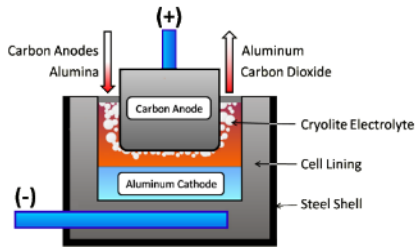


Metallic fuels treatment

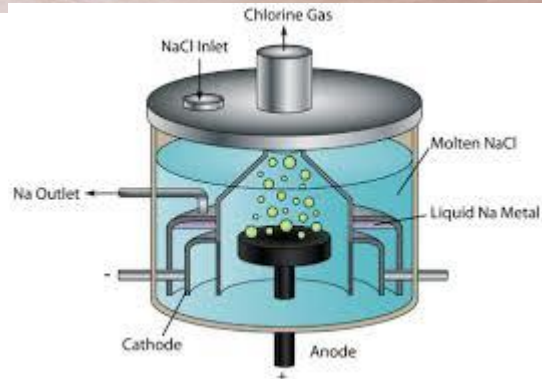
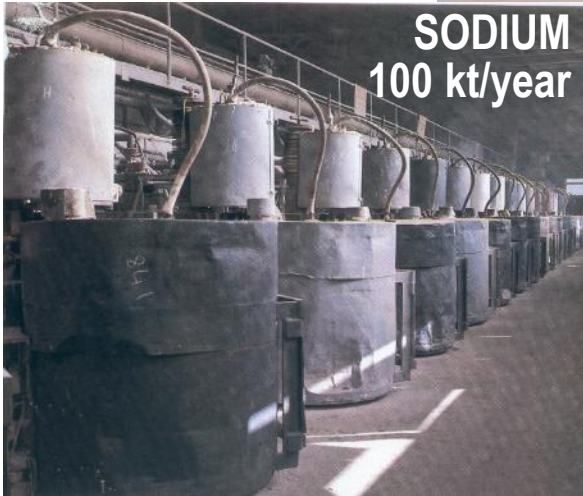


DE LA RECHERCHE À L'INDUSTRIE

ALUMINIUM 60000 kt/year



SODIUM 100 kt/year



		Half reaction					
	strongest oxidant	$\text{Au}^+(\text{aq}) + \text{e}^- \longrightarrow$	$\text{Au}(\text{s})$				weakest reductant
		$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \longrightarrow$	$2\text{H}_2\text{O}(\text{l})$				
		$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow$	$\text{Ag}(\text{s})$				
		$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow$	$\text{Fe}^{2+}(\text{aq})$				
		$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \longrightarrow$	$4\text{OH}^-(\text{aq})$				
		$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow$	$\text{Cu}(\text{s})$				
		$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \longrightarrow$	$\text{Sn}^{2+}(\text{aq})$				
		$2\text{H}^+(\text{aq}) + 2\text{e}^- \longrightarrow$	$\text{H}_2(\text{g})$				
		$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow$	$\text{Pb}(\text{s})$				
		$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow$	$\text{Sn}(\text{s})$				
		$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow$	$\text{Ni}(\text{s})$				
		$\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow$	$\text{Co}(\text{s})$				
		$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow$	$\text{Fe}(\text{s})$				
		$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow$	$\text{Cr}(\text{s})$				
		$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow$	$\text{Zn}(\text{s})$				
		$2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \longrightarrow$	$\text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$				
		$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow$	$\text{Al}(\text{s})$				
		$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow$	$\text{Mg}(\text{s})$				
		$\text{Na}^+(\text{aq}) + \text{e}^- \longrightarrow$	$\text{Na}(\text{s})$				
		$\text{Ca}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow$	$\text{Ca}(\text{s})$				
	weakest oxidant	$\text{K}^+(\text{aq}) + \text{e}^- \longrightarrow$	$\text{K}(\text{s})$				strongest reductant
		$\text{Li}^+(\text{aq}) + \text{e}^- \longrightarrow$	$\text{Li}(\text{s})$				

Increasing oxidising strength

Increasing reducing strength

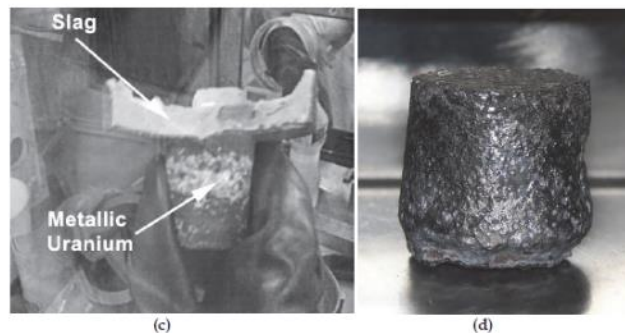
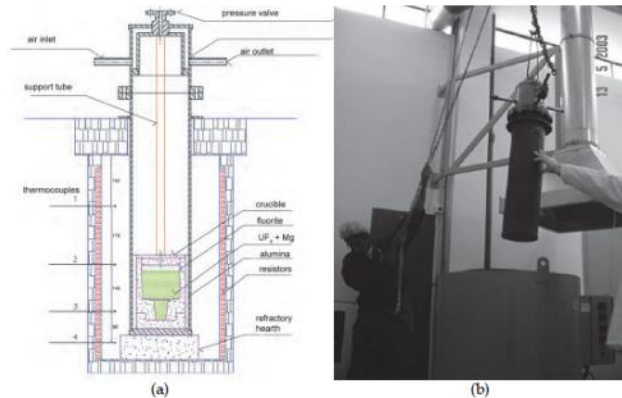
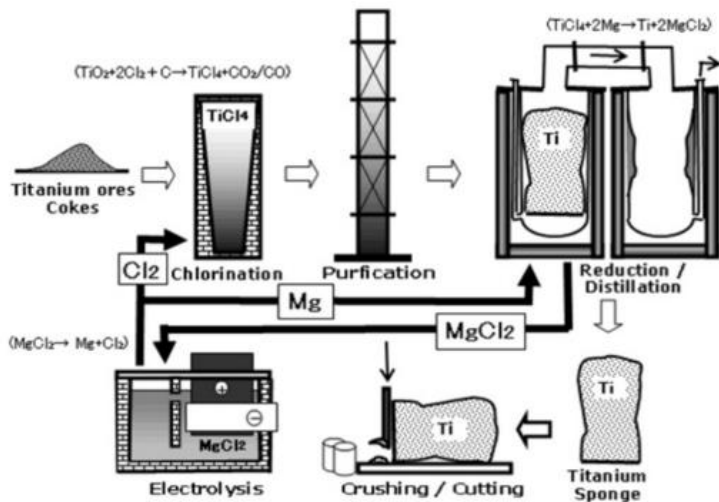
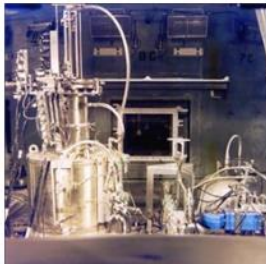


Fig. 8. (a) Schematic drawing of pit furnace, reactor vessel and crucible; (b) Charging of the reactor vessel inside the pit furnace; (c) Raw metallic uranium and upper deposited slag after removing from the crucible; (d) Metallic uranium after cleaning.

