TRANSURANIC MATERIAL RECOVERY IN THE INTEGRAL FAST REACTOR FUEL CYCLE

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ABSTRACT

The Integral Fast Reactor is an innovative liquid metal reactor concept that is being developed by Argonne National Laboratory. It takes advantage of the properties of metallic fuel and liquid metal cooling to offer significant improvements in reactor safety, operation, fuel cycle economics, environmental protection, and safeguards. The plans for demonstrating the IFR fuel cycle, including its waste processing options, by processing irradiated fuel from the Experimental Breeder Reactor-II fuel in its associated Fuel Cycle Facility have been developed for the first refining series. This series has been designed to provide the data needed for the further development of the IFR program. An important piece of the data needed is the recovery of TRU material during the reprocessing and waste operations.

INTRODUCTION

The Integral Fast Reactor is an innovative liquid metal reactor concept that is being developed by Argonne National Laboratory. It takes advantage of the properties of metallic fuel and liquid metal cooling to offer significant improvements in reactor safety, operation, fuel cycle economics, environmental protection, and safeguards (1). Many of the reactor-specific concepts have already been demonstrated with the Experimental Breeder Reactor II (EBR-II) at Argonne-West. The fuel cycle, including waste processing, is being developed at Argonne in Illinois with nonirradiated materials and modelled with thermodynamic data. Based on this work , the plans for demonstrating the IFR fuel cycle by processing irradiated EBR-II fuel in its associated Fuel Cycle Facility (FCF) have been developed. The objective of the FCF demonstration is to establish the technical and economic viability of the IFR Pyroprocessing System including transuranic (TRU) recycle, recycled fuel fabrication, and waste form preparation.

ELECTROREFINING

The spent fuel from EBR-II will be reprocessed by a pyrochemical method employing molten salts and liquid metals in an electrorefining operation at 500°C. Uranium and the TRU elements are electrochemically separated from the fission products in an electrorefiner and then fabricated into new fuel assemblies. The base molten salt for these operations is the eutectic of LiCl-KCl, and the base liquid metal is cadmium (2). To facilitate the reprocessing and recovery of actinides, actinide chlorides are also present in the salt. The FCF electrorefiner is a 101.6 cm diameter vessel with 30.5 cm of salt covering 15.2 cm of cadmium. Figure 1 is a schematic of the vessel.
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MASTER

With this system, chopped spent fuel is loaded into the electrorefiner in baskets. The fuel is

electrochemically dissolved into the system in an operation in which the baskets (anode baskets) are the anodes and either the cadmium pool or another electrode in the salt phase is the cathode. Electrochemical processes are also used to recover the uranium and TRU elements. Either the anode baskets or the cadmium pool serve as the anode for this operation. Uranium free of TRU material can be collected on steel electrodes (solid cathodes), and TRU materials can be codeposited with uranium in liquid-cadmium cathodes. A liquid-cadmium cathode is a ceramic crucible containing molten cadmium which can be lowered into the salt phase. The cadmium in the crucible is at cathodic potential. Because of the chemical activities of the TRU elements in cadmium, they can be easily deposited with uranium in liquid-cadmium cathodes but not on solid cathodes (3).

Assuming that no accountability or safety issues arise, fuel can be reprocessed in the FCF electrorefiner until the 6 kW fission product energy generation limit for the vessel is closely approached, the impurity levels in the recovered actinide products are too high for fuel production, or the composition of the salt has been changed so that its melting point is near the operating temperature. When one of these limits is reached, the salt and metal phases in the electrorefiner are treated to remove some of the fission products before more fuel is processed. An operating strategy for the first fuel refining series in FCF has been developed and evaluated. The computer code PYRO (4), developed by J. P. Ackerman of the Chemical Technology Division at Argonne in Illinois, has been used to model the electrorefiner operations for this campaign which includes the following four phases: start-up, irradiated fuel, actinide drawdown, and waste fission product removal.

Start-up Operations

The start-up operations consist of first loading the electrorefiner with the eutectic salt and cadmium and heating the system to 500°C. Salt treatment operations are then performed to lower the moisture and oxygen contents in the system. This operation is designed to decrease the actinide losses once they are placed in the system. Depleted uranium metal is then added to the system and oxidized to charge the salt phase with UCl_3. Stability testing is performed to ensure that the actinide concentration in the system remains constant and is not adversely affected by system contaminants. After the stability of the system is established, operations are performed with depleted uranium to test the equipment and operating procedures. The system is next charged with cold plutonium metal for further testing before irradiated fuel is added to the system. At the end of the start-up phase, the actinide concentration (UCl_3 and $PuCl_3$) in the salt will be approximately 2 mole percent, and the $PuCl_3$ to UCl_3 ratio in the salt will be 2 to 1.

