

CONF-840802-6

A PROPOSED PYROMETALLURGICAL PROCESS FOR RAPID RECYCLE OF DISCHARGED FUEL MATERIALS FROM THE INTEGRAL FAST REACTOR

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CONF-840802--6

DE84 015823

ABSTRACT

The Integral Fast Reactor (IFR) concept developed by Argonne National Laboratory includes on-site recycle of discharged core and blanket fuel materials. The process and fabrication steps will be demonstrated in the EBR-II Fuel Cycle Facility with IFR fuel irradiated in EBR-II and the Fast Flux Test Facility.

The proposed process consists of two major steps -- a halide slagging step and an electrorefining step. The fuel is maintained in the metallic form to yield directly a metal product sufficiently decontaminated to allow recycle to the reactor as new fuel. The process is further described and available information to support its feasibility is presented.

INTRODUCTION

The Integral Fast Reactor (IFR) Project at Argonne National Laboratory has the objective of demonstrating that a pool-type, sodium-cooled fast reactor using metallic fuel and an integral, simple fuel cycle can achieve low-cost power production, excellent safety, and overcome the perceived disadvantages of a plutonium-fueled reactor system. The IFR concept is based on: (1) a pool configuration for the reactor to reduce plant costs and achieve inherent safety, (2) a metallic fuel designed to further enhance reactor safety, and (3) a compact, simplified, integral fuel cycle to reduce the fuel cycle cost and provide deployment flexibility.

After the initial core loading of enriched uranium, reactor fuel will come from plutonium that is bred in the reactor core and blanket. Core and blanket processing and fuel refabrication will be done in on-site facilities that are closely coupled to the reactor. The reactor site can be closed so that no fuel shipments (except for startup and after plant shut down) cross the site boundaries. Waste will be processed on site to final disposal forms and shipped to permanent repositories only a few times during the plant lifetime.

The Argonne IFR concept takes advantage of several relatively recent developments. The performance of metallic alloys as reactor fuels has improved dramatically in the past 10-20 years, partly because the

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factors limiting fuel burn-up have become better understood. Thus, the 1-2% burn-up limit experienced in the 1960s on which the initial fuel performance of EBR-II was based has been supplanted by more recent 10-12% burn-up targets in the EBR-II reactor. Further, design studies and reviews of economic factors have shown that modest-sized, pool-type fast reactors can be built economically and could be attractive alternatives to the very large reactors that require expenditures often well beyond the fiscal capacity of prudent utilities.

Analyses of the behavior of pool-type designs that employ sodium-bonded metal alloy fuels indicate that these high thermal conductivity systems in which the fuel is compatible with the coolant exhibit safety-related features not found in other fuel-configuration combinations. Analyses of severe accident sequences show only modest temperature rise rates and peak temperatures far below sodium boiling where serious consequences would develop.

The fuel cycle requirements for a fast reactor can be relatively modest and the use of metallic fuel and sodium bond provide an opportunity to markedly simplify the ex-reactor fuel cycle. Both chemical composition and dimensional requirements are expected to be easily met by a reprocessing and fuel fabrication sequence that is based to a considerable extent on the experience obtained from the EBR-II fuel cycle operations conducted in the mid 1960s. The reprocessing is treated in detail subsequently. The EBR-II fuel fabrication process, based on remote injection casting of the alloy, is expected to be directly applicable to both core and blanket fuel for the IFR.

Selection of a pyrochemical procedure, coupled to a simple casting step as the main parts of the fuel cycle, is in concert with the use of a metallic fuel and the targets of economy and flexibility of scale set for the IFR concept. The current design of the pyrochemical process accommodates the modest requirements of the IFR for fission product removal and uses compact, simple equipment that is easily scaled to the anticipated requirements of one or a few reactors adjacent to the fuel cycle plant. Since the process is not amenable to production of highly purified plutonium, diversion resistance of the fuel cycle is assured. Wastes are converted to their final form and can be, if desired, stored on site for the life of the plant without requiring excessive facilities. Such a procedure could effectively eliminate the transport of radioactive materials into or out of the reactor complex. These factors result in the conclusion that a pyrochemical processing and fabrication procedure is a good choice for the IFR concept.

In operation of the EBR-II reactor and its adjacent fuel cycle facility, many of the techniques that are needed for the IFR have already been demonstrated. This considerable experience, coupled with the availability of a useful, decontaminated fuel cycle facility, makes the demonstration of the Argonne IFR concept a rather short and relatively inexpensive procedure. Since much of the fuel cycle background is

derived from the EBR-II, it is useful to review the experience that this previous application of pyrochemistry* has provided.

EBR-II METAL FUEL REPROCESSING EXPERIENCE

In the early 1950's Argonne National Laboratory embarked upon the design, development, construction, and operation of a integrated breeder-type nuclear power reactor and fuel cycling complex. The reactor was the Experimental Breeder Reactor II (EBR-II), a pool-type, unmoderated, heterogeneous, sodium-cooled fast breeder reactor with a thermal output of 62.5 MW and an electrical output of 20 MWe. The metallic reactor fuel consisted of 95% uranium (52%-U-235; 48%-U-238) and 5% fissionium.[†] The processing and refabrication plant, which was coupled to the reactor plant, was designated as the EBR-II Fuel Cycle Facility (FCF). The FCF consisted of a conventional rectangular air-atmosphere hot cell and a circular geometry argon-atmosphere hot cell. The two cells were joined together by a lock system. The fuel recycling complex is only 66 ft from reactor containment, and fuel was moved from the reactor to the fuel cycle facility in an enclosed passageway. Figure 1 shows an artist's cutaway sketch of the Fuel Cycle Facility.

Detail design of EBR-II and the FCF was initiated in 1955; construction started in 1957 at what is now the Idaho National Engineering Laboratory and was completed in early 1962. The first irradiated fuel was processed in the FCF in September 1964, and the first recycled fuel was returned to the reactor in April 1965. Processing of irradiated fuel and its refabrication continued in the FCF for the next four years. During this period, fuel was removed from the reactor, cooled, dismantled, processed, refabricated, and returned to the reactor in as short a time as 30 days. The typical turn-around time was 50 days, and the burnup was limited to 1.2 at. %. In all, about 400 reactor fuel assemblies containing 3 metric tons of irradiated metal fuel in 35,000 fuel pins were processed and recycled. Processing ceased when the mission of the reactor complex was changed from demonstration of a prototype breeder reactor complex to use of EBR-II as a test bed for oxidic fuel, and auxiliary operations were shifted to fuel examination.