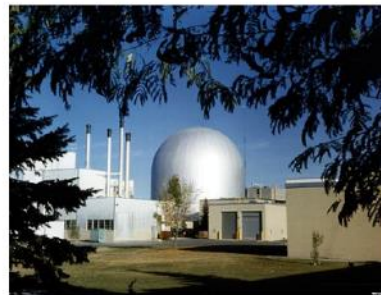
Pyroprocessing Background



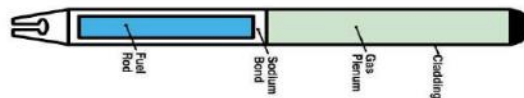
- Present generation of pyrochemical processing for recycling or treating spent fuel started in the 1980s.
- Reasons pyroprocessing pursued include:
 - Non-proliferation benefits due to low purity products
 - Resistance to radiation effects (hotter fuel can be processed)
 - Criticality control benefits
 - Potential compactness

Experimental Breeder Reactor-II

- EBR-II was a metallic-fueled sodium-cooled, fast reactor.
 - Operated from 1963 to 1995.
 - Uranium-10 wt % zirconium driver fuel.
 - High enrichment driver fuel (67-78%)
 - DU blanket (1% Pu--used for breeding)
 - High burnup (>30 atom %) achieved in some fuel pins.
 - All fuel sodium bonded
- Demonstration test reactor for Integral Fast Reactor System (1984 to 1995).
- Reactor shut down in 1995



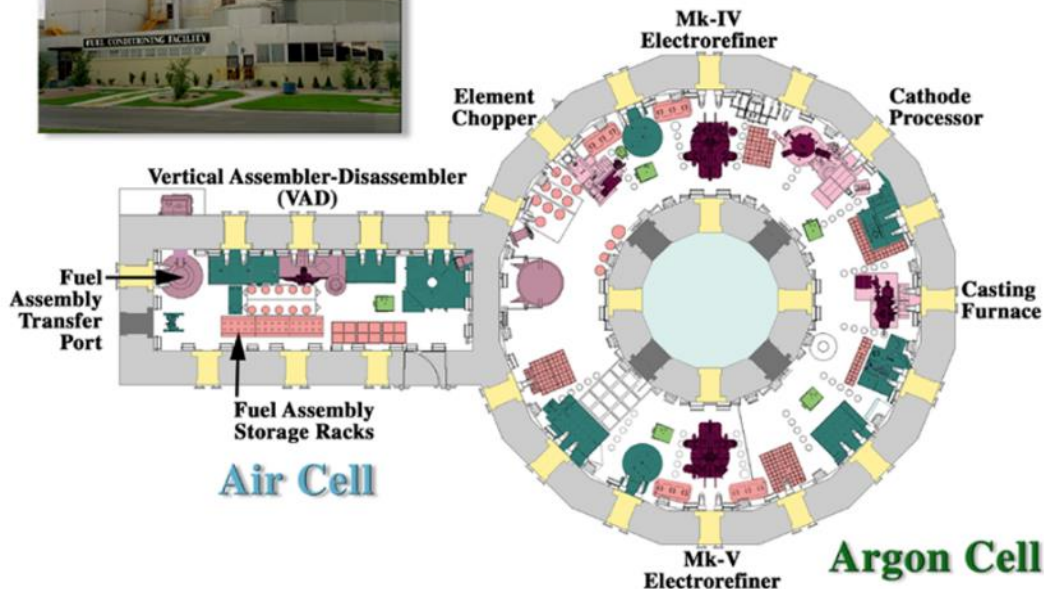
22.4 tons blanket
3.1 tons driver



Fuel Conditioning Facility

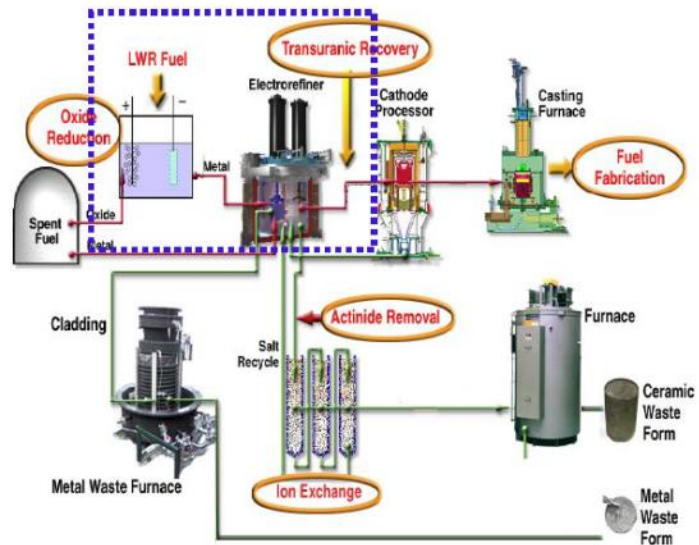
- **Constructed to support the EBR-II reactor**
- **Facility is now used for the treatment of EBR-II sodium bonded fuel**
 - **Controlled atmosphere within the shielded cells**
 - **Overhead and remote handling**
 - **In-cell process equipment**
 - **Decon spray chamber and suited-entry repair area**

