

CONF-790602-45

**MASTER**

PROCESS TECHNOLOGY ASSOCIATED WITH  
PYROCHEMICAL REPROCESSING

Charles E. Baldwin  
Rockwell International  
Rocky Flats Plant  
Boulder, Colorado

and

Kevin M. Myles  
Argonne National Laboratory  
Chemical Engineering Division  
Argonne, Illinois

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

**NOTICE**  
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MIN ONLY

MIN ONLY

NOTICE

PORTIONS OF THIS DOCUMENT ARE UNCLASSIFIED. It has been reproduced from the best available copy to permit the broadest possible availability.

**DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED**

*Handwritten signature*

## DISCLAIMER

**This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**

## PROCESS TECHNOLOGY ASSOCIATED WITH PYROCHEMICAL REPROCESSING

by

Charles E. Baldwin, Rocky Flats Plant, Rockwell International  
and  
Kevin M. Myles, Argonne National Laboratory

The pyrochemical coprocessing of spent nuclear fuels presents unique problems in design and remote engineering. The generally high operating temperatures and corrosive environments require materials of construction and unit operations specially designed for adverse conditions. The chemical flow sheet, shown in Fig. 1, illustrates the basic process steps found in pyrochemical processes currently under consideration. The process technology of the following three representative processes will be examined in detail: melt refining, zinc distillation, and salt transport.

The first full-scale application of pyrochemical technology in the nuclear field was the EBR-II melt refining of uranium alloys by the high temperature oxidation of fission products.<sup>1,2</sup> Over 35 000 fuel pins of spent metal fuel were reprocessed, refabricated, and recycled,<sup>3</sup> producing more than five reactor-core loadings.<sup>4</sup> The zinc distillation<sup>5</sup> and the salt transport<sup>6</sup> for coprocessing uranium and plutonium oxide and metal fuels are among the next generation of pyrochemical processes being considered. The process operations have been defined and the unit operations are currently being evaluated. As an example, the flow diagram for coprocessing oxide fuel by the salt transport process is shown in Fig. 2. The turntable, semi-continuous, batch concept<sup>7</sup> is being designed to be operated and maintained remotely and to process 1/2 metric ton of spent fuel daily.

The unit operations found in pyrochemical processes are unique in that they include remote processing, and containment of fluids and solids at up to 1400°C. Though all unit operations are difficult under remote conditions, the more significant unit operations that challenge the technical feasibility of pyrochemical processing are containment, phase separation, liquid transfer, distillation, reagent recycle, and by-product disposal.

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W 31 109 ENG 33. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

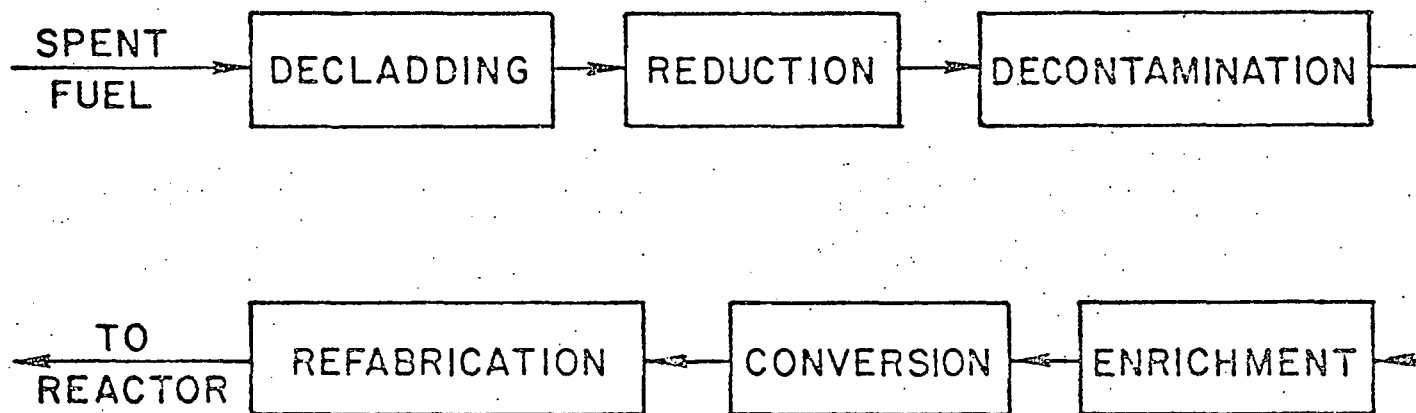


Fig. 1. Basic Pyrochemical Process Steps.

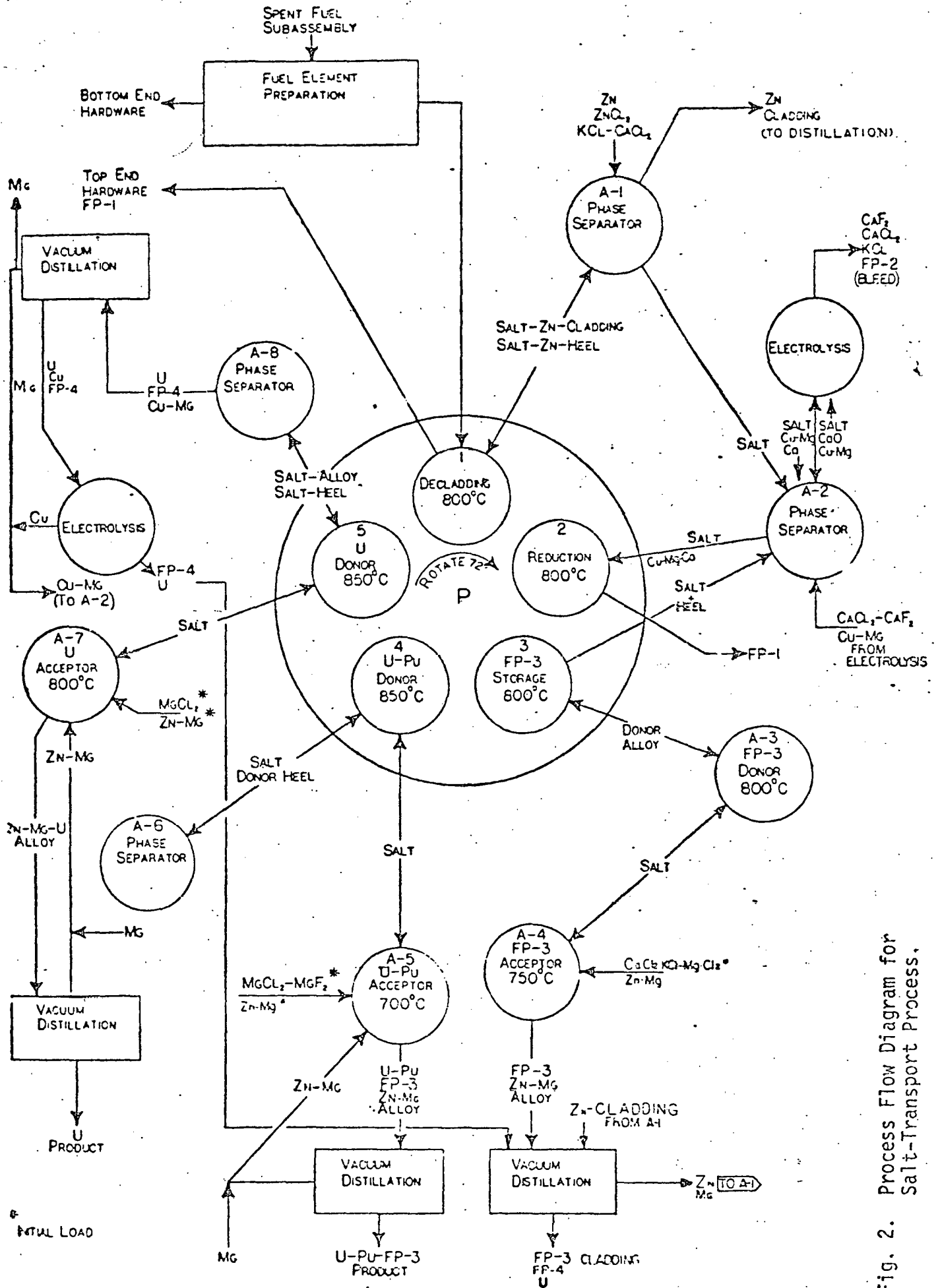


Fig. 2. Process Flow Diagram for Salt-Transport Process.