Essentially all of the information known about the EBR-II Fuel Cycle Facility--design of plant and equipment, costs, description of processes, and operational experience--have been compiled in a monograph,

*The EBR-II process is usually designated as a pyrometallurgical process, the fuel remaining in its metallic state throughout the process. The broader term "pyrochemical" is applied here to processes in which reactions or phase changes of the major fuel constituents takes place.

†Fissionium is a mixture of noble element fission products at a composition calculated to be at their equilibrium level in reprocessed, recycled fuel. The normal composition is: molybdenum - 2.46 wt %; ruthenium - 1.96 wt %; rhodium - 0.28 wt %; palladium - 0.19 wt %; zirconium - 0.1 wt %; niobium - 0.01 wt %.

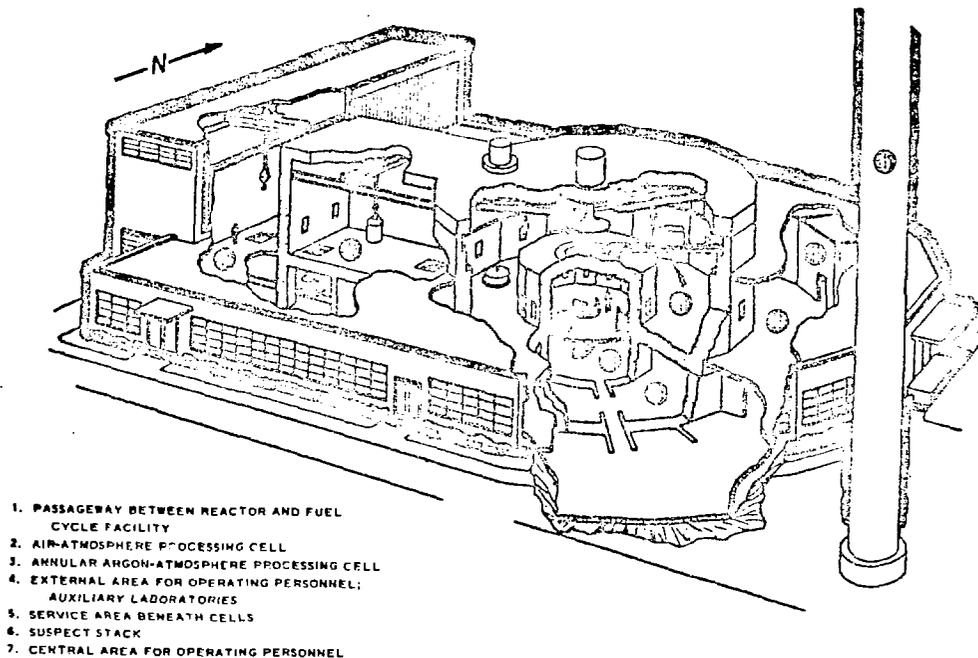


Fig. 1. Cutaway View of EBR-II Fuel Cycle Processing Facility

the EBR-II Fuel Cycle Story,¹ which is now in publication by the American Nuclear Society. References 2 through 7 have also been selected to give pertinent information about the facility and the processes developed for it.²⁻⁷

IFR CONCEPT

The Integral Fast Reactor Concept (IFR) consists of a sodium-cooled metal fuel fast reactor, a fuel reprocessing facility, a fuel refabrication facility, and a waste processing facility, all colocated on a single closed site. Colocation of facilities (The Integral Concept) has a number of advantages. Studies of this concept have shown that shared facilities and services lead to capital and operating cost savings. Shipments of fuel involving fissionable material are eliminated, thereby increasing diversion resistance. Wastes are processed to their final form for permanent disposal, allowing shipments to be infrequent. Plutonium production (breeding gain) can be adjusted to match plant site needs. One of the more attractive features of the Argonne IFR concept to a commercial user is that virtually all the uncertainties of the fuel cycle are removed for the customer prior to plant startup since the fuel cycle remains under the user's control. The primary feed of natural or depleted uranium can be purchased in advance and stored on site.

The pool-type reactor arrangement is a key in lowering reactor plant cost, reducing construction schedule, providing high reliability and easy maintainability, and assuring inherent safety. Reduction of costly construction commodities is achieved by eliminating the complex primary piping (and associated support system) and the primary component housings. Studies of nuclear island construction have shown that the bulk construction materials for a pool type can be reduced by a factor of two or more, compared to the loop-type LMFBR or standard PWRs. In the pool concept, the entire inventory of radioactive sodium is contained within the reactor vessel, thereby reducing occupational exposure of maintenance workers to an order of magnitude less than for LWRs. The large thermal inertia of the cool sodium pool, combined with the thermal response characteristics of the overall reactor assembly, results in safe inherent shutdown of the reactor even under the extreme of loss of primary flow with failure to scram. Highly reliable decay heat removal is achieved by passive systems and natural convection, independent of the normal heat transport systems. The high thermal conductivity of metal fuel results in a much bigger safety margin for loss of flow accidents as compared to oxide fuel. For slow transient overpower events, the metal fuel provides a bigger safety margin than oxide fuel, due to enhanced axial fuel expansion.

In the 1960's, metal fuel development was discontinued because it was believed that metal fuel could not achieve high burnup and would be incompatible with anticipated high temperatures of the reactor coolant outlet. Subsequently, it has been found that, by proper fuel pin design, high burnups are achievable as evidenced by the 11.5% burnup design specification for present EBR-II Mark II fuel and expected burnups of 18% on Mark II-A fuel. High burnup metal fuel pin design is achieved by using a fuel smear density of 75%. This allows the fuel to swell without cladding stress until the porosity within the fuel matrix becomes interconnected allowing release of fission gases to the fuel pin plenum. The expectation of achieving very high reactor outlet coolant temperatures did not materialize (due to temperature limits of core structural materials); therefore, the currently planned temperatures for future LMFBRs are quite compatible with metal fuel. Extensive experience with metal fuel in EBR-II has shown that metal fuel performance and failure mechanisms are well-characterized and predictable. Transient tests have demonstrated that cladding breach does not result in fuel-coolant interaction, as in oxide fuel, and the response is completely benign. A further advantage for metal fuel is its high internal conversion. This allows the fuel cycle to be started on enriched uranium, and as the ^{235}U is burned out, it is replaced by plutonium bred in the core or blanket without need for fissionable material makeup from external sources.