Fuel Conditioning Facility for Spent Nuclear Fuel Treatment

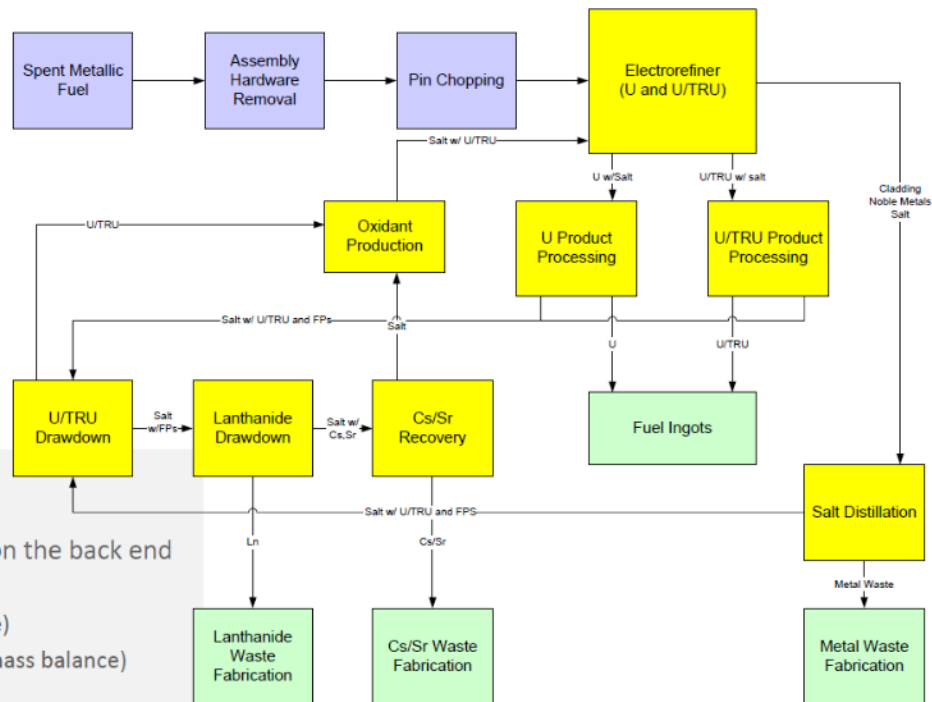


Introduction of Pyrochemical Separation

- Present generation of pyrochemical processing for recycling was started in the 1980s by ANL and INL
- Electrolytic reduction and electrorefining are key separation steps in pyroprocessing
- The electrorefining process can treat different types of spent fuel (metal, oxide, and nitride) and produce a pure metallic product
- The use of the electrorefining processes for material recycle and purification is expanding across the globe



Flowsheet modifications (Metal Fuel)

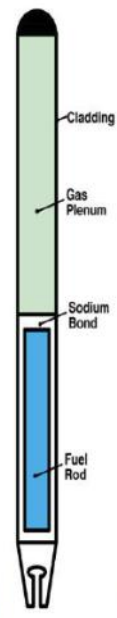


- Minimize waste by maximizing salt recycle
- Sequential drawdown on the back end
 - U/TRU (complete)
 - Lanthanides (complete)
 - Cs/Sr (sufficient for mass balance)

Typical Significant Constituents of Spent Fuel

(Spent Driver Fuel from Experimental Breeder Reactor, Sodium Bonded U-10Zr Alloy)

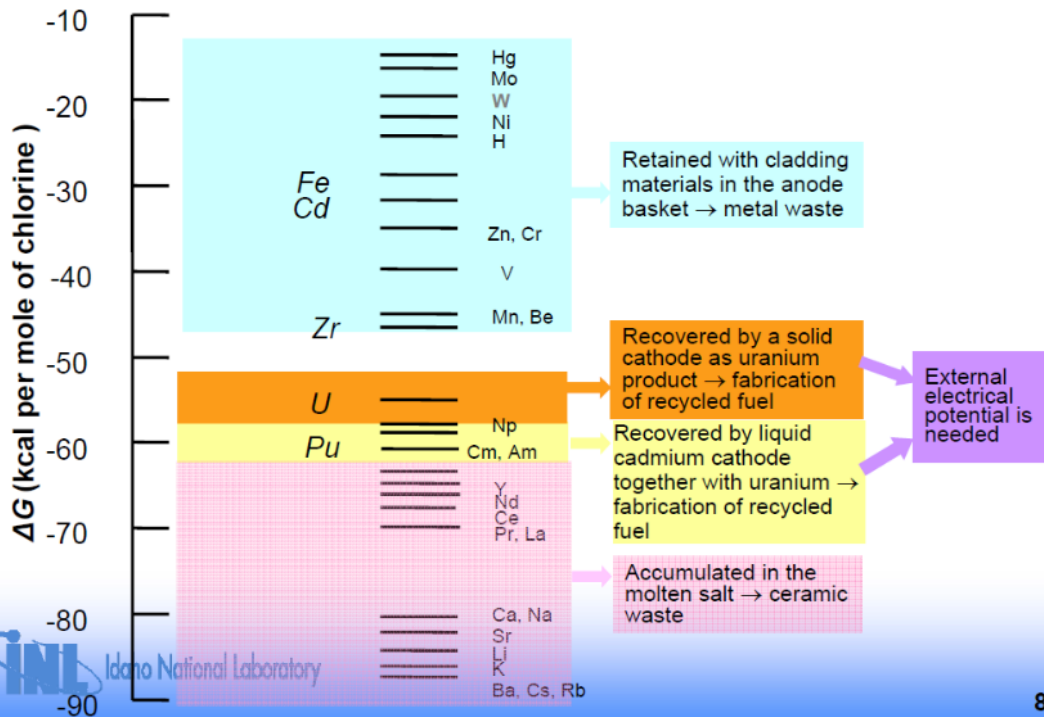
Element	Wt%	Element	Wt%
U	80.60	Sr	0.22
Zr	10.81	Tc	0.18
Na	2.16	Sm	0.18
Mo	0.77	Y	0.13
Nd	0.93	Te	0.11
Cs	0.77	Rh	0.11
Ce	0.54	Rb	0.09
Pu	0.41	Pd	0.09
Ru	0.41	Ti	0.08
Ba	0.33	I	0.05
Si	0.29	Np	0.04
La	0.28	Se	0.02
Pr	0.27	Total	99.86