Recent effort in the fabrication of tungsten and tungsten alloys as well as the impregnation and coating of ceramics have shown promise in solving the containment problems. It is anticipated that containers up to 10 ft<sup>3</sup> will be required and studies in tungsten fabrication including spinning, sintering, plasma spraying, and joining are currently underway. Several tungsten crucibles that were recently fabricated by the various techniques are shown in Fig. 3.

The separation of immiscible liquids, solids from liquids, solids from solids, and vapor from solids or liquids are inherent to pyrochemical processing. Remote, high temperature processing, however, mandates minimizing the handling of solids: therefore, the majority of phase separations are with liquids with specially designed equipment. For example, pressure transfer of alloys and salts at 800°C are accomplished in heated molybdenum-tungsten tubes. Vacuum distillation is employed for the separation and recycle of volatile components, such as cadmium and zinc, from liquid solutions.<sup>8,9,10</sup>

Reagent recycle to minimize waste disposal is a continuing challenge and responsibility. An investigation is underway to recover calcium from calcium oxide, a major by-product from the reduction operation. One concept involves the electrolysis of CaO in fused salt where calcium forms at the cathode and CO/CO<sub>2</sub> at the anode.<sup>11</sup> The waste from pyrochemical processes are readily converted to solids that are compatible with the current national policy concerning radioactive waste management.

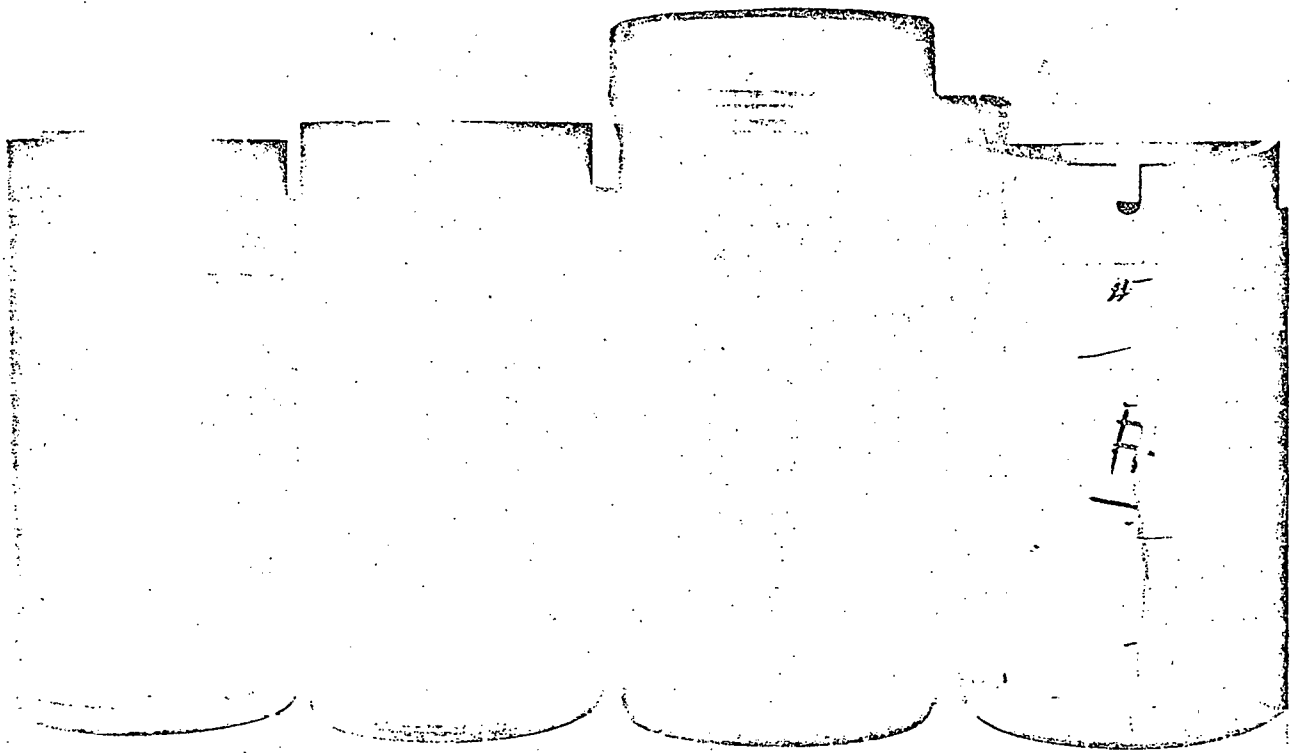


Fig. 3. Tungsten Crucibles: Joined, Plasma Sprayed, Draw Spun, and Sintered (from left to right). (approximately 5 in. diameter by 10-1/2 in. high)



REFERENCES

1. L. Burris, Jr., *et al.*, "The EBR-II Skull Reclamation Process--Part I. General Process Description and Performance," Argonne National Laboratory, ANL-6818 (1964).
2. D. C. Hampson, *et al.*, "Melt Refining of EBR-II Fuel," Symposium on Reprocessing of Nuclear Fuels, Nuclear Metallurgy, Volume 15, USAEC-TID-4500 (1969).
3. H. F. Jelinek, *et al.*, "Fabrication of EBR-II, CORE-I, Fuel Pins," ANL-6274, Argonne National Laboratory (1962).
4. M. J. Feldman, *et al.*, "Remote Refabrication of EBR-II Fuels," Symposium on Reprocessing of Nuclear Fuels, Nuclear Metallurgy, Volume 15, USAEC-TID-4500 (1967).
5. K. M. Myles, personal communication.
6. J. B. Knighton, *Radiochimica Acta*, to be published.
7. D. S. Webster, *et al.*, Chemical Engineering Division Fuel Cycle Technology Quarterly Report--April-June, 1970, Argonne National Laboratory, ANL-7735 (1970).
8. P. Nelson, *et al.*, "Distillation of Magnesium," Argonne National Laboratory, ANL-5996 (1959).
9. I. O. Winsch, *et al.*, "Concentration of Simulated Plutonium Product Solution by Evaporation," Argonne National Laboratory, ANL-6725 (1963).
10. W. Miller, *et al.*, "Recovery of Uranium Product by Retorting," Argonne National Laboratory, ANL-7125 (1966).
11. W. D. Threadgill, *J. Electrochem. Soc.* 111, 1408(1964).