The choice of metal fuel for the IFR leads to lower fuel fabrication costs compared to oxide fuel. Conservative estimates at ANL show that the cost of fabricating fuel assemblies of metal fuel will be less than 60% of the cost of fabricating with oxide fuel. Oxide fuel requires tight specifications, resulting in multiple process steps and costly recycle in fuel preparation. Specifications for metal fuel pins are more relaxed, leading to little recycle, and fuel recycle is simple. Foremost in lowering fuel cost, however, is that injection casting of metal fuel and

loading the metal rod into a cladding tube are much simpler operations than the fabrication of oxide pellets from powders and assembly of pellets into fuel pins.

Rapid turnaround of short-cooled fuel has been demonstrated using pyrochemical processes. As a result, inventory charges and requirements for storage facilities are reduced. The pyrochemical process is simple and compact, as will be shown below, requiring a minimum of modest-sized equipment. For a small on-site plant, this attribute results in lower hot cell space requirements compared to the conventional or even the advanced Purex plant designs. Pyrochemical processes, which are carried out in inert atmospheres and always behind heavy shielding, are freed of the usual safety and diversion concerns. These features also allow a closely coupled facility to exhibit reliability and operational simplicity that is in accord with the need to maintain the operation of the reactor and does not place the burden of excessive complexity on the utility customer.

Mass flows for core and blanket processing of uranium plus plutonium for a typical IFR facility (330 MWe reactor) are given on Table I. The daily processing rate will be about 10.5 and 30.5 kg HM (U + Pu) for core and blanket, respectively. The material for the core and blankets are 39 core pins, each 91.0 cm (36 in.) long; 78 axial blanket pins, each 35.5 cm (14 in.) long, and 5 radial blanket pins, each 162.5 cm (64 in.) long. The reference core fuel composition is U-Pu-Zr (75-15-10 wt %) and the reference blanket is uranium. The reference core fuel pin is about 5.4-mm in diameter and is sodium bonded inside the cladding jacket.

Processing of short-cooled fuel requires attention to fission product decay heating. Fission products fall into three groups that distribute to separate process streams: (1) the volatile fission products; (2) the chemically active fission products, which distribute to the chloride salt phases present in the process; and (3) the noble metal fission products, which distribute to the liquid metal waste phase. Table II shows the heat

Table I. Mass Flow Data for the Reference IFR
(330 MWe)

	Number of Assemblies	Total Heavy Metals (kg)
Equilibrium Loading, kg/yr		
Core	36	2852
Axial Blanket	—	3382
Radial Blanket	14	4380
Equilibrium Discharge, kg/yr		
Core	36	2618
Axial Blanket	—	3371
Radial Blanket	14	4364

Table II. Fission Product Heating (kW) from Fission Products Associated with the Daily Processing Batch (10.5 kg HM) of IFR Core Fuel

	Days Out of Reactor			
	30	90	180	365
1. Salt Phase (Cs, Sr, Ba, R.E.)	0.96	0.49	0.33	0.21
2. Metal Phase (Zr, Nb, Ru, Rh)	0.74	0.46	0.24	0.09

generation by core fuel for a daily processing batch as a function of time out of the reactor and distribution of the important fission product elements between the salt and metal process waste streams.

PYROCHEMICAL PROCESSING FOR IFR

Fig. 2 shows the overall fuel cycle for the IFR. It differs in several important respects from the EBR-II fuel cycle. For the low burnup EBR-II fuel, the cladding of the core fuel was removed mechanically. For the IFR core fuel this will probably not be possible since the cladding

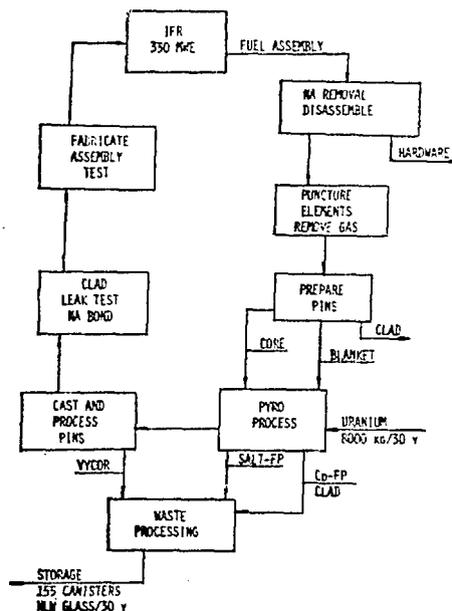


Fig. 2. IFR Fuel Cycle

gap will have been closed by the end of the high (10 a/o) burnup expected to be achieved. The pyroprocess will therefore have to accommodate the cladding elements from core fuel within the process. Although it is started on enriched uranium, the IFR fuel cycle subsequently becomes plutonium-based, whereas the EBR-II fuel cycle was based on enriched uranium. Blanket processing to make the reactor self-sufficient is part of the IFR concept, whereas EBR-II had no blanket. Lastly, the EBR-II process depended on the formation of solids in the crucible, whereas the IFR process depends on molten salt as a processing medium. In the balance of this paper, some of the details for processing of the IFR core and blanket pins to produce purified metal suitable for refabrication of fresh core or blanket fuel will be discussed.

Laboratory pyrochemical work at ANL earlier than 1964 was reviewed by Pierce and Burris.⁸ Much of the work done earlier than 1969 was presented in a series of papers given at Ames.⁹ Much of the pyrochemical process work done at ANL after 1960 was based on zinc as a liquid metal solvent phase. Although uranium and plutonium have high solubilities in zinc, materials of construction useful with zinc are limited, and phase separations and solvent removal are somewhat complicated. Therefore, other types of pyroprocesses were considered for the IFR.

A reference process flowsheet has been devised for IFR fuel that consists of two main steps, halide slagging and electrorefining. Although the current focus is on this reference process, it must be emphasized that a number of attractive alternatives are available for these process steps. The available information on the reference process is being expanded and refined. Final selection of flowsheet steps will require both verification of the chemistry of the steps and demonstration that the process steps can be carried out under conditions that meet process and product criteria.