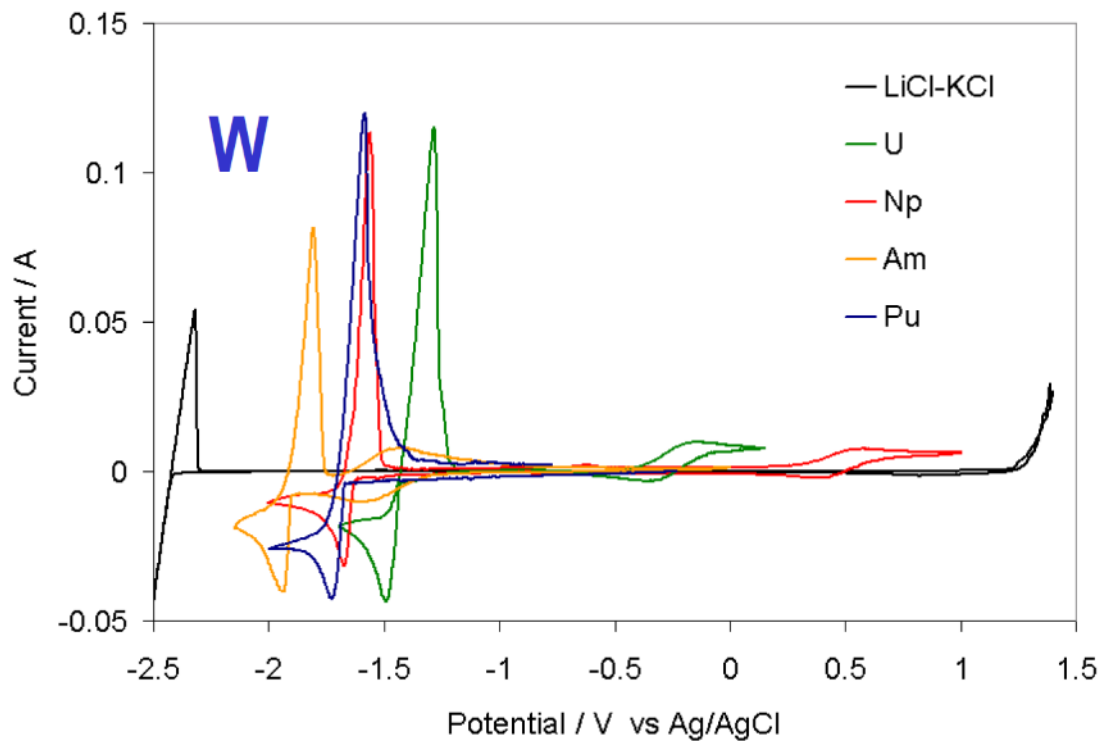


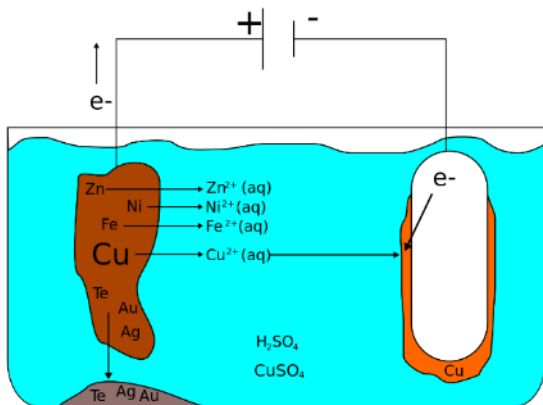
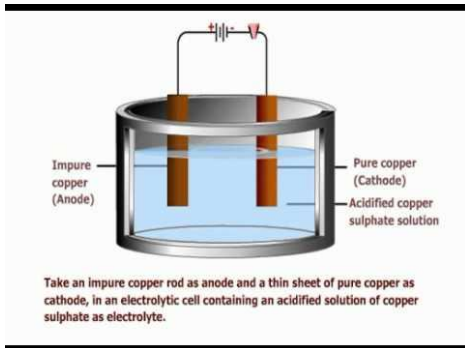
Spent metal
fuel element

4

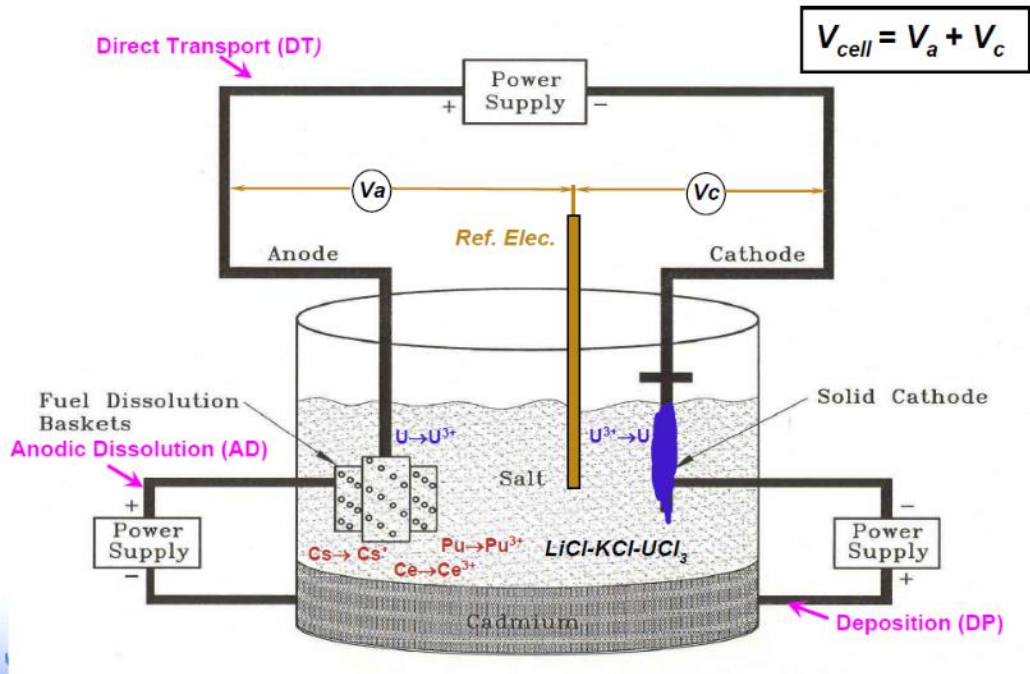
Spent Fuel Constituents are Partitioned According to Free Energy of Formation of Chlorides at 500°C



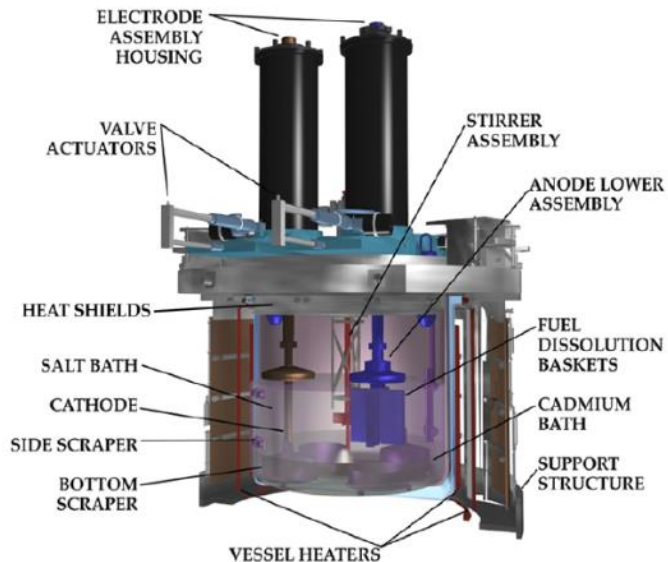




Schematic of Electrorefining Process to Treat Spent Fuel



Mark-IV Electrorefiner (Mk-IV ER)