PROCESS TECHNOLOGY ASSOCIATED WITH  
PYROCHEMICAL REPROCESSING

By

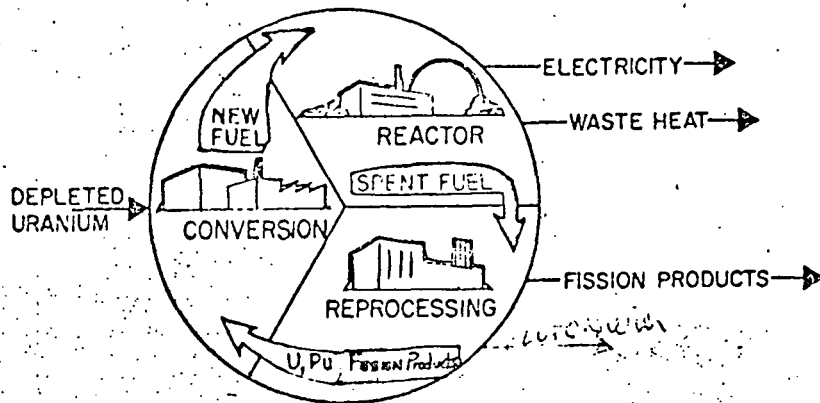
Charles E. Beldrin  
Rocky Flats Plant  
Rockwell International

and

Kevin M. Hyles  
Argonne National Laboratory

SCOPE OF  
PRESENTATION

- I. FAST BREEDER FUEL CYCLE
- II. BASIC PYROCHEMICAL PROCESS
- III. CANDIDATE PYROCHEMICAL PROCESSES
- IV. UNIT OPERATIONS OF CANDIDATE PROCESSES
- V. DESIGN CONCEPT FOR CANDIDATE PROCESS
- VI. EBR-II PROCESS
- VII EBR-II FUEL REPROCESSING FILM



The practical, economic operation of a Fast Breeder Reactor requires a <sup>complete</sup> closed fuel cycle including spent fuel reprocessing to recover the required enrichment, conversion to new fuel, and return of the fuel to the reactor.

In the following slide, a closed LMFBF fuel cycle is illustrated. Depleted uranium is introduced into the system where it is combined with plutonium generated in the system, converted to fuel, placed in the reactor, producing electricity, waste heat, fission products and plutonium in excess of that which is consumed. The uranium and plutonium are coprocessed, removing certain fission products while enriching the fuel, with respect to plutonium, and converting it back to usable fuel, thus completing the cycle. The excess plutonium can be used to provide fuel for additional reactors. This plutonium must be safeguarded to prevent diversion to weapons. ~~Exportable fast breeder fuel reprocessing technology should not provide an attractive path, in terms of time and resource requirements, for production of weapons - usable fissile material~~

~~or other alternative path.~~ In the design of such a fuel cycle, effort must be made to minimize the potential for diverting fissile materials (diversion) and to minimize the potential for producing nuclear weapons (proliferation). Maintaining certain fission products and uranium with plutonium provides the diversion resistance and proliferation resistance.

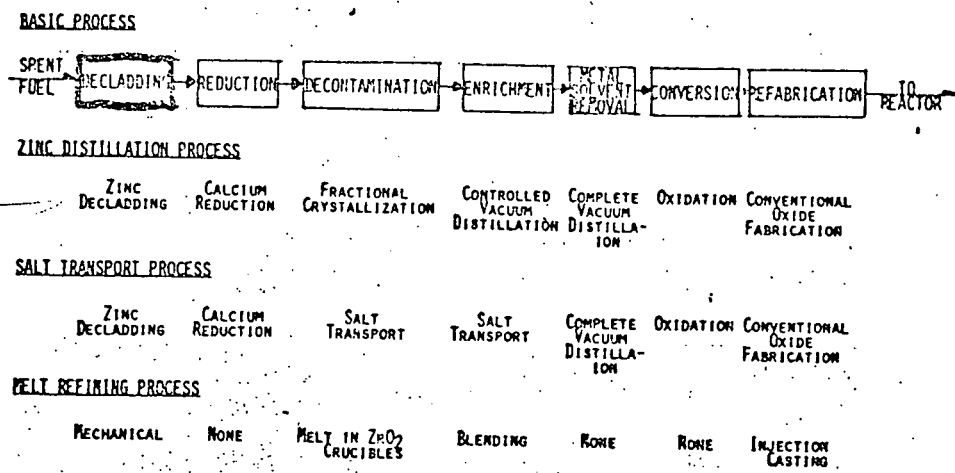
The pyrochemical (nonaqueous) co-processing of spent nuclear fuels presents unique problems in design and remote engineering. The generally high operating temperatures and corrosive environments require materials of construction and unit operations specially designed for unique conditions.



#### BASIC PYROCHEMICAL PROCESS STEPS

A chemical flow sheet is presented illustrating the basic process steps found in pyrochemical processes currently under consideration.

> During a brief discussion of the basic flow sheet, the process technology of several representative pyrochemical processes (Melt Refining, Zinc Distillation, and Salt Transport) will be examined. An analysis of the key unit operations associated with the Zinc Distillation and Salt Transport Processes finally will be made culminating in a basic conceptual design incorporating these unit operations into an overall processing scheme.



The following slide compares the basic pyrochemical flow sheet with three representative pyrochemical processes. This is not intended to be comprehensive, since the chemistry has already been discussed, but merely presents a general understanding of pyrochemistry.

Decladding is the removal of the fuel assembly hardware and the cladding associated with the active section of the fuel assembly. This may be done either mechanically or chemically, or both. The majority of the gaseous fission products are vented during decladding.

DECLADDING

- MELT DECLADDING
- OXIDATIVE DECLADDING
- MOLTEN METAL DECLADDING
- MOLTEN SALT DECLADDING
- MECHANICAL DECLADDING

Some typical non-aqueous decladding methods include:

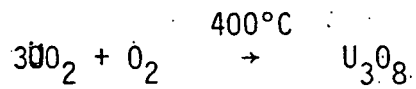
- a. Melt Decladding is a method in which a fuel assembly is heated until the cladding melts and drains away from the fuel. Melt decladding was investigated at Argonne National Laboratory in the temperature range of 1400-1650°C. using pellets clad in type 304 stainless steel tubes.



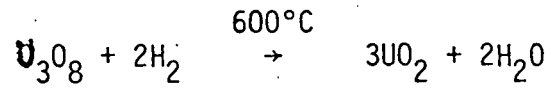


# CYCLIC OXIDATION

## Oxidation Reaction



## Reduction Reaction



This slide shows the chemical reaction by which the fuel is pulverized by cyclic oxidation.

PAGES 9 to 10  
WERE INTENTIONALLY  
LEFT BLANK

-11-

DECLADDING

- o MELT DECLADDING
- o OXIDATIVE DECLADDING
- o MOLTEN METAL DECLADDING
- o MOLTEN SALT DECLADDING
- o MECHANICAL DECLADDING

c. Molten Metal Decladding involves contacting the oxide fuel assembly with a molten metal or alloy in which the cladding and fuel assembly hardware is dissolved. Two such candidates are copper-antimony at 900-1000°C. and zinc at 800°C. A physical separation is required to separate the fuel from the molten alloy-cladding mixture.

For both the Zinc Distillation and Salt Transport Processes molten zinc is used to remove the cladding from the spent fuel. After cropping off the bottom hardware the fuel is immersed in molten zinc at approximately 800°C. Only the active section is dissolved, allowing the top hardware to be removed.

DECLADDING

- o MELT DECLADDING
- o OXIDATIVE DECLADDING
- o MOLTEN METAL DECLADDING
- o MOLTEN SALT DECLADDING
- o MECHANICAL DECLADDING

d. In Molten Salt Decladding of zirconium and zircaloy cladded fuels, the cladding is removed from the fuel by the reaction of the cladding with molten lead chloride or zinc chloride at 600-800°C. This decladding method may apply to LWR fuels.

THIS PAGE  
WAS INTENTIONALLY  
LEFT BLANK

#### DECLADDING

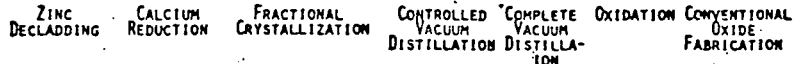
- o MELT DECLADDING
- o OXIDATIVE DECLADDING
- o MOLTEN METAL DECLADDING
- o MOLTEN SALT DECLADDING
- o MECHANICAL DECLADDING

e. In Mechanical Decladding the cladding is mechanically removed from the fuel. In the EBR-II Melt Refining Process the decladding was accomplished by complete disassembly of the fuel assembly and mechanical removal of the cladding from each pin.