Irradiated Fuel Operations

After the start-up phase is complete, the typical operations with irradiated spent fuel begin. The reference fuel for the IFR program is a ternary alloy of uranium, plutonium, and zirconium. Most of the spent fuel available for reprocessing is a uranium-zirconium binary alloy from EBR-II. In order to demonstrate the recovery of plutonium in the presence of large quantities of fission products, ternary fuel will be simulated by reprocessing batches of irradiated binary fuel mixed with cold plutonium metal. The loading for these operations consists of 13 kg of irradiated binary fuel and 5 kg of plutonium metal. From each 18 kg loading, two solid cathode products and two liquid cathode products are recovered. The anticipated heavy metal products from each of these operations, based on the campaign simulation with PYRO, are given in Table I.

Based on the strategy simulation, fuel can be reprocessed until the energy generation limit for the vessel is approached. Before this limit is reached, reprocessing will be terminated, and the electrorefiner waste operations will begin. Fifteen of the 18 kg (13 kg of irradiated fuel and 5 kg of Pu) batches will be processed prior to waste operations.

WASTE OPERATIONS

Operationally, the goal of the waste operations is to remove a significant fraction of the fission products so that the heat content of the electrorefiner is reduced. The lanthanide fission products are responsible for the bulk of the energy generation in the electrorefiner and are therefore the ones that need to be removed.

Minimizing the loss of TRU material is a goal of the IFR program and is therefore essential to the waste processing demonstration. The TRU material must be removed from the electrorefiner before the lanthanides are removed if the TRU loss in the lanthanide waste stream is to be minimized. The TRU removal occurs during the actinide drawdown operations, which are the first phase of the electrorefiner waste processing operation.

There are a number of options for proceeding after a large portion of the actinides are removed from the electrorefiner. In order to meet the operational goal and the need to demonstrate adequately some of the advanced waste treatment options, the following operations will be performed at the end of the first refining series: 1) actinide drawdown from approximately 7.6 to 2 weight percent in the salt, 2) removal of approximately 80 kg of salt for use in an extractor (an advanced processing option) demonstration, 3) continued actinide drawdown of the remaining material in the electrorefiner, 4) removal of the lanthanide fission products by salt stripping in the electrorefiner, 5) filtering of the salt and cadmium in the electrorefiner to remove particulates, 6) removal of a portion of the salt for treatment with zeolites and eventual waste form production, and 7) reloading the salt with actinide products from the drawdown operation so that reprocessing can resume.

Actinide Drawdown

The first step in the actinide drawdown phase of electrorefiner operations is to remove from the system any actinides that are not present in the salt phase. This step will be accomplished initially by electrotransport from the cadmium pool to solid cathodes. Once the actinide concentration in the cadmium pool becomes small, this operation will become increasingly slow and will be replaced by chemical oxidation of the remaining actinides in the cadmium to their chlorides by the addition of $CdCl_2$ to the system. At this point, only the active metals (alkali, alkaline earth, and lanthanide metals) and the actinides will be present in the salt phase. The noble metals will be in the cadmium phase.

As noted earlier, the first electrorefiner operating campaign has been modelled with the computer code PYRO. The actinide drawdown and waste fission product removal phases have also been modelled with PYRO. The contents of the salt and cadmium phases at the end of the first refining series when all the actinides are present in the salt are given in Table II. PYRO assumes that all the noble metals and zirconium in the fuel segments which are placed in the electrorefiner are released into the cadmium phase, or that there is no retention of these components in the anode baskets. It also assumes that no zirconium is transported with the uranium products.