Vessel ID: 1M

Temperature: 500°C

Electrolyte: LiCl-KCl +

~10 wt% UCl₃

Cd Pool: ~ 10 cm

Anode: Stainless steel
baskets or the
Cd pool

Cathode: Steel mandrel



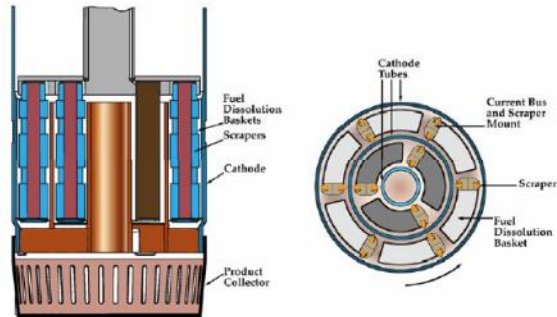
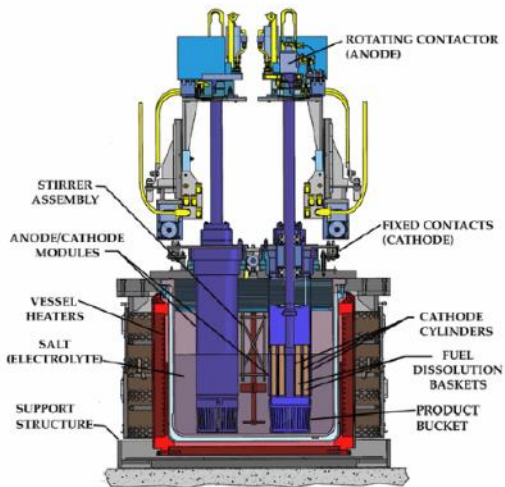
Anode Assembly



Cathode Deposit

14

Mark-V Electrorefiner Treats Blanket Fuel Up to 5 MTHM Per Year

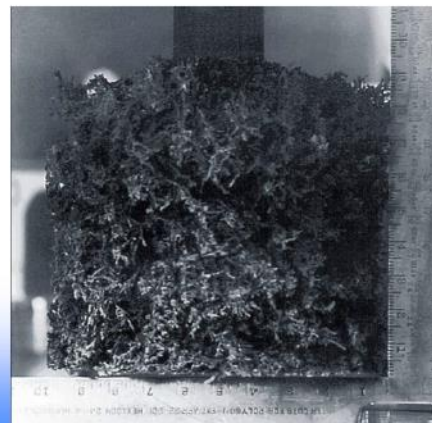


*Concentric Anode Cathode Details
(4 units per electrorefiner)*

Large electrode surfaces
Low solution resistance
High current capacity

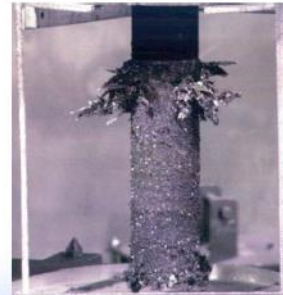
Pyroprocessing Background

- Cathode products from electrorefining have adhering salt and cadmium that require separation from the uranium
- Method of salt and cadmium separation during pyroprocessing is high temperature distillation
- Distillation or retort process is called “cathode processing”
- Cathode processing includes initial consolidation of uranium
- Following cathode processing, another high temperature process (casting) is employed for final consolidation
- Purpose of casting furnace is currently for sampling but historically for fuel fabrication
- Materials of construction are unique to both processes

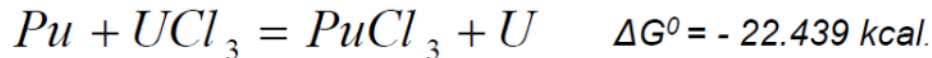


Dendritic Deposit at Solid Cathode

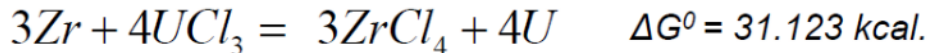
- The morphology of uranium product collected on a solid cathode in a high temperature molten salt is dendritic in general
- The loose dendritic material is easily dislodged from the cathode as the rotating mass grows out toward the scrapers located on the interior sidewalls of the ER
- This results in low current efficiency and limits the process rate
- The formation of loose dendrite was caused by mass transport limitations at the cathode/salt interface



Examples of Exchange Reactions Among Spent Fuel Components and LiCl-KCl-UCl₃ Salt at 500°C

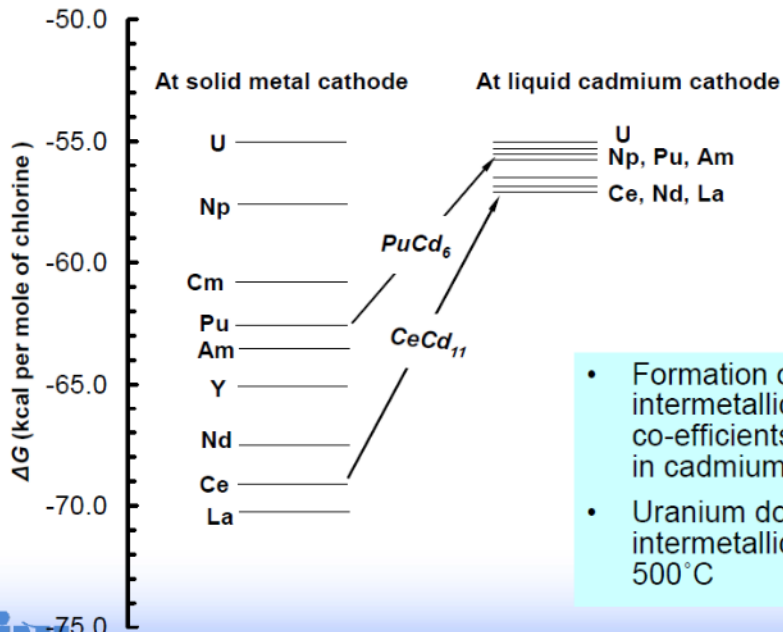


This is a spontaneous chemical reaction



This is an non-spontaneous chemical reaction

Free Energy of Formation of Metal/Chlorides and Intermetallic/chlorides in LiCl-KCl at 500°C



- Formation of metal/cadmium intermetallics reduces activity co-efficients of minor actinides in cadmium
- Uranium does not form intermetallic with cadmium at 500°C

- Initial gram-scale tests of U/Pu at ANL in 1990's
- Kg-scale tests of U-only at ANL in 1990's
- Kg-scale of U-Pu LCC at INL in early 2000's
- Results all are consistent
 - Difficult to prevent U dendrite formation
 - U/TRU ratio in deposit is a function of U/TRU ratio in the molten salt
 - Composition agrees with prediction of equilibrium thermodynamic model

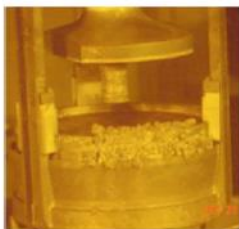
Recap of liquid cadmium cathode development

TABLE III

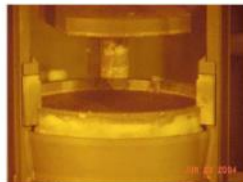
Results of Transuranic Recovery Experiments