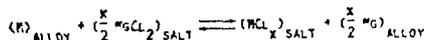
In halide slagging, melted fuel is contacted with a molten halide salt that contains an oxidant chosen such that chemically active fission products (alkali metals, alkaline earth metals, rare earth metals) are oxidized to the salt, thus separating them from the fuel melt. In addition, plutonium may be selectively oxidized and transferred to the salt, thus achieving separation of plutonium from the uranium. Electrorefining is a process in which uranium and plutonium are oxidized anodically in a molten salt electrolysis cell and deposited cathodically as solids. Under proper cell conditions, the remaining class of fission products (the noble metals) will not oxidize and thus will remain at the cell anode. The only significant contamination expected in the product uranium-plutonium is electrolyte salt, which will be occluded in the cathode product. This will be separated from the metal by melting and freezing to give two separate consolidated solids.

Halide Slagging

Some process development work on the halide slagging process was done at ANL in the period 1963-1964.¹⁰ The chemical principles underlying the halide slagging process are shown on Fig 3. It is similar to melt refining, except that a liquid chloride salt is the slagging medium instead of a solid oxide such as zirconia.

PYROCHEMICAL PROCESSING OF IFR FUELS

HALIDE SLAGGING STEP



$$\text{IF } D_H = \frac{[MCl_x]_{\text{SALT}}}{[M]_{\text{ALLOY}}}$$

$$\text{LOG } D = \frac{\frac{x}{2} \Delta G_F^{\text{MgCl}_2} - \Delta G_F^{\text{MCl}_x}}{2.3 RT} + \text{LOG} \left[\frac{y_M}{x/2} \right] - \text{LOG} \left[\frac{y_{MCl_x}}{x/2} \right]$$

(A)

(B)

(C)

A RELATES TO THE DIFFERENCE IN FREE ENERGY OF FORMATION OF THE CHLORIDES

B RELATES TO THE COMPOSITION OF THE ALLOY, AND T

C RELATES TO THE COMPOSITION OF THE SALT, AND T

EXAMPLE: $D_{\text{CE}}/D_{\text{PU}} \geq 88.1/1.6 \times 10^{-3} \geq 5.5 \times 10^4$

AT 1600°K, $a_{\text{MgCl}_2} = 4.2 \times 10^{-3}$

Fig. 3. Principles of the Halide Slagging Step

Thermodynamic data for the chloride salts of interest are shown on Table III. One carrier salt used for high temperature halide slagging is 81 wt % BaCl₂-19 wt % CaCl₂. Magnesium chloride in stoichiometric amounts dissolved in this salt may be used as an oxidant to separate the active fission products from uranium and plutonium, as required for core fuel processing. At the temperature used for the high temperature slagging (>1150°C), magnesium metal, which results from oxidation of the active fission products, distills from the salt, driving the reaction to completion. For blanket processing, UCl₃ may be used as an oxidant to remove bred plutonium from the blanket metal melt. The uranium, added as the chloride, provides the blanket makeup requirement for depleted uranium. For high temperature halide slagging, BeO is a satisfactory, nonreactive crucible material.

The results of small scale (750 grams of metal) halide slagging experiments carried out at ANL in 1964 are shown in Table IV. These results indicate excellent separation of active fission products. Loss of plutonium to the salt will be controlled by the amount of excess oxidant (MgCl₂) used and is expected to be less than 0.3%. The same crucible was used for all experiments, and appeared to be unaffected by continued reuse. The molten uranium alloy did not wet the crucible. The small amount of metal that remained in the crucible was removed between runs to make a material balance. In the case of a process, the crucible heel would either be physically removed or carried forward to the next run, the result in either case being a higher product yield. Figure 4 shows the laboratory apparatus used for halide slagging work.

Table III. Standard Free Energies of Formation of Chlorides at 1000°K

	$-\Delta G_f^\circ$ (kcal/g-equiv. Cl)		$-\Delta G_f^\circ$ (kcal/g-equiv. Cl)
BaCl ₂	83.4	PuCl ₃	58.9
KCl	81.4	MgCl ₂	57.7
RbCl	81.2	UCl ₃	54.0
SrCl ₂	81.0	ZrCl ₂	49.2
CsCl	80.0	MnCl ₂	42.3
SmCl ₂	80.0	ZnCl ₂	35.0
LiCl	78.8	CrCl ₂	31.9
CaCl ₂	77.9	CdCl ₂	30.4
NaCl	75.7	FeCl ₂	26.6
LaCl ₃	67.0	NbCl ₅	24.6
PrCl ₃	66.3	CuCl	22.0
CeCl ₃	66.3	NiCl ₂	20.0
ThCl ₃	65.3	MoCl ₂	8.0
NdCl ₃	64.2	TcCl ₃	7.0
YCl ₃	61.2	RhCl	5.8
		PdCl ₂	3.8
		RuCl ₃	1.4

Table IV. Melt Refining of Plutonium-Containing Fuels by use of Halide Fluxes^a

Metal Charge ^b		Excess Oxidant ^d (%)	Ingot Yield ^e (%)	Ce Removal (%)	Pu in Flux ^c (%)	Ce/Pu Separation ^g
Total (g)	Ce (w/o)					
737	.335	N/A ^f	97.1	62.3	0.05	-
743	.335	10	98.3	98.2	0.45	7400
716	.468	10	97.5	97.6	0.29	7200
691	.751	100	96.9	99.1	1.88	4100

^aAll runs held at 1150°C for 1 h under Ar; flux poured off at 860°C, and ingot poured at 1300°C.

^bCompositional (w/o) 80.97 U, 10.02 Pu, Ce as shown, 2.87 Mo, 3.20 Ru, 0.54 Rh, 1.13 Pd, 0.93 Zr.

^cFlux 81 w/o BaCl₂, 19 w/o CaCl₂, charge-to-flux 7:2.

^dOxidant is MgCl₂.

^eCrucible is isopressed, high-density, high-purity BeO.

^fNo MgCl₂ added.