The actinides are removed from the salt phase with the use of an anode of LiCd and recovered in liquid-cadmium cathodes. For this operation, the anode baskets are loaded with a LiCd alloy (5.8 weight percent lithium and a melting point of 549°C) instead of spent fuel. Two liquid-cadmium cathodes are also used. This operation employs electrochemical and chemical reactions and can be described as occurring in the following steps: 1) the lithium in the alloy chemically reduces any actinide chlorides that contact it to metals, 2) most of the reduced actinide metals adhere to the anode baskets or alloy, 3) the actinide metal at the anode is electrochemically oxidized to the +3 state, and 4) simultaneously with the electrochemical oxidation, actinide chlorides are electrochemically reduced to metals at the liquid-cadmium cathode.

The actinide drawdown operations will continue until the amount of TRU material left in the electrorefiner is expendable. For the purpose of strategy development, the recovery 99.9% of the TRU material input to the electrorefiner has been assumed. Based on the modelled results with PYRO, this goal can be achieved with approximately six LiCd anode operations. Each of the first four operations requires two anodes and two liquid-cadmium cathodes. The last two of the six require only one anode and one cathode. The compositions of the products from these six operations are given in Table III.

The liquid-cadmium cathode products from these operations will primarily be used to recharge the electrorefiner's actinide concentration for the second campaign. The lanthanide concentration in the products from drawdown operations 1, 2, and 3 are low enough that they could be used to make normal subassemblies for EBR-II. Some of the material from the products with higher lanthanide concentrations may be used to make experimental subassemblies to determine the maximum lanthanide concentration that can be tolerated in the reactor fuel.

Because the liquid-cadmium cathodes that are recovered during the actinide drawdown phase are recycled back to the electrorefiner for the next campaign, the quantity of lanthanides in these products will affect the duration of the next campaign. Therefore, an attempt has also been made to minimize the amount of lanthanides in the products. In this proposed strategy, less than 25% of the quantity of lanthanides present in the electrorefiner at the end of the campaign is recycled back to the electrorefiner for the next cycle.

An additional goal of the waste operations is to generate data for developing waste processing methods that might be employed in commercial facilities and for evaluating the waste processing options for the IFR program. Between drawdown operations 3 and 4, a quantity of salt, approximately 80 kg, can be removed from the electrorefiner for demonstrating an advanced waste process option, the extractor system (5). The extractor is a pyrocontactor (high temperature centrifugal contactor) that serves to mix the salt with a U-Cd alloy to recover TRU material. A multi-stage pyrocontactor may be used to recover most of the TRU material from the electrorefiner in a commercial operation. The 80 kg of salt will be used to demonstrate the remote operation of a single-stage pyrocontactor in a high radiation field.

Waste Fission Product Removal

The goal of the waste fission product removal operations is to strip the lanthanide fission products and the remaining actinides from the electrorefiner. From a waste processing position, the removal of essentially all of the TRU material is desirable. At the end of the actinide drawdown operations, 75% of the lanthanides, or approximately 4.0 kg, and 119 g of actinides, or 107 g of TRU and 12 g of uranium, remain in the system. These items are removed using LiCd anodes and liquid-cadmium cathodes as with the actinide drawdown operations.

The present waste processing strategy calls for three LiCd anode operations each using two anodes and two cathodes to remove the remaining lanthanides and actinides from the electrorefiner. The resulting products from these operations are depicted in Table IV. These six products, two from each of the three operations, are part of the metal waste stream from the electrorefiner. They will eventually be combined with the other metal wastes and placed in a stable matrix for disposal. Most likely the bulk of the cadmium in the products will be distilled off and at the same time the waste will be alloyed with copper-aluminum to provide a stable matrix and dissipate the fission product heat (5).

The waste fission product removal operations in the electrorefiner will serve to demonstrate the stripping process that will be needed for a commercial fuel cycle facility. In such a facility, this operation may occur in a vessel separate from the electrorefiner in order to provide a larger contact area between the salt and the reductant alloy, but for demonstration purposes, the electrorefiner vessel will be adequate.

Filtration Operations

After the stripping operation, the noble metal fission products and any remaining zirconium from the fuel matrix can be removed. Filtration is the reference position for the removal of noble metals from the electrorefiner. After the first campaign, the quantity of noble metals and zirconium in the system will probably not be enough to cause operational problems, but removing them may still be desirable to demonstrate the process. If the noble metals are to be removed by filtration, the bulk of the zirconium will probably need to be removed first since it appears to form a "sticky" intermetallic with cadmium that may inhibit pumping the liquids through a filter (5).