Results	TRU #1	TRU #2	TRU #3
Heavy metal recovered (g)	1365	1739	1313
Pu in casting furnace ingot (g)	1024	1080	492
²³⁷ Np in casting furnace ingot (g)	4.5	1.2	0.6
U in salt at end of test (wt%)	0.47	0.74	0.83
Pu in salt at end of test (wt%)	2.67	2.46	2.38
MC of recovered metal	1.65	2.11	1.59
Integrated current (MC)	1.81	2.13	2.09
Transport efficiency (%)	91.5	99.2	76.1

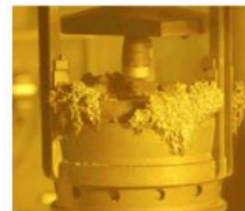
D. Vaden et. al., Nuclear Technology, 162, 2008, 124-128



(a)

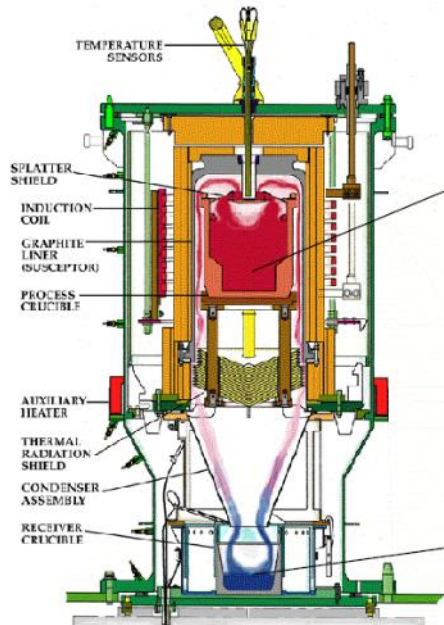


(b)



(c)

Cathode Processor



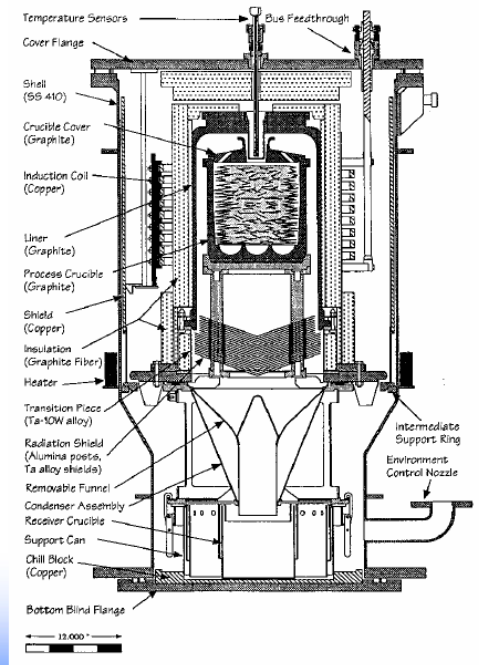
Uranium



Salt

Cathode Processor Distillate Control

- Challenge
 - To Control the Path of Distillate (Both Salt and Cadmium) During Cathode Processing
- Loss of Control
 - Cadmium Migration into the Induction Coil Region and the Vacuum System
 - Intermittent Coil Shorting
 - Failed Vacuum Pumps
 - Salt Migration into the Graphite Components and Induction Coil
 - Salt Holdup/Intercalation
 - Intermittent Coil Shorting



Cathode Processor Crucible

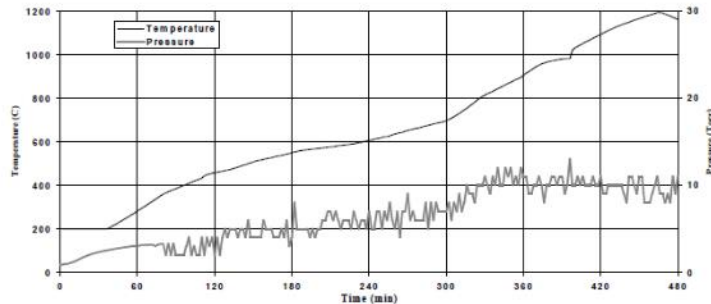
- **Challenge**
 - To Find a Material/Coating Compatible with Reactive Chloride Salts, Molten Uranium, and Harsh Thermal Environment (up to 1300°C)
- **Initial Testing Showed ZrO₂ Coating on Graphite to be the Best Performer**
 - Other Materials/Coatings Tested Include Y₂O₃, CaO, ThO₂, Er₂O₃, MgO, HfO₂, Al₂O₃, BeO, Plasma-Sprayed W-Re and Mo-Re, W, Nb-30Ti-20W, AlN, TiN, ZrB₂, and TiC



Cadmium Distillation

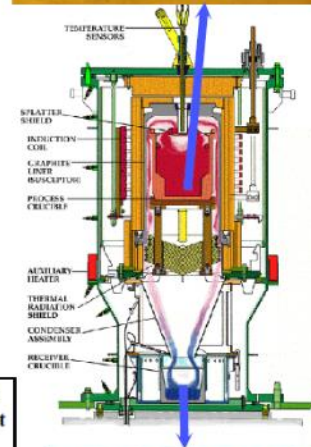
- Operating parameters have been developed for the distillation of cadmium in large quantities (>25 kg) following LCC operations.

FCF CP - CPLCC01 (March 8, 2004), Crucible Temperature and Vessel Pressure



Cathode Processor Batch	Date	Condensate* Charged (kg)	Condensate* Recovered (kg)	Condensate* Recovered (%)	Cadmium in TRU Product (ppm)
CD001	6/17/2003	28.513	28.224	99%	NA
LCC01	3/8/2004	26.505	26.545	100%	<20
LCC02	7/21/2004	26.531	26.662	100%	<25
LCC03	8/9/2005	25.901	25.988	100%	<85
LCC04	2/23/2007	26.710	27.114	100%	<10