^gSeparation Factor = $\frac{\text{Ce in Flux/Ce in Metal}}{\text{Pu in Flux/Pu in Metal}}$

SCHEMATIC DIAGRAM OF INDUCTION FURNACE AND GLOVE BOX
FOR MELT REFINING OF URANIUM-PLUTONIUM-FISSIUM ALLOY

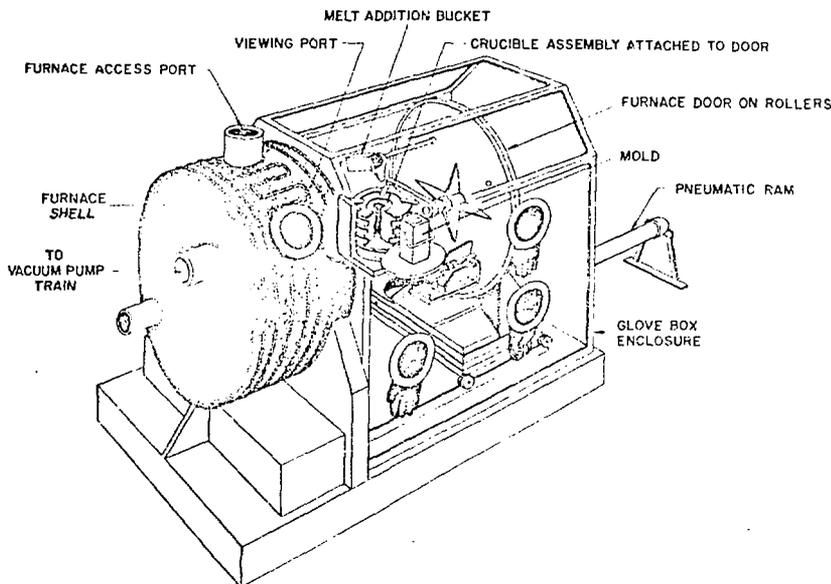


Fig. 4. Apparatus Used for Halide Slagging

Halide (chloride) slagging was also investigated at Los Alamos as means of purifying molten plutonium.¹¹ Using a LiCl-KCl flux and MgCl_2 as an oxidant at 600°C , quantitative removal of cerium and lanthanum from a plutonium, iron, molybdenum, ruthenium alloy occurred in one hour of contact time. When the amount of excess MgCl_2 oxidant was restricted to 10%, plutonium recovery in the metal ingot was greater than 99%. Similar experiments using $\text{MgCl}_2\text{-NaCl-KCl}$ flux at 700°C and alloys of Pu, Fe, Zr, Mo, Ru, Ce, and La, gave similar results with only cerium and lanthanum oxidized to the salt and greater than 99% recovery of plutonium in the metal ingot after one hour contact time.

Equipment for the halide slagging process for IFR is expected to be very similar to that used for melt refining of EBR-II fuel that has been described by Hampson¹² and Stevenson.¹ The melting furnace and process differ, however, in several ways: (1) an inert crucible material, BeO , will be used instead of reactive ZrO_2 , (2) a halide salt flux (about 1.5 liters) will be added to the crucible, along with the core fuel charge of 10 kg that represents the design basis for both EBR-II and IFR, and (3) the mold and demolding equipment must accommodate the salt ingot as well as the metal ingot.

Electrorefining

The principle of electrorefining may best be explained with the aid of Table III. Consider the equilibrium conditions when uranium-plutonium alloy containing noble metals such as Mo, Ru, Rh, Fe, Cr, Zr, and Cd

is brought into contact with a molten salt such as LiCl-KCl eutectic into which about 2 mol % UCl_3 - $PuCl_3$ has been added. At thermodynamic equilibrium, only a very small concentration of noble metal chlorides will appear in the salt phase. An electrorefining cell is obtained if the metal phase becomes a cell anode and a cathode where chlorides can be reduced is introduced into the salt phase. When a direct current is passed at low voltage from anode to cathode, the bulk of the current will pass through the cell as uranium and plutonium ions, which are reduced and collected at the cathode as metals. Separation of uranium and plutonium from noble metals occurs, since only a very small fraction of the current is carried through the salt by noble metal ions because of their very low concentration.

Electrorefining has been applied at Los Alamos for many years for the purification of plutonium. Table V, taken from one of their reports¹³, summarizes the kind of purification that has been routinely achieved. In their cell, impure liquid plutonium was the cell anode and purified liquid plutonium was deposited and collected at the cathode. The electrolyte was

Table V. Behavior of Impurity Elements in Electrorefining of Plutonium

Element ^a	$-\Delta G^\circ$, KCal per Gram Atom Cl ^b	Concentration, g Element/ 10^6 g Pu		Element Concentrated In
		Feed	Product	
Ir	2	4,500	110	---
Ni	18	1,000	<0.5	Anode
Cu	21	500	<1.5	Anode
Ta	27	5,000	80	Anode
Pb	27	2,000	<0	---
Fe	27	25,000	20	Anode
Si	28	320	<5	Anode
Cr	32	340	<5	Anode
Ga	32	10,000	<25	Anode
Mn	41	70	<2	---
Ti	43	15,000	10	---
Al	46	2,700	<5	Anode
U	54	330	<20	Anode
Zr	56	10,000	14	---
Th	59	1,300	10	Anode
Pu	59	---	---	---
Ce	66	527	<25	Electrolyte
Am	67	850	82	Electrolyte

^aListed in order of increasing stability of their chlorides.

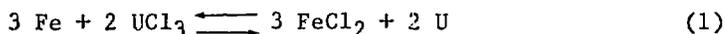
^b $-\Delta G^\circ$ at 1000K is tabulated. For elements having a multiplicity of oxidation states, the $-\Delta G^\circ$ for the most stable form of the chlorides is given.

NaCl-KCl that contained about 2 mol % PuCl₃. The noble elements, as expected, remained in the anode. Uranium, which was present initially in the anode at low concentration, 0.03 wt %, tended to stay in the anode because of its low activity in the liquid plutonium. The behavior of cerium and americium is worthy of note because it illustrates the behavior of elements whose chlorides are more stable than that of plutonium. These elements tend to concentrate in the cell electrolyte and do not deposit cathodically with the plutonium. In effect, they behave like the normal cell carrier salt, in this case NaCl-KCl.