**BASIC PROCESS**



**ZINC DISTILLATION PROCESS**



**SALT TRANSPORT PROCESS**



**MELT REFINING PROCESS**



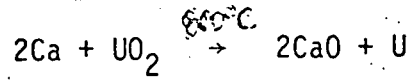
Reduction converts oxide and carbide fuel into metals which are more amenable to subsequent pyrochemical operations for fission product removal and enrichment.

In the Zinc Distillation and Salt Transport Processes, the oxide fuel is converted to a metal form by the calcium reduction of the oxide fuel. This is done in the presence of zinc or a copper-magnesium alloy and a salt containing calcium chloride. Intense agitation must be employed to insure a continuous movement of the liquid alloy and salt past the oxide.

Mixing brings calcium to the reaction site, removes the reaction products from the reaction site, and equilibrates the salt and metal phases. The alkali-alkaline earth, chalcogen, and halogen fission products are taken up by the salt. The actinides and remaining fission products remain with the alloy.

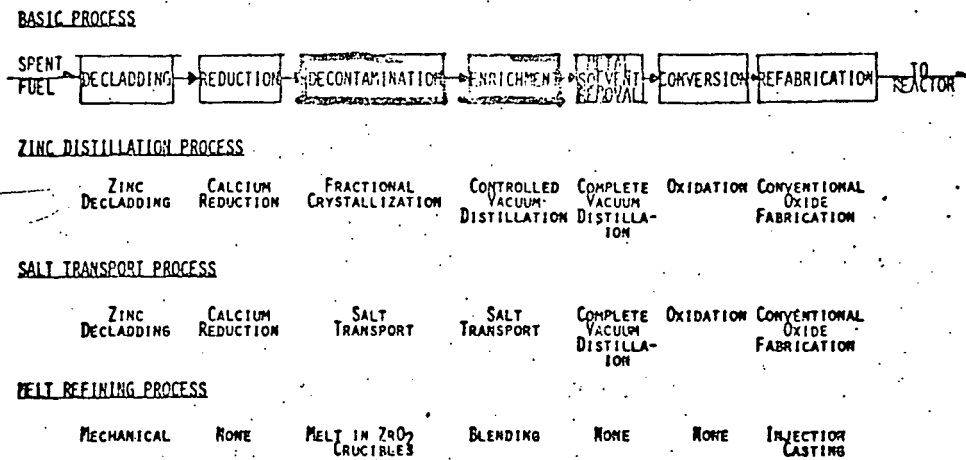
Since the EBR-II fuel is in a metallic state to begin with, no reduction is required.

Typical Reduction Reaction



This slide illustrates the basic calcium reduction for both Zinc Distillation and Salt Transport.





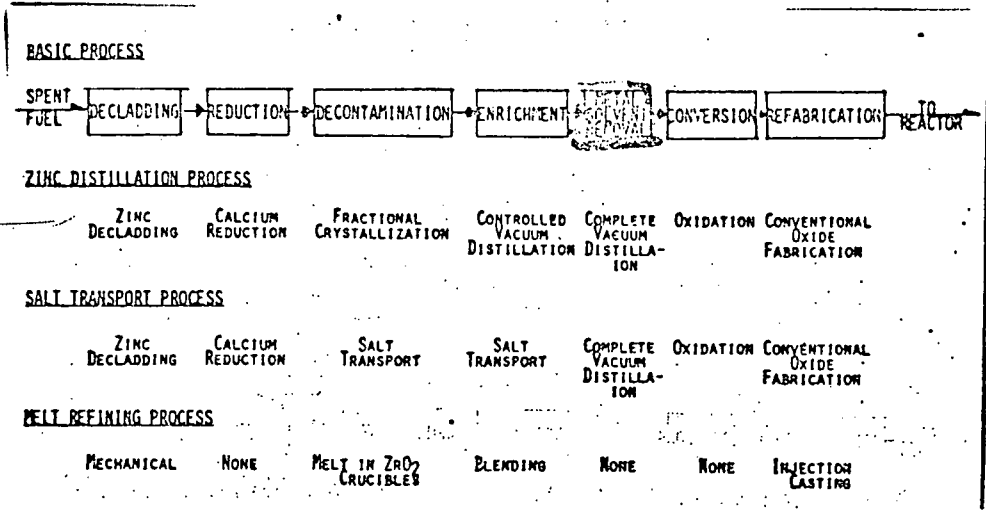
Separation methods for removal of fission products and for enrichment of fissile materials may be accomplished in a number of different ways and can be classified into two groups: physical and chemical.

- a. Physical separations include such processes as distillation and evaporation, fractional crystallization, and liquid-liquid extraction. Removal of highly volatile fission products can be made by distillation. Fractional crystallization can be employed for fission product separations. Fission product removal and plutonium enrichment can also be accomplished by partitioning between immiscible liquid metal phases.
- b. Chemical Separations can be achieved by selective chemical oxidation and reduction reactions.

In the Zinc Distillation, Salt Transport, and Melt Refining Processes, decontamination and enrichment are performed in two separate operations. These operations could be performed in any order; however, in the Zinc Distillation Process the order is reversed from the basic flow sheet, with enrichment being performed first by controlled vacuum distillation followed by separation of certain fission products by fractional crystallization. Salt Transport uses liquid-liquid extraction involving molten salts and liquid metals as the immiscible process solvents for partial fission product removal and enrichment.

In both the Zinc Distillation and Salt Transport Processes, the enrichment is accomplished by removing depleted uranium from plutonium during processing.

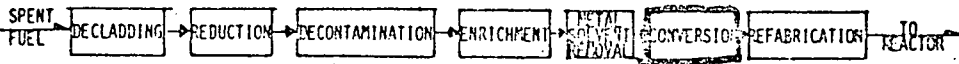
Melt Refining removed certain fission products by oxidation with a zirconia crucible used to contain the melt. The fission product oxides were retained in the crucible as a skull. Enrichment after Melt Refining was accomplished by the addition of enriched uranium to the recycled uranium.



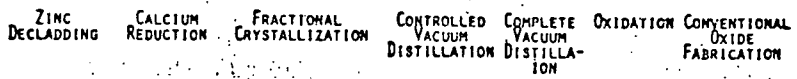
In some pyrochemical processes where solvent metals are employed, proper selection of the solvents is necessary to insure complete solvent separation later on in the process. Solvent removal is generally accomplished by relying on the high vapor pressures of solvent components, affecting separation by distillation techniques. Both the Zinc Distillation and Salt Transport processes use distillation for complete removal of metal solvents.

Since no solvents were present in the EBR-II Melt Refining Process, solvent removal was unnecessary.