* Includes both cadmium and salt



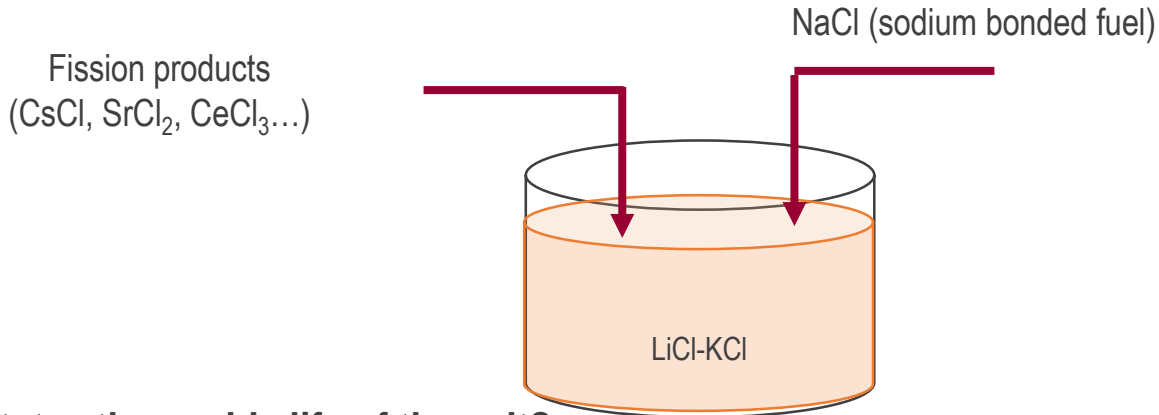
High-Level Wastes

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



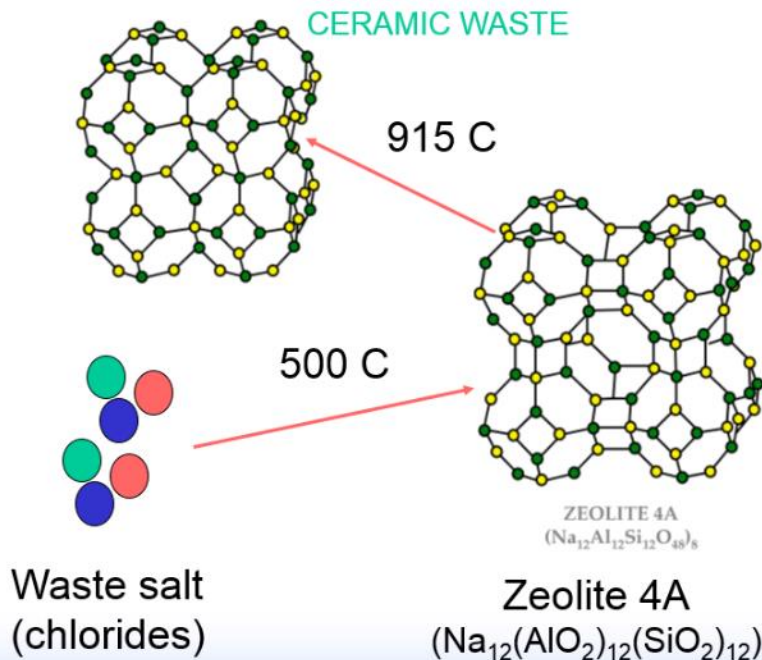
Electrorefiner Salt Contamination

- Contaminants accumulate in the electrorefiner:



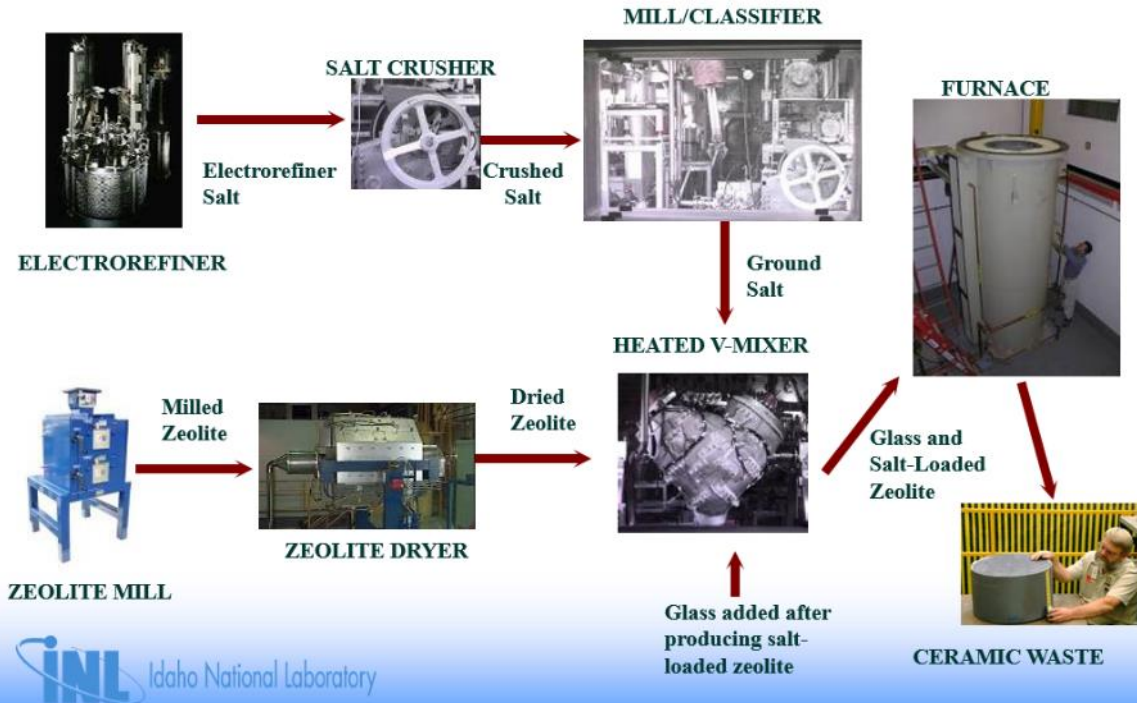
- What dictates the usable life of the salt?
 - NaCl concentration in the case of sodium-bonded fuel (melting point)
 - Fission product chloride concentration in the case of other fuel (decay heat)

Waste Salt Processing



- Zeolite is a crystalline aluminosilicate material containing micropores
- Zeolite 4A absorbs salt at 500 C.
- Salt occluded zeolite-A is then mixed with glass and heated to form sodalite.
- Most salt is bound by sodalite, while some partitions into the glass phase.

Ceramic Waste Process



Pressureless Consolidation

- After blending salt-loaded zeolite with glass, conversion to monolithic sodalite waste form is the final step.
- Pressureless consolidation method replaced Hot Isostatic Press after the 1999 technology demonstration for DOE.
- Furnace for out-of-cell, full-scale testing installed in 2005.
 - Maximum operating temperature of 1025 °C
 - Sealed with atmosphere control
 - Capable of processing waste forms 320-400 kg



Salt Occlusion in Zeolite-A

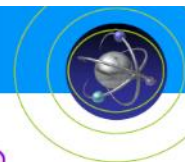
- This is known as the “throw-away process,” since it involves discarding all of the salt, including the useful LiCl and KCl
- Approximately 10 wt% salt is accommodated in the zeolite-A structure
- Since fission product concentration will not exceed 30 wt% in the salt, this means that only 3 wt% fission product loading possible in this waste form.
- This is good motivation for developing an advanced, selective process.