Considerations for IFR Electrorefining Cell Design

The basic cell design for the IFR uses a pool of liquid cadmium for the anode. There are a number of reasons for choosing a liquid anode pool and a number of reasons why cadmium was chosen as the liquid. Cadmium will dissolve uranium and plutonium (solubility of uranium is greater than 2 wt % and plutonium is greater than 3 wt % at 500°C) in sufficient quantity to serve as a liquid anode for uranium as well as plutonium. Further, the solubility of iron in liquid cadmium is extremely low (0.00076 at. % at 500°C and 0.007 at. % at 600°C). This indicates that liquid cadmium in an iron container could be a strong candidate for the pool anode. As shown in Table III, cadmium and iron are noble elements with respect to cell electrolyte chloride melts such as LiCl-KCl containing UCl₃-PuCl₃ or BaCl₂-CaCl₂ and containing heavy metal chlorides.

The chemical equilibrium for the cell electrolyte in contact with its iron container and the liquid cadmium pool containing dissolved fuel is given by:

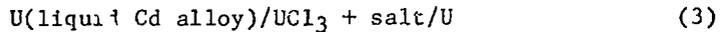


$$K_a = \frac{[a_U]^2 [a_{\text{FeCl}_2}]^3}{[a_{\text{Fe}}]^3 [a_{\text{UCl}_3}]^2} = \exp - \left[\frac{\Delta G}{RT} \right] \quad (2)$$

where the a's represent the activities of the product and reactants and ΔG° is the standard free energy change for the reaction.

A quantity of interest is the ratio ($a_{\text{FeCl}_2}/a_{\text{UCl}_3}$) since this will indicate the magnitude of the corrosion problem and also the extent to which the cathode product is likely to be contaminated with iron, since any FeCl₂ which appears in the salt would result in iron deposits on the cathode. This ratio will be highest at the end of the electrolysis since at that time a_U will have the lowest value. We use as this value 8.6×10^{-4} , which is the activity of uranium in cadmium¹⁴ at a uranium concentration that is 0.1% of the saturation value at 500°C, representing conditions in the anode after 99.9% transfer of uranium to the cathode. Since iron is essentially insoluble, $a_{\text{Fe}} \approx 1$, and a ratio $a_{\text{FeCl}_2}/a_{\text{UCl}_3}$ of 4×10^{-12} is calculated for a UCl₃ concentration of 2 mol %. We, therefore, conclude that iron container corrosion and product contamination from this source should be insignificant. When the interaction of cadmium with the electrolyte is analyzed in this same manner, the results are similar.

The above-described interaction of the container material or cadmium with the cell electrolyte is chemical. Electrochemical corrosion reactions can also occur. For instance, a reaction (1) requires a voltage of 1.26 V to cause reduction of UCl_3 . If cadmium is substituted for iron in Eq. (1), the cell voltage required is 1.08 V. Therefore, during electrolysis the cell voltage needs to be restricted to less than one volt. The minimum voltages required for electrorefining transport of uranium and plutonium have been calculated.¹⁴ For instance, for the cell.



The minimum EMF, E , of this cell is given by $E = (RT/3F)\ln a_U$, where R is the gas constant, T the absolute temperature, F the Faraday constant, and a_U the activity of uranium in the liquid anode. Similar expressions apply to plutonium transport. It is assumed here that the uranium and plutonium are at unit activity at the cathode. If alloy formation takes place at the cathode, the activities will be less than unity and the minimum EMF will be less. The minimum values for uranium and plutonium transport (500°C) after 99.9% transfer out of the anode are 0.16 V and 0.49 V, respectively. At higher concentrations, the required voltages are less. Therefore, for the cell design considered, there is ample driving force to cause transport of uranium and plutonium without driving reactions involving cell structural materials. Since iron and cadmium are separable from uranium-plutonium as shown above, the noble metal fission products are expected to be separated in the same manner.

Electrorefining to purify uranium (or plutonium) from noble elements can be done in a cell without a liquid cadmium pool anode.¹⁵ In this case, solid reactor fuel is made into the cell anode, and uranium and plutonium are collected on a cathode suspended in the cell electrolyte. In cells of this type, however, it is very difficult to get high recoveries of material, since part of the anode material can lose electrical contact with the electrode as the electrolysis proceeds. Also, any material that becomes disengaged from the cathode may be lost if, subsequently, it does not make contact with the anode. A liquid anode pool such as cadmium overcomes these problems.

A cell design that has both a positive electrode and the cadmium anode pool may have some advantages. If core fuel is first melted in a melting furnace (the halide slagging furnace) and cast, the cladding will alloy with the fuel to form an ingot. If this ingot is added directly to a cadmium anode pool its rate of dissolution is likely to be slow because of the insolubility of the contained iron. However, if this ingot becomes part of an electrode in the electrolyte phase of the cell, it should readily dissolve anodically to start the electrorefining process. The fuel ingot could be loaded into a detachable, perforated iron basket that would be part of a rotatable, vertically movable electrode. The electrolysis would be finished in the cadmium phase; this would dissolve any uranium and plutonium residue that had become detached from the electrode during the anode dissolution in the electrolyte phase. The perforated iron basket would be a daily process waste since it would contain the cladding and those noble metal fission product elements that are insoluble in the bulk cadmium anode pool. Removal of these insolubles on a routine basis as part of a waste stream also prevents the buildup of insoluble

sludge in the cadmium anode pool. The cadmium anode lifetime is limited by accumulation of sludge to an unacceptable level.

The design of the cathode is not yet determined. Some information is available for solid uranium deposition¹⁵ but not for uranium-plutonium. The product is assumed to collect as a solid, rather uniformly deposited on a rotating, cylindrical mandrel. The deposit is expected to be dendritic in nature and to be covered with cell electrolyte. The mandrel surface will be either iron, molybdenum or zirconium, from which the deposit may be removed mechanically. The product will be consolidated and separated from the occluded electrolyte by melting, casting, and phase separation. The latter operation is to be done in equipment similar to the halide slagging furnace.

Figure 5 shows an electrorefining cell concept. The metal ingot from the vacuum melt step may be dropped down a slug chute of the electrorefining furnace into the cadmium anode pool for direct dissolution and electrolysis, or it may be added to a perforated iron basket attached to the positive electrode. The electrorefining furnace remains at operating temperature (500°C) throughout the operating cycle and between cycles and is shut down and cooled only for maintenance. The anode crucible is about 16 in. inside diameter and 30 in. tall. It is of mild or low chromium-molybdenum steel, and contains the cadmium anode pool and the cell electrolyte. The anode pool is about 43 liters of cadmium, which will dissolve all the uranium and plutonium in the daily processing batch. The cell electrolyte, about 35 liters, is the basic LiCl-KCl eutectic salt containing 2 mol % UCl_3 - $PuCl_3$ and about 7 mol % active metal fission product chlorides.