The recovery of zirconium from the electrorefiner is still being developed. The zirconium does appear to be capable of electrotransport and recovery on solid cathodes (5). In fact, the bulk of it may be removed on cathodes with the actinides during the typical operational and actinide drawdown phases. If not, the zirconium will need to be removed from the system, probably by electrotransport, prior to filtration.

Once the zirconium is out of the system, the filtration operations occur as follows: 1) the pump and filter system is placed in the electrorefiner with the inlet of the apparatus positioned so that only the salt is pumped, 2) the salt phase is pumped and filtered thoroughly, 3) the pump inlet is lowered to the cadmium phase, 4) the cadmium phase is pumped and filtered thoroughly, and 5) the pump and filter apparatus is removed from the system with the filter housing still full of cadmium. Filtering the salt before the cadmium phase allows the cadmium to flush the salt, which still may contain some TRU chlorides, out of the apparatus. Leaving cadmium in the filter housing after the operations serves to lessen the build-up of the soluble noble metal fission products in the cadmium.

At the end of the operation, the filter housing contains the insoluble noble metals and cadmium with some dissolved noble metals. These components will eventually be retorted to separate the cadmium which will be recycled. The noble metals will be combined with the cladding hulls and metal waste stream from the waste fission product removal operations and placed in a stable matrix for characterization to support the technical evaluation and waste form licensing (5).

Because of the issues associated with the removal of the noble metals and zirconium from the electrorefiner, tests will also be performed to examine the retention of these elements in the anode baskets during the dissolution operations. The use of fine mesh screens to cover the baskets will be explored in either the FCF electrorefiner or other small-scale systems. If these tests are successful, the electrotransport of zirconium and filtration operation may be eliminated in future designs.

After the stripping and filtration operations, a portion of the salt, approximately 100 kg, will be removed from the electrorefiner and used to make waste formations for stability tests. The current plan is for it to be run through a zeolite column which will sorb and stabilize a number of the more active fission products (5). Additionally 10 to 20% of the salt will be occluded. The salt that passes through the zeolites can be reused in the electrorefiner. The zeolite will be processed into a stable waste form that will be characterized.

Soon after the demonstration of the stripping operations, stability testing of salt and metal waste formations made with real fission products will begin, and the initial electrorefiner waste demonstration work will be complete. It will now be reloaded with actinides. The products removed during the actinide drawdown operations can be used to charge the salt to the appropriate actinide concentration and plutonium to uranium ratio. Once the salt is reloaded, the second reprocessing series can commence.

SUMMARY

During the first refining series in FCF, irradiated fuel is processed with plutonium metal to demonstrate the IFR fuel cycle and provide ternary fuel for EBR-II. Additionally, much of the technical data needed for developing a commercial IFR fuel cycle are acquired; these include the following: 1) the heavy metal processing rate, 2) the deposit rates on the solid and liquid cathodes, 3) the fission product carry-over for both cathodes, 4) the accountability capabilities, and 5) the characteristics of the process and waste streams leaving the electrorefiner.

For the waste treatment demonstration after the first refining series, the salt and metal phases are initially treated in the electrorefiner to remove essentially all the uranium and TRU material. The actinides are removed by a combination of chemical reduction and electrotransport operations. The recovered actinides are used to charge the salt for the second processing series. Additionally, electrorefiner salt is used to test more advanced waste treatment methods including a pyrocontactor extractor.

Next, many of the rare earth fission products are removed from the system as metals in a similar operation. Zirconium, which is used as an alloy in the metallic fuel, can also be removed electrochemically and recycled. The noble metal fission products, which are distributed primarily as insolubles in the metal phase of the electrorefiner, are to be removed by filtration and retorting. The zirconium and noble metal removal operations may be eliminated in future systems by retaining these elements in the anode baskets. Excess salt and metal are also removed from the system. Therefore, the primary wastes produced from the electrorefining operations are excess salt and a metal waste stream, each containing fission products but relatively little TRU material. The waste materials are then stabilized in an appropriate matrix for final waste disposal.

