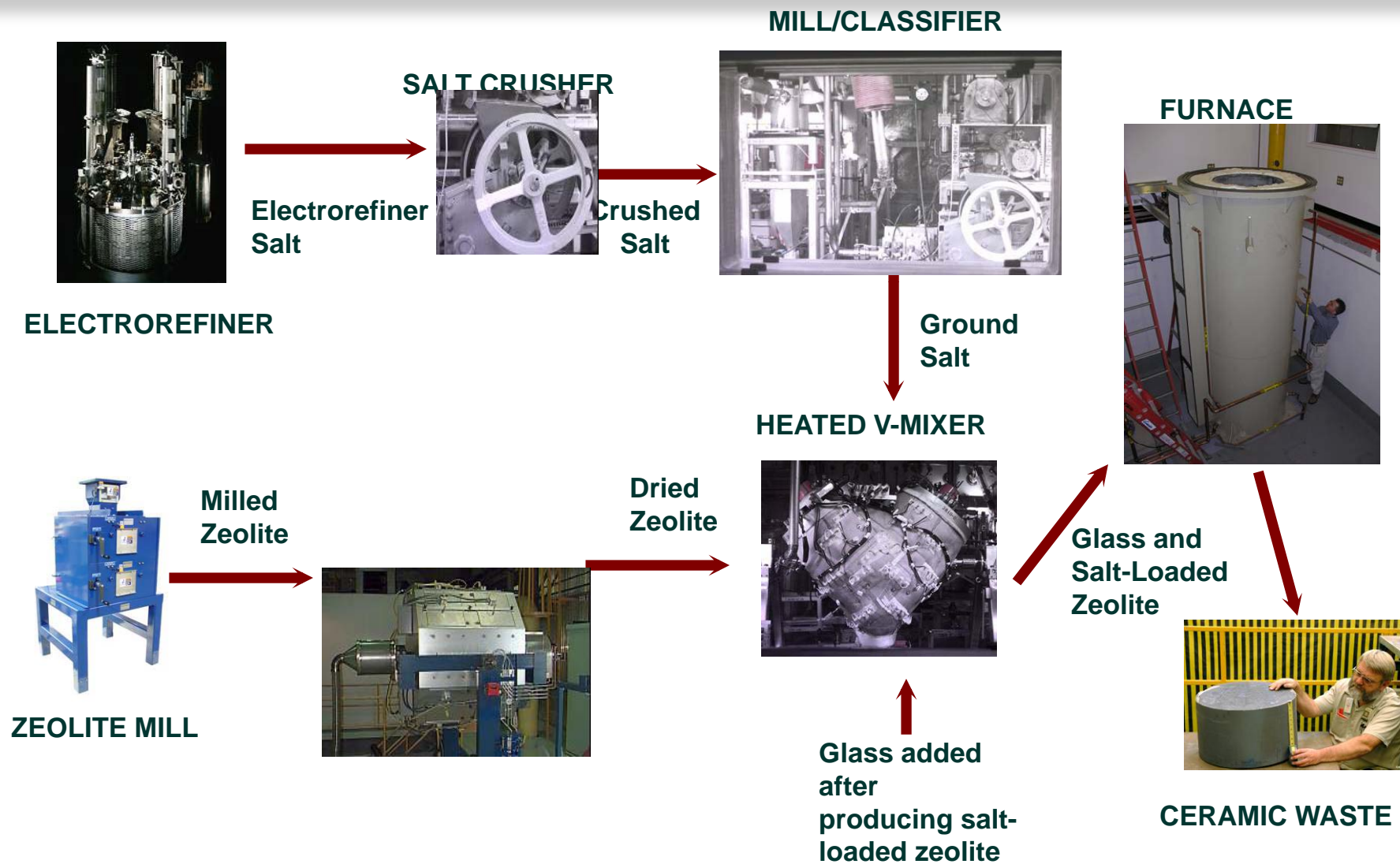
Unit Cell of Zeolite A :
 $\text{Na}_{12} [(\text{AlO}_2)_{12} (\text{SiO}_2)_{12}]$



*Fe-Zr Phase Diagram
for Metal Waste*



Ceramic Waste Process





Metal Waste Form Process



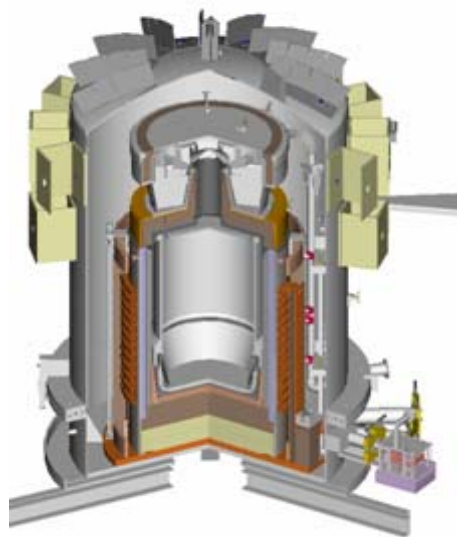
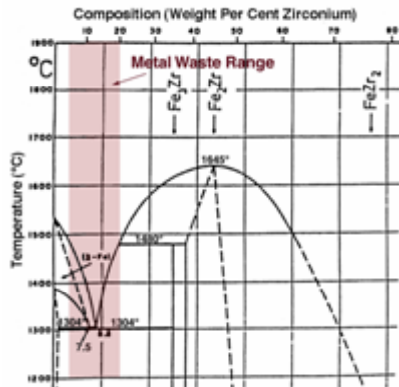
CLADDING HULLS



SALT



ELECTROREFINER



INDUCTION FURNACE



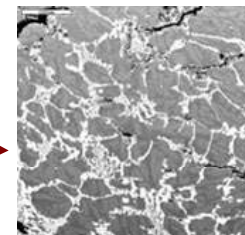
CERAMIC WASTE



ZIRCONIUM



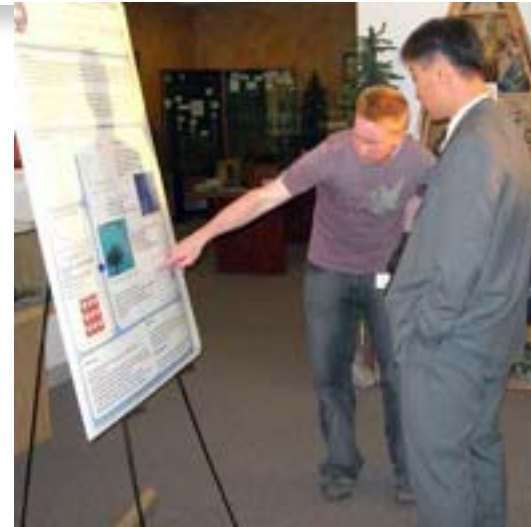
INGOTS





International Pyroprocessing Conference

- **INL hosted first International Pyroprocessing Research Conference in August 2006.**
- **There were approximately 75 attendees, 34 from outside US.**
- **Papers were presented from 7 countries:**
 - US
 - ROK
 - Japan
 - France
 - United Kingdom
 - India
 - Russia
- **70 presentations were made.**
- **Follow-on conference was in Korea.**





Summary

- **Non-aqueous technologies have been/are still being assessed for recycle of spent nuclear fuel.**
- **Non-aqueous technologies offer benefits for treatment of spent nuclear fuels compared to aqueous technologies.**
- **Non-aqueous technologies in general do not result in high purity products.**
- **Technology has been implemented for treatment of fast reactor spent fuel.**