Functionality of the Metal Waste Furnace

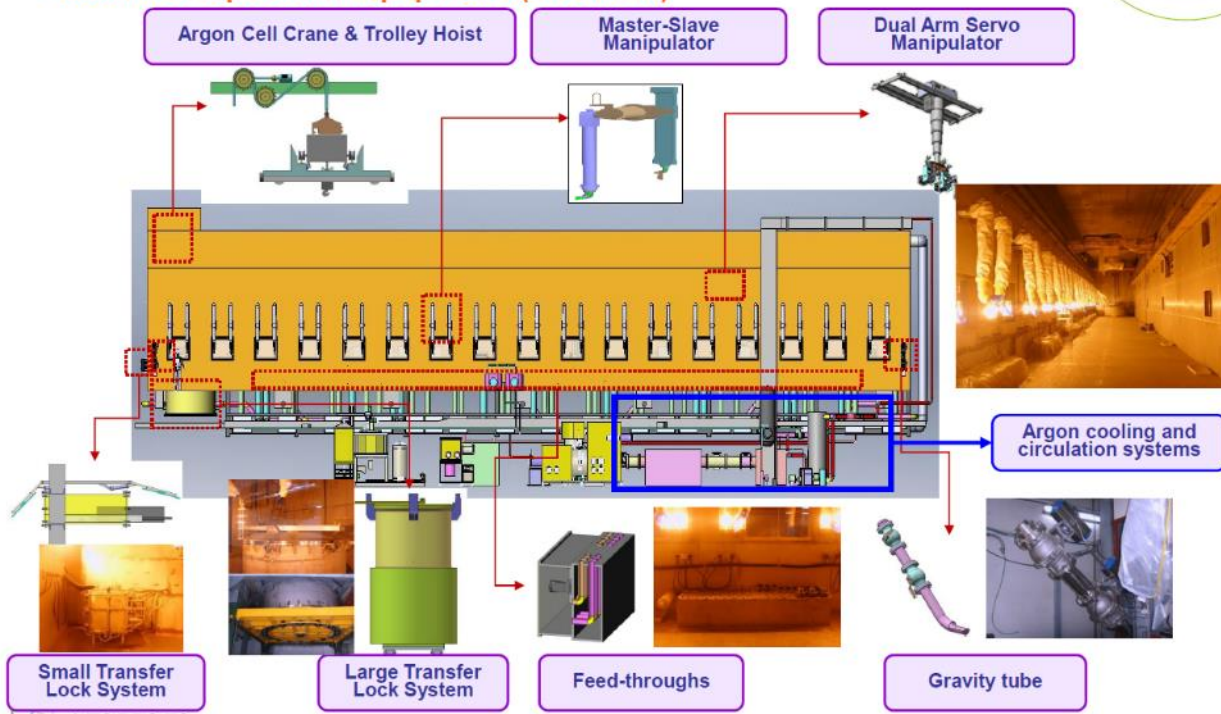
- Metallic sodium in the cladding plenum sections is reacted with ferrous chloride to form stable sodium chloride and metallic iron.
- Salts (primarily LiCl, KCl, and NaCl) are vacuum distilled from the cladding hulls between 800-1350°C.
- Hulls and zirconium wire are melted and alloyed for approximately three hours at 1600°C to form a homogeneous alloy.



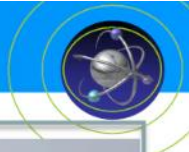
PRIDE Facility Brief Overview



Main Cell Operation Equipments (side view)



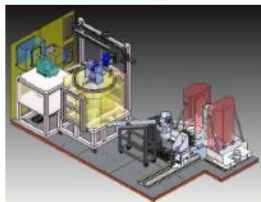
V. PRIDE 시설



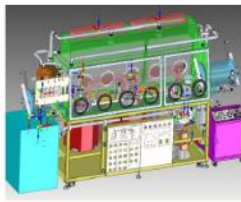
2 nd Floor



1 st Floor



Waste solidif.



U-Chlorinator

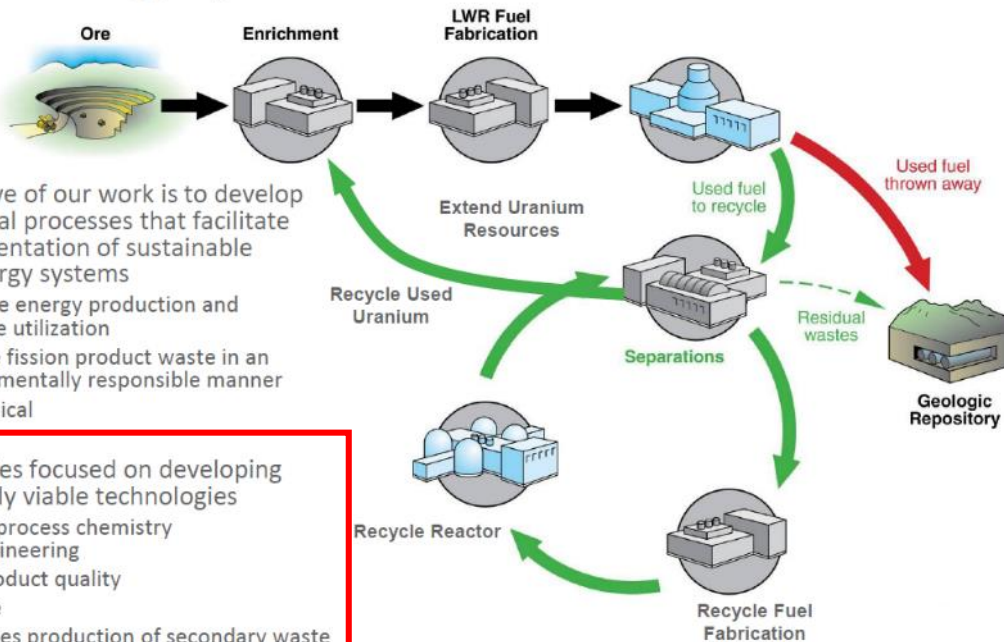


Ingot casting furnace



pretreatment

A Comprehensive Vision for an Expanded, Sustainable Nuclear Energy System



- The objective of our work is to develop pyrochemical processes that facilitate the implementation of sustainable nuclear energy systems
 - Optimize energy production and resource utilization
 - Manage fission product waste in an environmentally responsible manner
 - Economical
- R&D activities focused on developing commercially viable technologies
 - Robust process chemistry and engineering
 - High product quality
 - Scalable
 - Minimizes production of secondary waste
 - Meet U.S. non-proliferation objectives

Advanced electrorefiner prototype

- Electrorefiner development efforts center on optimizing process efficiency and throughput
 - Interleaved anode and cathodes for simplified operations
 - Intermittent scraping of cathodes allows increased product removal efficiency
 - Uranium product recovered by automated system to minimize downtime and maximize throughput



Prototype
Test
Module



U product collected during advanced refiner tests



QUESTIONS?