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DISCLAIMER

Table I

Products from the Typical Operating Cycle

PRODUCT TYPE	NUMBER OF BATCHES	URANIUM (kg/batch)	PLUTONIUM (kg/batch)
Solid Cathode	2	5.9	-
Liquid Cathode	2	0.65	2.5

Table II

Electrorefiner Contents After the First Campaign

ELEMENT(S)	SALT PHASE (kg)	CADMIUM PHASE (kg)
URANIUM	7.6	0.0
PLUTONIUM	24.3	0.0
LANTHANIDES	5.3	0.0
NOBLE METALS	0.0	2.1
ZIRCONIUM	0.0	37.4
TOTAL	442.3	1049.6

Table III

Cathode Products from the Actinide Drawdown Operations

OPERATION NUMBER	PLUTONIUM (kg)	URANIUM (kg)	RARE EARTHS (kg)	PRODUCT TOTAL (kg)
1 - (2 LCCs)	5.7	1.4	0.017	7.2
2 - (2 LCCs)	5.4	1.8	0.024	7.3
3 - (2 LCCs)	5.4	1.8	0.041	7.2
4 - (2 LCCs)	5.1	1.7	0.12	7.0
5 - (1 LCC)	2.2	0.78	0.60	3.5
6 - (1 LCC)	0.40	0.083	0.47	0.95
TOTAL	24.2	7.6	1.27	33.1

Table IV

Waste Fission Product Removal Products

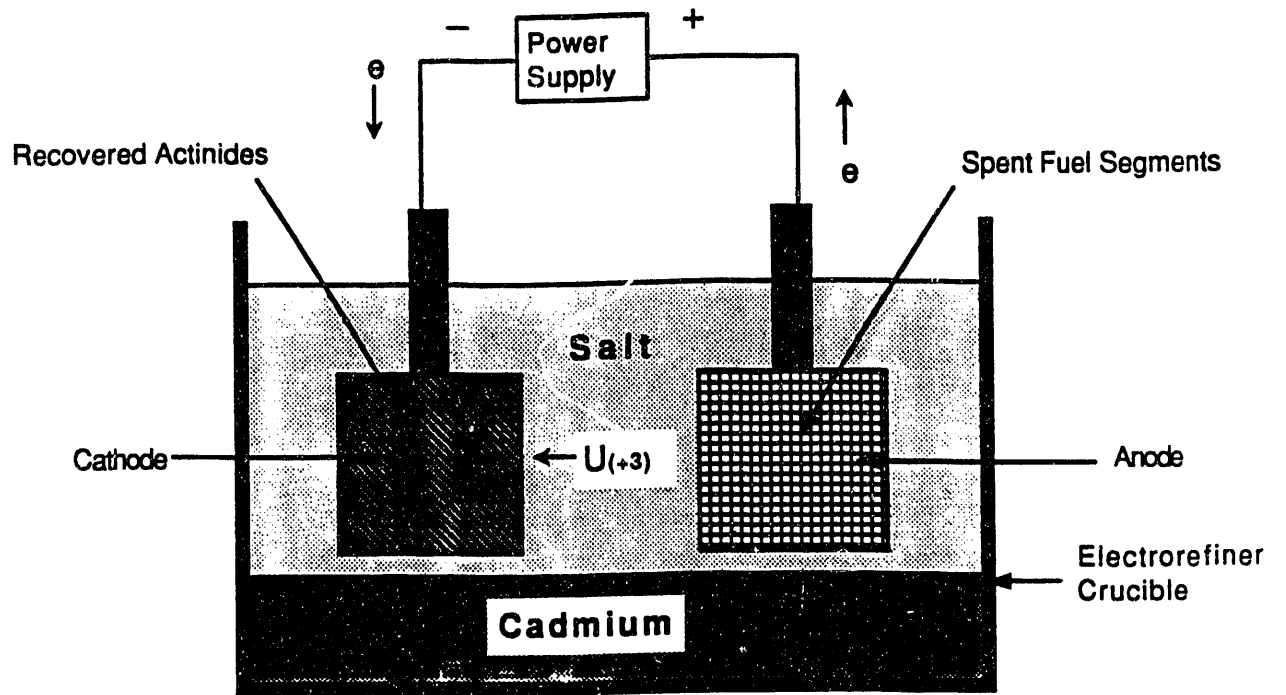| OPERATION NUMBER	PLUTONIUM (kg)	URANIUM (kg)	RARE EARTHS (kg)	PRODUCT TOTAL (kg)
1 - (2 LCCs)	0.099	0.011	1.2	1.4
2 - (2 LCCs)	0.008	0.000	1.3	1.3
3 - (2 LCCs)	0.000	0.000	1.3	1.3

Fig. 1. Electrorefiner Schematic

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