BASIC PROCESS



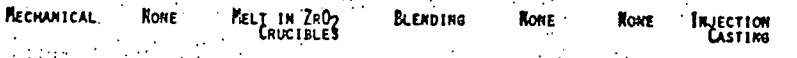
ZINC DISTILLATION PROCESS



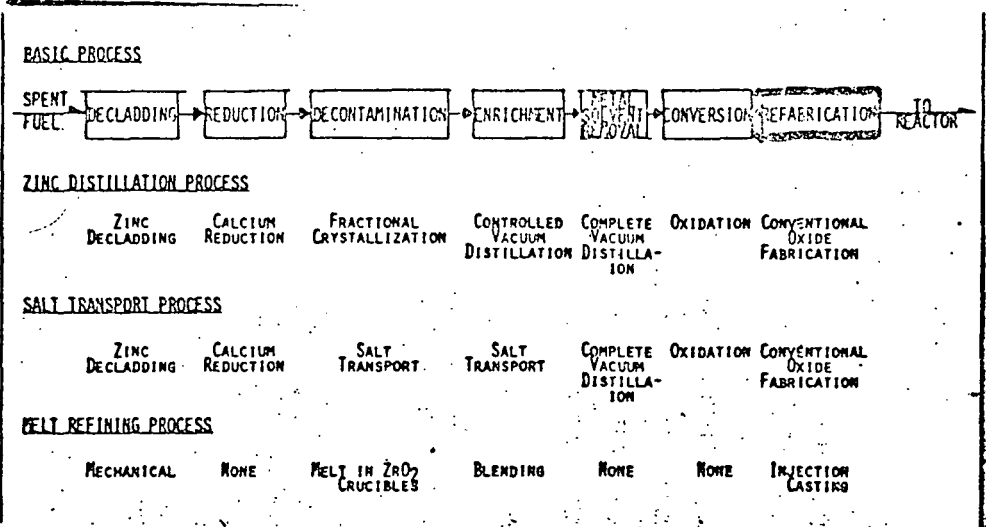
SALT TRANSPORT PROCESS



MELT REFINING PROCESS



The product from the process must be converted to a form compatible with refabrication operations. For metal fuels, such as were handled by the EBR-II Process, a metal product can be cast into the required shape used in refabrication. For oxide fuels, such as those handled by the Zinc Distillation and Salt Transport Process, the metal product must be converted to an oxide product, which meets the proper isotopic, chemical and physical specifications suitable for refabrication. Volatilization of fission products, such as Ruthenium 106, during oxidation, must be considered to maintain proliferation resistance.



Fabrication of new fuel from oxide powders requires additional treatment such as compaction, granulation, tableting, and sintering to produce a product acceptable for use in new fuel. The fabrication of metal fuel can be accomplished by injection casting as was performed in the EBR-II Fuel Cycle Facility.

-21-

MAJOR UNIT OPERATIONS

- MIXING
- CONTAINMENT
- PHASE SEPARATION/ LIQUID TRANSFER
- DISTILLATION
- REAGENT RECYCLE/ BYPRODUCT DISPOSAL

To accomplish the process operations of both the Zinc Distillation and Salt Transport Processes the following major unit operations required are: mixing, containment, phase separation, liquid transfer, distillation, reagent recycle, and by-product disposal. Each will be addressed in more detail.

MAJOR UNIT OPERATIONS

- ① MIXING
- CONTAINMENT
- PHASE SEPARATION/ LIQUID TRANSFER
- DISTILLATION
- REAGENT RECYCLE/ BYPRODUCT DISPOSAL

For oxide reduction and for equilibration of salt and metal phases, mixing is provided using a "pot and paddle." These process operations are performed in a cylindrical vessel. This equilibration is accomplished by intermixing the salt and metal phases. An impellor may be rotated in the molten materials.

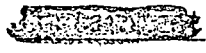
← P.F. SID

# POT & PADDLE SCHEMATIC

==

MAJOR UNIT OPERATIONS

- o MIXING
- o CONTAINMENT
- o PHASE SEPARATION/ LIQUID TRANSFER
- o DISTILLATION
- o REAGENT RECYCLE/ BYPRODUCT DISPOSAL



Due to the corrosive nature of the process reagents at operating temperatures up to 1000<sup>o</sup>C, special materials of construction are required for containment.

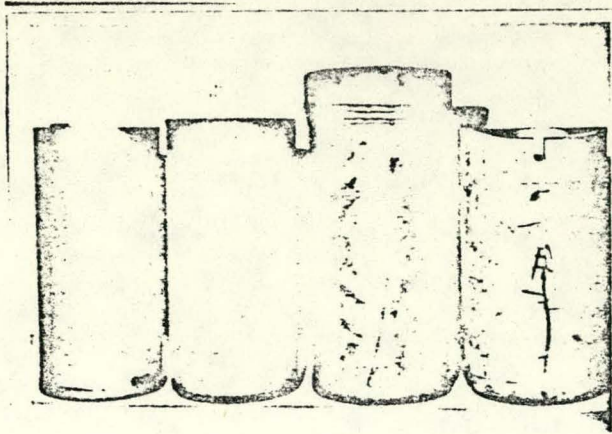


<u>PRIMARY PROCESS OPERATIONS</u>	<u>OPERATION TEMPERATURE C</u>	<u>MTL. OF CONSTRUCTION</u>
<u>ZINC DISTILLATION</u>		
o CRYSTALLIZATION	1000	TANTALUM CARBIDE-COATED GRAPHITE
o DISTILLATION	1000	TANTALUM CARBIDE-COATED GRAPHITE
o TRANSFER LINES	800	POLYBIDENUM-30% TUNGSTEN
o SHAFTS/PADDLES	800	POLYBIDENUM-30% TUNGSTEN
o CRUCIBLES	800	TUNGSTEN
<u>SALT TRANSPORT</u>		
o DISTILLATION	800	TUNGSTEN
o TRANSFER LINES	800	POLYBIDENUM-30% TUNGSTEN
o SHAFTS/PADDLES	800	POLYBIDENUM-30% TUNGSTEN
o CRUCIBLES	800	TUNGSTEN

Estimated operating temperatures and proposed materials of construction are presented for both Zinc Distillation and Salt Transport.

Studies are currently underway at Argonne National Laboratory and Rocky Flats to determine the corrosion resistance and fabricability of materials of construction. At this point in time tungsten is the most attractive material of construction for containment of molten salts and metals used in these processes.

Tungsten is a difficult material to fabricate. At Room Temperature tungsten is brittle, but may be formed at high temperatures with difficulty.



This slide shows four tungsten vessels fabricated by four different methods. These methods are, from left to right: joining, plasma spraying, spinning, and pressing and sintering.

(1) Joining is a fabrication method whereby a sheet of tungsten is roll-formed and joined by welding, diffusion bonding, or brazing. Welding causes recrystallization at the weld, resulting in failure at the grain boundaries. Diffusion bonding requires some interface metal such as niobium or molybdenum-niobium and high pressures and temperatures. Because of the high pressures and temperatures, severe alignment problems arise during bonding. The interface metal provides a path for corrosion. Brazing is the most attractive of the joining techniques. The brazing development focuses on the selection of a brazing alloy that will bond below the tungsten recrystallization temperature, yet remain strong at the service temperature. Also some corrosion resistance to molten salts and metals is desired. The joints may be coated with tungsten either by plasma spraying or chemical vapor deposition to prevent direct contact of the molten alloy with the braze material.

Two joining attempts have been made at Rocky Flats culminating in a 5 by 10 1/2 inch tungsten crucible, 0.040 inches wall thickness

(2) Plasma spraying is a fabrication method whereby a tungsten powder is sprayed at 3500 C onto a mandrel to produce the desired shape. The mandrel is then removed from the tungsten by dissolving in acid and the tungsten piece is then sintered to improve density. This plasma sprayed free standing crucible 5 inch diameter by 10 1/2 inch high by 0.100 inch thick was made by *LUDE, DIVISION OF UNIV. CARBIDE* and will be sintered.

(3) Spinning is a fabrication method in which a cup, formed from a flat sintered tungsten blank, is extrusion spun at 1150 C to the desired length (Slide -3). Three such crucibles have been successfully spun at Rocky Flats. This ~~last~~ technique does not appear to be an acceptable method since tungsten blanks are not commercially available in a size large enough to produce a full scale crucible. It is not likely that blanks large enough will be available in the near future.