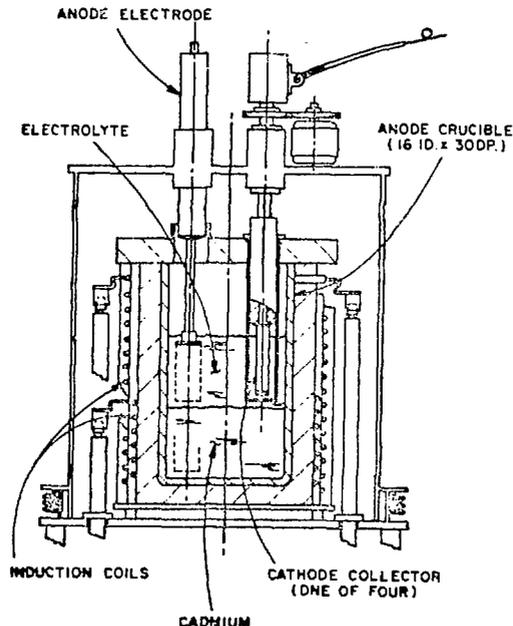


Fig. 5. Electrorefining Cell

To electrorefine 10.4 kg of HM at 80% current efficiency requires 4392 A-hr. For the 16 in. diameter anode, this gives an average anode current density of about 0.5 A/cm^2 for an 8-h transfer. If four cathodes are used, the cathode current density is about equivalent to the anode current density. After transport of the bulk of the uranium and plutonium, the anode becomes depleted and at a fixed current the voltage rises to cutoff to complete the electrorefining step.

The liquid anode is continuously mixed by 60-cycle induction power which is coupled directly to the liquid cadmium. Stirring the cadmium promotes fuel dissolution and reduces concentration gradients in the molten salt. The steel crucible is baffled so that vortexing is avoided and turbulence created in the cadmium phase will stir the electrolyte phase. The objective, during electrolysis, is to stir both phases sufficiently so that the rate of transfer is not controlled by bulk diffusion but not to cause bulk mixing of the two phases.

Flowsheet for IFR Pyroprocess

Figure 6 gives a conceptual flowsheet for core processing and Figure 7 is for the reactor blanket. These flowsheets show one way in which the two major processing steps, halide slagging and electrorefining, may be employed to process the fuel. The development program for the IFR fuel reprocessing is in a very preliminary phase, and it should be understood that these are selected flowsheets that are essentially conceptual in nature at this time.

For core fuel elements, the cladding jacket is punctured in a vacuum chamber to release the "free" gaseous fission products. The fission gases are collected from this and later processing steps in vacuum, in order that, with subsequent compression, the storage volume will be minimal, about 1.5 ft^3 (STP)/day including flush gas (argon) from all sources. The core fuel pins are chopped into short (5 cm) lengths with the cladding left in place. Entire axial blanket sections are separated and processed with the radial blanket (see below). The core fuel is vacuum melted in a BeO crucible to complete the release of the gaseous fission products in vacuum as the fuel cladding melts. The sodium bond, iodine, probably as a compound, and volatile fission product metals such as cesium and rubidium will be released during the melting. For the 39-pin batch, 115 g of sodium must be removed. Molded Fiberfrax* is used as an absorbent to trap the sodium fumes, and the material also effectively traps small amounts of iodides and alkali metal fission products which are released from the fuel as it is heated. About 14 g of absorbent are required per gram of sodium. The bulk density of the molded Fiberfrax is about 0.45 g/cm^3 , so the volume of the material needed is about 3.7 liters for the required 1680 g of absorbent. After use, the bulk of the absorbent bed can be reduced to about 0.7 liter by compaction to give a small waste volume.

*A product of Carborundum Corporation. The material is vacuum molded from fibers whose composition is aluminum oxide - 51.2%; silica - 47.4%; boron oxide - 0.7%; and sodium oxide - 0.7%.

