“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 LiCl+KCl or LiF+CaF2) or fused metals such as cadmium, bismuth or aluminium.”

From Wikipedia
“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
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 UF₆
- UF₆ 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

EBR-II Reactor

Spent Fuel Assembly

New Fuel Assembly

Construct Assembly and Test

Clad Fuel, Leak Test & Bond Test

Re-cast pins, separate VYCOR and inspect

VYCOR scrap

Scrap Fuel Alloy

Melt Refining Furnace (1400 °C)

Rejected Elements

U & Pu from oxide

Crucible & Fission Products to Waste

Skull Oxidation

235U to enrich

Disassemble & Remove Elements

Remove Cladding & Chop Fuel

Clean Assembly (Remove Sodium)

Fuel Cycle Facility

Remove Cladding & Chop Fuel

Construct Assembly and Test

Re-cast pins, separate VYCOR and inspect

VYCOR scrap

Scrap Fuel Alloy

Melt Refining Furnace (1400 °C)

Rejected Elements

U & Pu from oxide

Crucible & Fission Products to Waste
Molten Salt Electrolysis

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

(Kcal per equivalent)

-10
-20
-30
-40
-50
-60
-70
-80
-90

Metal Waste
Uranium Product
Ceramic Waste

Fe
Cd
Zr

Hg
Mo
W
Ni
H
Zn, Cr
V
Mn, Be

U
Sc
Mg
Cr, Am
Y
Nd
Ce
Pr, La

Pu

Ca, Na
Sr
Li
K
Ba, Cs, Rb
Electrochemical Process Flowsheet

- LWR Fuel
- Oxide Reduction
- Spent Fuel
- Oxide
- Metal
- Metal Waste Furnace
- Cladding
- Actinide Removal
- Electrorefiner
- Cathode Processor
- Casting Furnace
- Fuel Fabrication
- Ceramic Waste Form
- Metal Waste Form
- Ion Exchange
- Salt Recycle
Electrorefining

[Diagram of electrorefining equipment with labels for electrode assembly housing, valve actuators, heat shields, salt bath, cathode, side scraper, bottom scraper, vessel heaters, stirrer assembly, anode lower assembly, fuel dissolution baskets, cadmium bath, and support structure.]
Recovery of plutonium on a solid cathode is not feasible because the following reaction is favorable:

\[ \text{Pu} + \text{UCl}_3 \rightarrow \text{PuCl}_3 + \text{U} \quad \text{(free energy change is } -21 \text{ kcal/mol)} \]

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 (~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.
Salt must be separated from recovered actinides.
Salt is distilled and recycled back to electrorefiners.
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
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.
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).
Processing Lines in FCF

Driver and Blanket Fuel are Treated in Parallel
Electrochemical processing has been performed on the engineering-scale with irradiated fuel since 1996.

Approximately 4.5 MTHM of fuel, including highly enriched uranium fuels from EBR-II and the Fast Flux Test Facility, 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.
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

- 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.

- Engineering-scale electrorefining operations continue to demonstrate high dissolution of actinides (99.7%).
Electrochemical Processing Accomplishments

- 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 amendable to remote fabrication.
- Metallic fuels are capable of high burnups.
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

(Kcal per equivalent)

Metal Waste

Uranium Product

Ceramic Waste

Fe
Cd
Zr

Hg
Mo
W
Ni
H

Zn, Cr
V

Mn, Be

Pu

Np
Sc
Mg
Cr, Am
Y
Nd
Ce
Pr, La
Ca, Na
Sr
Li
K

Ba, Cs, Rb
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.
Ceramic Waste Process

**MILL/CLASSIFIER**

**SALT CRUSHER**
- Crushed Salt

**ZEOLITE DRYER**
- Dried Zeolite

**ELECTROREFINER**
- Electrorefiner Salt

**MILLED ZEOLITE**
- Milled Zeolite

**HEATED V-MIXER**
- Ground Salt
  - Glass and Salt-Loaded Zeolite

**ZEOLITE MILL**
- Glass added after producing salt-loaded zeolite

**CERAMIC WASTE**
- Salt Crusher
- Furnace
Metal Waste Form Process

CLADDING HULLS → ELECTROREFINER

SALT → CERAMIC WASTE

INGOTS

ZIRCONIUM

INDUCTION FURNACE
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 conferences were in Korea and Russia.
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.