(4) Pressing and sintering is a fabricating method whereby powdered tungsten is isostatically formed and sintered between 1800 and 2200 C producing an average tungsten density of 92% theoretical. Two sintered crucibles 5 inch by 10 1/2 inch high by 0.300 inches were made by GTE Sylvania at 96% theoretical density. A large wall thickness is required to support the crucible during sintering. Electrochemical grinding will be used to reduce the wall thickness.

Molybdenum-30 wt.% tungsten is an acceptable material for fabricating transfer tubes, agitator shafts, and paddles.

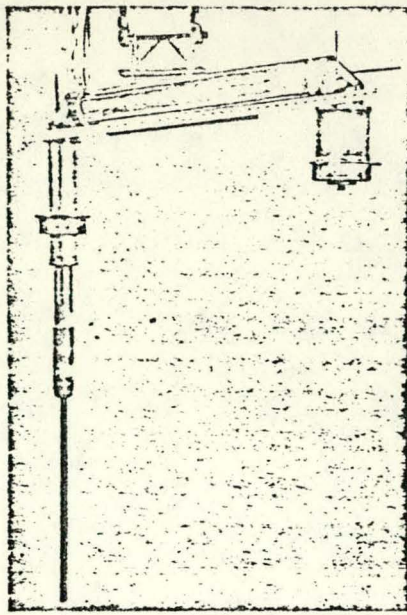
THIS PAGE  
WAS INTENTIONALLY  
LEFT BLANK

MAJOR UNIT OPERATIONS

- MIXING
- CONTAINMENT
- PHASE SEPARATION/ LIQUID TRANSFER
- DISTILLATION
- REAGENT RECYCLE/ BYPRODUCT DISPOSAL

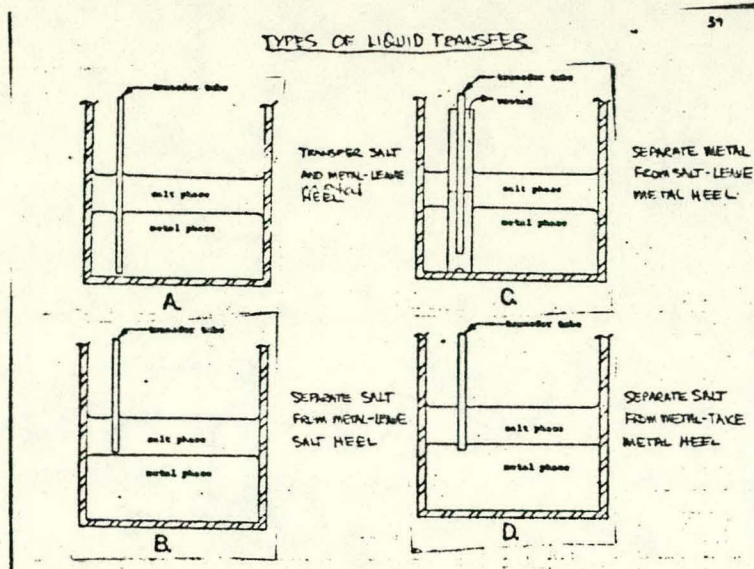
Sufficient time must be allowed after equilibration of salts and alloys for phase disengagement of the immiscible phases. Phase disengagement must be done prior to phase separations to prevent carryover of undesired phases during liquid transfer. Liquid transfer will be accomplished by pressure transfer through heated transfer lines from one vessel to another. The transfer lines through which the liquid will be transferred is wrapped with resistance heaters and insulation to maintain the temperature of the liquid above its melting point. Transfer lines used for transferring molten salts and liquid metals will be fabricated from molybdenum-30 wt.% tungsten.





Slide shows a resistance-heated transfer line which was designed, built, and used at Argonne National Laboratory.

The inlets of the transfer tubes will be positioned so as to remove only the desired liquid phases.



Slide illustrates the four types of separations to be accomplished in the Salt Transport and Zinc Distillation Processes.

Device →  
 Phase  
 transfer  
 to interface



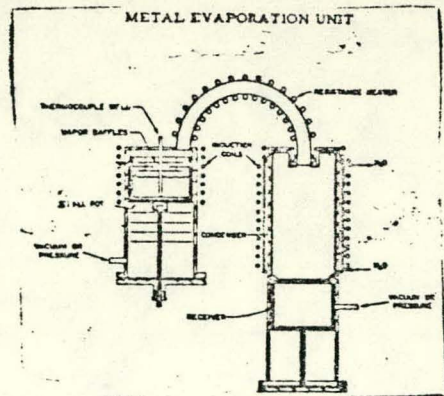
-32-

MAJOR UNIT OPERATIONS

- o MIXING
- o CONTAINMENT
- o PHASE SEPARATION/ LIQUID TRANSFER
- o DISTILLATION
- o REAGENT RECYCLE/ BYPRODUCT DISPOSAL

Distillation is a key operation in both the Salt Transport and Zinc Distillation Processes. Salt Transport uses distillation for separation of metal solvents from the product and recycle of process solvents. To minimize new process reagents and reduce waste, zinc and magnesium may be separated from the cladding and spent acceptor alloys. In the Zinc Distillation Process not only is distillation important to solvent recycle but it is vital in obtaining the required enrichment and fission product removal.





This slide shows a distillation furnace developed by Argonne National Laboratory for removal of zinc and magnesium from uranium. This equipment was developed for the Skull Reclamation Process. The Skull Reclamation Process was developed but not installed at EBR-II.

MAJOR UNIT OPERATIONS

- MIXING
- CONTAINMENT
- PHASE SEPARATION/ LIQUID TRANSFER
- DISTILLATION
- REAGENT RECYCLE/ BYPRODUCT DISPOSAL

Byproduct Disposal

The Zinc Distillation and Salt Transport Processes have several waste streams in common.

PROCESS WASTE STREAM

TREATMENT

*Zinc Distillation and Salt Treatment Processes*

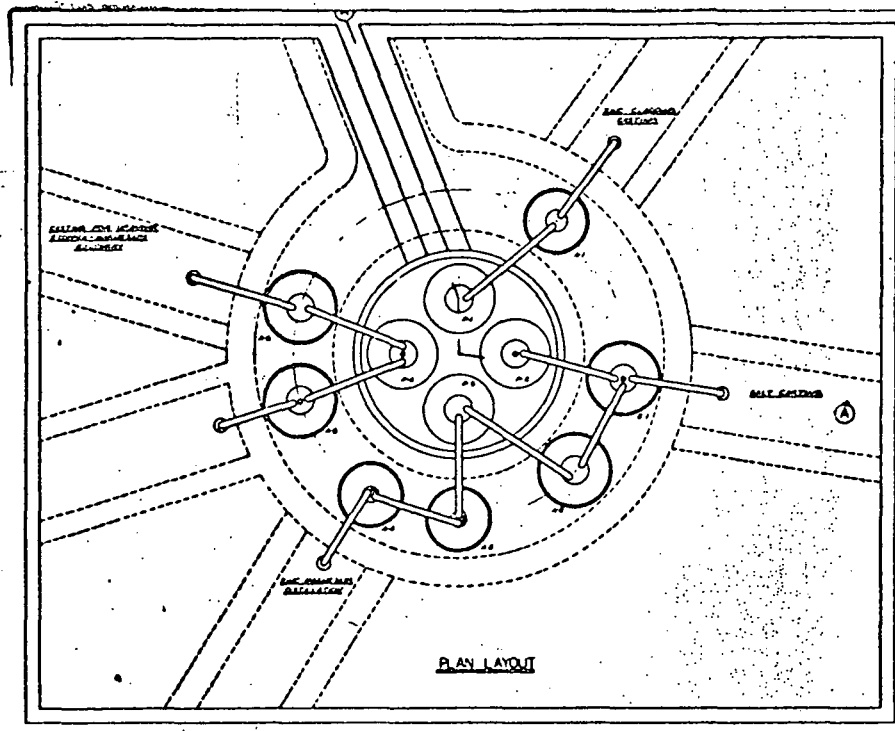
WASTE STREAM	ACTION	FINAL FORM
FP-1	COMPRESS AND STORE IN CYLINDERS	COMPRESSED GAS <i>vented to atmosphere after cooling</i>
CLADDING, FP-3, FP-4	REMOVE ZINC BY DISTILLATION	STORE IN SEALED, HIGH INTEGRITY S.S. CONTAINERS
REDUCTION SALT, CAO, FP-2	ELECTROWIN CAO REMOVE SMALL FP-2 BLEED STREAM	STORE WITH CLADDING IN SEALED, HIGH INTEGRITY S.S. CONTAINERS