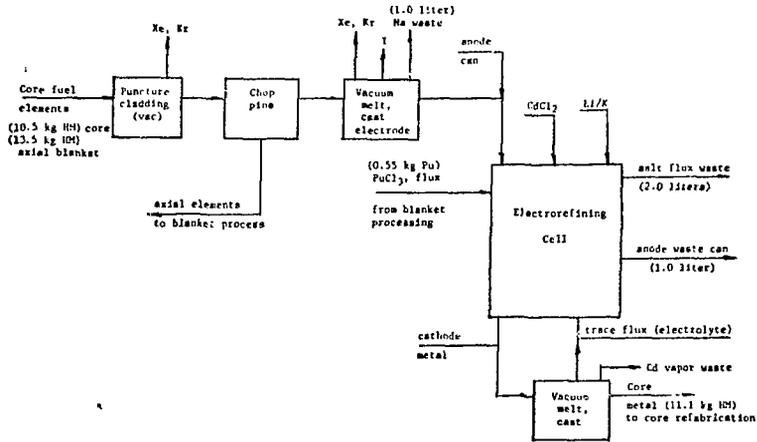


Fig. 6. Core Fuel Process for IFR

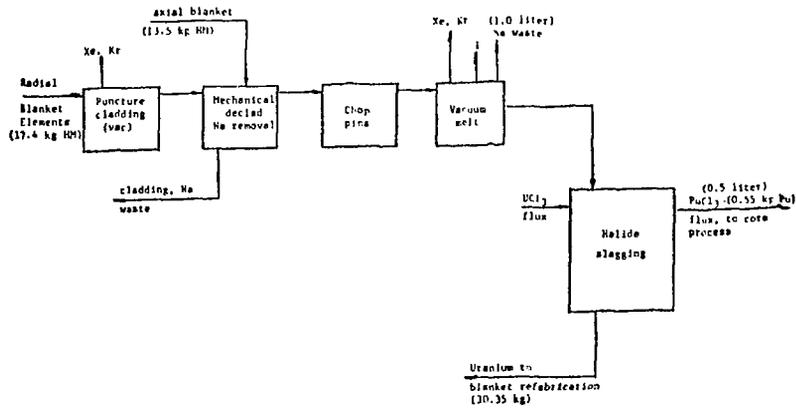


Fig. 7. Blanket Process for IFR

The cast product of the vacuum melting operation is a fuel ingot shaped for loading into a perforated iron basket which attaches to the anode (+) electrode of the electrorefining cell. The anode basket may be rotated in the electrolyte and the fuel will be attacked anodically, resulting in transport and deposition of uranium and plutonium to the cathode. Alternatively, CdCl_2 may be added to the electrolyte to attack the fuel, since it will oxidize the uranium, plutonium, and reactive fission products (alkali metal, alkaline earth, and rare earths) to the salt phase. Cadmium metal, one of the reaction products, passes to the cadmium anode pool at the bottom of the cell. The base electrolyte phase which is used repeatedly consists of LiCl-KCl with about 7 mol % active fission product chlorides (alkali, alkaline earth, and rare earth chlorides). Sufficient CdCl_2 is added to oxidize all the active fission products in the new fuel charge, plus enough to oxidize sufficient uranium and plutonium to give an electrolyte which contains ~ 2 mol % U/Pu (4.45 kg U/Pu in the salt phase). About 5.8 moles of CdCl_2 are needed to oxidize the fission products and 28.1 moles are added to oxidize the required amount of U/Pu. Insufficient CdCl_2 is added to oxidize all of the U/Pu. Under these conditions, zirconium is not expected to oxidize and will act like a noble metal. After partial reaction of the anode material, the basket is lowered into the cadmium phase with continuing rotation until the dissolution process is completed. All of the CdCl_2 will be consumed since there is excess U/Pu and this reaction is completed prior to the start of the electrorefining step.

At the start of electrorefining, the bulk of the active fission products will be in the electrolyte with sufficient UCl_3 and PuCl_3 in the salt to provide for electrorefining transport. After the transport, the U/Pu product is removed with the cell cathodes and the deposits are processed by melting to provide the pin casting feed. At the end of this step, the U/Pu in the cadmium phase should be reduced to as low as practicable. If this cannot be obtained rapidly near the end of the electrolysis, then small amounts of CdCl_2 would be added to the salt phase to oxidize the residual U/Pu in the cadmium to the salt phase.

The electrolyte phase is withdrawn from the cell (liquid transfer) and stored in a holding tank. The electrolyte withdrawal step of the process is necessary to reduce process losses since the salt contains the uranium and plutonium, and losses of these metals would occur if the basket were withdrawn through an upper salt phase. A small amount of the cadmium is taken in this transfer to assure that no salt remains. The anode basket is next withdrawn and becomes the noble metal, cladding and cadmium waste. In the first process step, 33.9 moles of CdCl_2 were used for reaction with the fuel. This gives 3.8 kg (0.44 liters) of cadmium, which is withdrawn from the cadmium anode pool with the basket of waste. In this process we also expect zirconium to act as a noble metal and be removed in the process dragout.

The salt phase that was stored in the holding tank is returned to the electrorefining cell. Metallic lithium and potassium (Li-K) then added to the salt phase to reduce the UCl_3 and PuCl_3 . The Li/K ratio is the same as that in the bulk salt. Sufficient Li-K (56.1 moles) is added to reduce all of the heavy metal chloride. The Li-K when added will float on the salt phase to start a salt phase reaction. The Li-K has

sufficient reducing power to reduce some of the active fission product chlorides in the salt phase. However, the UCl_3 and $PuCl_3$ are the least stable chlorides, so the reduced active fission product metal will, in turn, reduce the heavy metal chloride with the resultant transfer of the heavy metal to the cadmium phase. Some excess Li-K may be required in order to reduce all of the $UCl_3/PuCl_3$ at equilibrium, and this may result in transfer of some of the active fission products to the cadmium phase. This would cause some inefficiency since these would be oxidized by $CdCl_2$ (in the first process step) on the next cycle.

After the reduction of $UCl_3/PuCl_3$ by the Li-K, about 2.0 liters of salt is withdrawn as a process waste. This would contain the 56 moles of LiCl-KCl (from the heavy metal chloride reduction step) and 4.4 moles of active fission products which entered the process in the new fuel. This means that when the electrolyte in the electrorefining cell reaches steady state, the active fission product content would be 7.3 mol %. With this reasonably low active fission product content it is likely that this very complex salt would be a single liquid phase. This salt waste will have a maximum heating rate of 250 W/liter if we start to process the fuel at 30 days cooling and run one batch per day thereafter.

The radial blanket pins are punctured under vacuum as are the core pins. The axial blanket sections and the punctured radial pins are mechanically deacid as was done in the case of EBR-II fuel.¹⁶ The pins are vacuum melted to remove and collect the volatiles and sodium. The metal is then halide slagged using UCl_3 in a flux as the oxidant to remove the active fission products and the bred plutonium. After pouring and casting, the salt ingot containing bred plutonium and active fission products is fed to the core process electrorefining cell. Uranium metal with noble metals left in is returned to blanket pin refabrication.

SUMMARY

A closely coupled fuel cycle similar to that demonstrated for EBR-II in the mid 1960s has been conceived for the Integral Fast Reactor. The fuel cycle is based on a compact pyrochemical process, especially designed for a metallic fuel, and a fuel fabrication process based on injection casting. This fuel fabrication method was demonstrated in remote operation in the EBR-II Fuel Cycle Facility between 1964 and 1969 and is presently employed for manufacture of fresh fuel for EBR-II.

The proposed process for recovering uranium and plutonium from core and blanket fuels consists of two major steps--halide slagging and electrorefining. The process promises considerable improvement over the melt refining process used to recover EBR-II fuel in providing higher yields and adequate removal of all fission products. Perceived advantages of the process are the following: compactness (only two major steps); retention or ready availability of metal form throughout--especially direct production of a metal product suitable for injection casting of fuel pins; high resistance to radiation damage through use of inorganic reagents (therefore, capable of handling short-cooled fuels); flexibility--can accommodate a variety of fuel compositions; high resistance to diversion or proliferation for weapons use because of low decontamination from

fission products and limited access to fuel materials within the processing facility; small volumes of waste; and low cost--based on process simplicity and previous experience at EBR-II.

The process is in early developmental stages, but is well grounded in experiments and thermodynamic information developed at ANL in 1960s and early 1970s and at Los Alamos. It is anticipated that process feasibility will be adequately demonstrated by the end of FY 1986.

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