- FP-1: Xe, Kr, <sup>3</sup>H
- FP-2: I, Br, Cs, Rb, Ba, Sr, Eu, Se, Te
- FP-3: La, Ce, Pr, Nd, Pm, Gd, Tb
- FP-4: Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb

Slide gives the type of waste stream, the waste stream treatment, and final form for interim and long term storage. The FP-1 fission gases will be collected from sealed furnaces, compressed, and stored in gas cylinders. Process solvents such as zinc and magnesium as well as salts, with the exception of fission product bleed streams, will be recycled. The stainless steel cladding will be used as a disposal matrix for FP-3 and FP-4 elements. The FP-2 elements in the reduction salts may be cast with the cladding into high integrity steel containers which can be sealed for interim and long term disposal. The adequacy of this method must be verified.

## BLANK SLICE

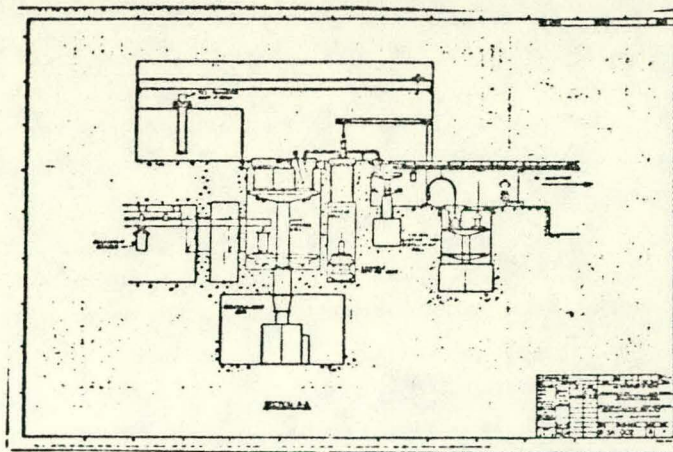
In the conceptual process for either Zinc Distillation or Salt Transport the initial operations have solids present. To avoid transferring of solids, a turntable with several operating positions is proposed. Three positions are proposed for the Zinc Distillation Process. Four are proposed for the Salt Transport Process. The turntable concept provides a method for avoiding removal of the solids from the crucible by moving the crucible and solids from position to position through the process.



For example, in the Salt Transport Process, the primary process-operations operations are conducted sequentially in the same tungsten crucible. These primary operations are conducted in a circular processing assembly with ~~operation~~ stations dedicated for each operation. Each station has the necessary apparatus to conduct the desired unit operations (introduction of spent fuel, induction heating, stirring, and transfer of liquid metal and molten salt phases into and out of the crucibles).

Auxiliary operations are conducted in stationary furnaces surrounding the rotatable turntable. Flow of material between crucibles is made by pressure transferring through heated transfer tubes.





This slide illustrates an elevation view of the conceptual facility. Ancillary operations such as distillation, casting and product oxidation are conducted in separate process bays extending radially from the main process operations.

After each operation is completed the turntable is rotated for the next operation. Prior to rotation, the turntable (and crucibles) are lowered so that the stirrers and transfer tubes will not obstruct the rotation of the crucibles. After rotation the crucibles are raised back to the operating level at the new operating positions. A preliminary design volume of 250 liters was selected for the primary operations. In the Salt Transport Process a design volume of 30 liters was selected for the FP-3 removal operations. The small volume of the FP-3 removal vessels builds in a tamper-proof feature to prevent higher than desired removals of FP-3 elements.

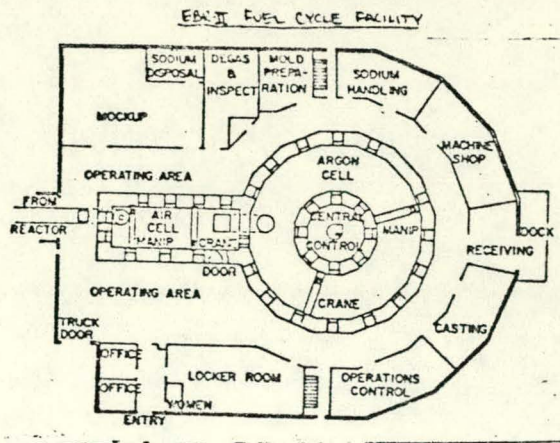
>BLANK SLIDE<

EBR-II, Experimental Breeder Reaction II, and its associated pyrochemical fuel cycle facility, was an early demonstration of closing the fuel cycle. EBR-II was one of the first reactors to produce electrical power, producing 20 MW electrical. The fuel reprocessing, refabrication, and testing were performed remotely and operated successfully for four years.



THIS PAGE  
WAS INTENTIONALLY  
LEFT BLANK

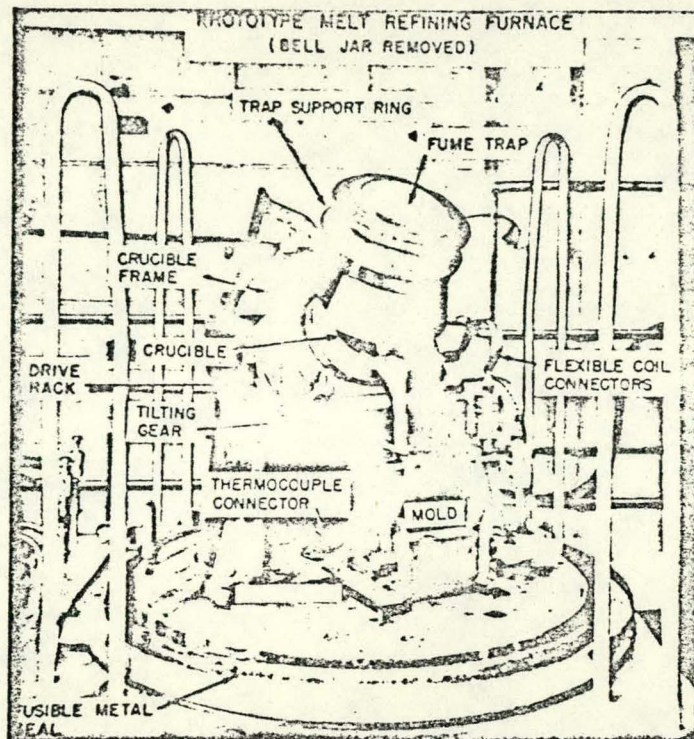




The Fuel Cycle Facility (FCF) is located adjacent to and integrated with the EBR-II at the National Reactor Testing Station in Idaho. Within the National Reactor Testing Station was a two-cell complex consisting of a 700 sq. ft. air cell and a 2200 sq. ft. argon atmosphere cell. This facility was designed by Argonne to demonstrate remote, close coupled, pyrochemical reprocessing of the irradiated metallic fuel from EBR-II, a part of the Liquid Metal Fast Breeder Reactor (LMFBR) program. Construction was completed in 1963 and irradiated fuel introduced into the facility in 1964. From that time to 1968, when the facility was dismantled, 35,000 fuel elements with burnups to 2 at .% were processed.

Melt Refining was the process selected for removal of the more reactive fission products from the irradiated EBR-II fuel. At this time, fully enriched uranium was also added to the charge to maintain the proper enrichment level.

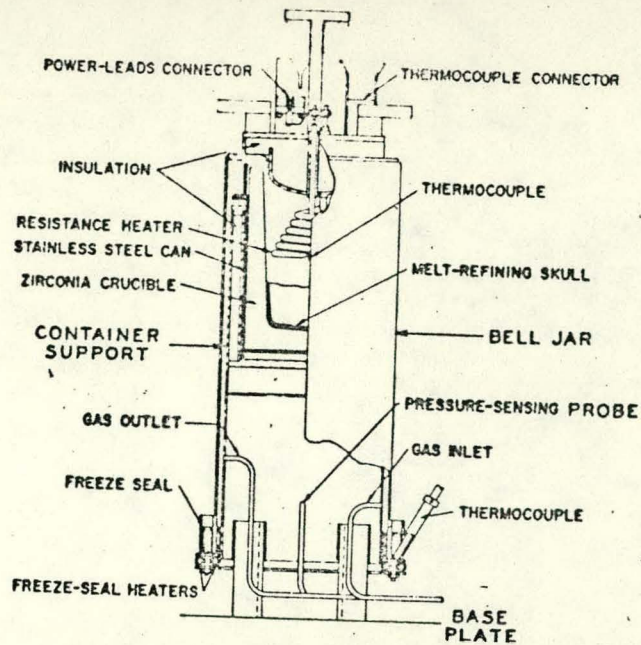




The spent chopped fuel was charged into a lime-stabilized zirconium oxide crucible containing the enriched make-up material. The fuel alloy was melted and liquated for 3 hrs. at 1400 C under an inert argon atmosphere. A ceramic-fiber fume trap was used to trap cesium and iodine (CsI). After purification, the fuel alloy was poured into a graphite ingot mold. Melt refining removed three classes of fission products from the fuel which represent about two-thirds of the total fission yield. The chemically inert fission gases, xenon and krypton, were evolved on melting. Some of the FP-2 fission products were volatilized and trapped by the fume trap. The remaining FP-2 and the FP-3 elements, reacted with the oxygen in the zirconia crucible to form oxides. These oxides remained with the crucible when the alloy was poured into a mold.

THIS PAGE  
WAS INTENTIONALLY  
LEFT BLANK





EBR-II Skull-oxidation Furnace, Cutaway View

Skull oxidation was designed to free the uranium trapped in the slag from the melt refining crucible. The oxidation operation was designed to form a free-flowing oxide powder. The crucible was charged into the oxidation furnace, the bell jar was lowered and sealed to the furnace, the temperature was raised to 700 C and alternate cycles of pure oxygen feed and furnace evacuation were initiated. The cyclic process was controlled automatically and was terminated when the skull ceased to consume oxygen.

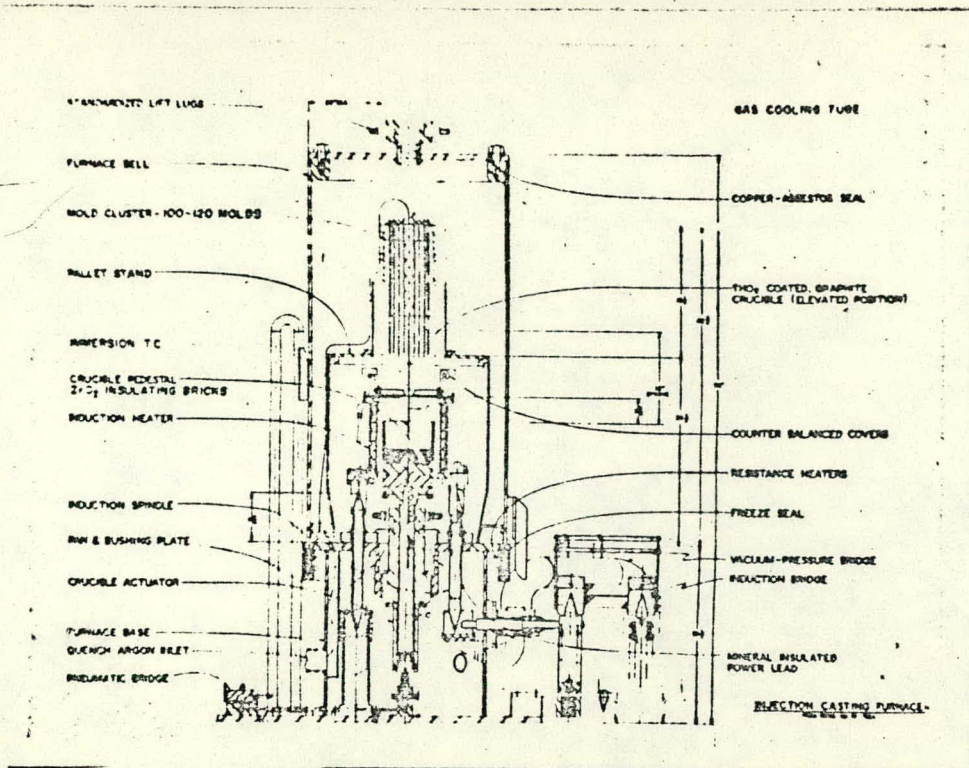
After oxidation, the skull oxide was removed from the furnace and mechanically dumped into a container and stored.

BLANK SLIDE

A skull reclamation process, designed for recovering uranium from the oxide skulls, was developed, but was never installed due to changes in the mission of EBR-II

The melt refining process produced an ingot (about 10 kg.) of partially decontaminated fuel.





The initial fabrication step was injection casting molten fuel into precision bored Vicor glass molds. The resultant fuel rod<sup>was</sup> demolded, sheared to length, and subjected to quality-control inspection. The fuel rod was placed in a cladding tube containing a predetermined amount of sodium. The assembly was vibrated at elevated temperature to settle the fuel to the bottom of the cladding assembly, a top closure plug was added, and the assembly was welded closed. Leak detection operation was performed on the closure weld. The leak-tight fuel element was then subjected to a high-temperature impacting operation to affect a continuous, sodium heat-transfer envelope between the fuel rod and the cladding. The element was then tested to ascertain the bond quality and to determine the sodium level. Acceptable elements were then fabricated into a fuel assembly. The assembly was tested<sup>for</sup> adequacy of weld penetration, quality, and for straightness. Completed subassemblies were then transferred to the reactor for insertion into the core.

CONCLUSIONS

- o PYROCHEMICAL REPROCESSING SUCCESSFULLY DEMONSTRATED
- o CURRENT PROCESS CONCEPTS POTENTIALLY PROLIFERATION AND DIVERSION RESISTANT
- o PROCESS WASTE IS SOLID
- o FURTHER DEVELOPMENT IS REQUIRED

In conclusion fully remote pyrochemical processing and fabrication of spent LMFBR fuel is viable as has been demonstrated by the successful Melt Refining operation conducted at EBR-II from 1964 to 1968.

The requirement for coprocessing uranium and plutonium and maintaining adequate levels of fission products qualify certain pyrochemical processes such as Zinc Distillation and Salt Transport as potential exportable proliferation and diversion resistant fuel reprocessing options. Advantages of pyrochemical processing are that all operations are non-aqueous and short cooled fuel can be processed. Waste generation is in solid form, requiring no subsequent conversion from aqueous solutions to solids.

Further development effort, however, must be conducted before these pyrochemical processes can be performed on a production scale.