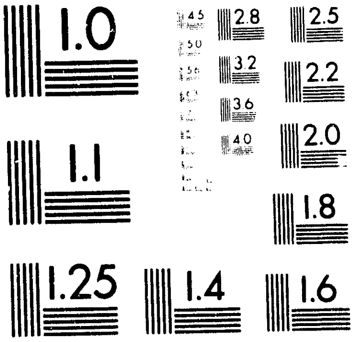
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DEVELOPMENT OF IFR PYROPROCESSING TECHNOLOGY*

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DEVELOPMENT OF IFR PYROPROCESSING TECHNOLOGY

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ABSTRACT

A metallic fuel alloy, nominally U-20Pu-10Zr, is the key element of the IFR fuel cycle. This metallic fuel permits the use of an innovative reprocessing method, known as "pyroprocessing," featuring fused-salt electrorefining of the spent fuel. Electrorefining separates the actinide elements from fission products, without producing a separate stream of plutonium. The fuel product is contaminated with the higher actinides and with a minor amount of rare earth fission products, making it self-protecting and thus diversion-resistant while still perfectly suitable as a fuel material in the fast spectrum of the IFR core.

I. INTRODUCTION

The Integral Fast Reactor (IFR) fuel cycle[1] is based on the use of a metallic fuel alloy, with nominal composition U-20Pu-10Zr. This fuel system offers excellent high-burnup capabilities, with test fuel having been carried to burnups in excess of 20 atom % in EBR-II irradiations, and to peak burnups over 15 atom % in FFTF. The metallic fuel possesses physical characteristics, in particular, very high thermal conductivity, that facilitate a high degree of passive inherent safety in the IFR design. The fuel has been shown to provide very large margins to failure in overpower transient events. Rapid overpower transient tests carried out in the TREAT reactor have shown that the IFR fuel can withstand up to 400% overpower conditions before failing. An operational transient test conducted in EBR-II at a power ramp rate of 0.1% per second reached its termination point of 130% normal power without any fuel failures. The IFR metallic fuel also exhibits superior compatibility with the liquid sodium coolant; intentionally defected fuel pins have been operated in EBR-II for over 230 days beyond the point of cladding breach without the release of fuel material or solid fission products into the primary coolant.

Equally as important as the performance advantages offered by the use of metallic fuel is the fact that this fuel system permits the use of an innovative reprocessing method, known as "pyroprocessing," featuring fused-salt electrorefining of the spent fuel. Development of the IFR pyroprocess has been underway at the Argonne National Laboratory for over five years, and great progress has been made toward establishing a commercially viable process. Pyroprocessing offers a simple, compact means for closure of the fuel cycle, with anticipated significant reductions in fuel cycle costs.

II. PYROPROCESSING

Pyroprocessing refers to the complete set of unit operations required to recover actinide elements from spent fuel and recycle them to the reactor for use as fuel materials. In the case of the IFR spent fuel, these operations begin with the dismantling of the irradiated fuel assembly and the removal of individual fuel rods. These fuel rods are sent to a chopper, where they are chopped into short (typically, 6.5 mm) lengths. The chopped fuel rod segments are loaded into perforated steel baskets and placed in an electrorefiner. The operation of the electrorefiner will be described in detail below; it performs the task of separating the actinide elements from the fission products present in the spent fuel. The process is the same as the electrorefining process used for many years in the minerals industry: an impure metal is made the anode, and it is deposited at a cathode in a condition of greater purity by electrotransport through a suitable electrolyte. In the IFR electrorefiner, virtually pure uranium is collected at a solid mandrel cathode and a mixture of plutonium, americium, neptunium, curium, uranium, and some rare earth fission products is collected at a liquid cadmium cathode suspended in the electrolyte salt. The cathode deposits are recovered after the desired amount of material has been collected and then sent to a cathode processor, which is basically a high-temperature vacuum furnace. The deposits are consolidated in the cathode processor by melting; in the process, any volatile materials that were included in the cathode deposits are removed by vaporization. This includes the electrolyte salt, in the case of the solid mandrel uranium deposits, and cadmium, in the case of the liquid cadmium cathode deposits. The distillates from the process crucible are transported to the condenser region of the cathode processor, where they are collected for recycle to the electrorefiner. The metal ingots resulting from the cathode processing operation are free of unwanted impurities and become the feed material for the next operational step, injection casting.

The function of the injecting casting system is to obtain the appropriate blend of uranium, plutonium, minor actinides, and zirconium and then cast the fuel alloy into slugs suitable for loading into new fuel rods. The fuel batch is induction-melted under vacuum and homogenized, after which the system is pressurized and the fuel alloy is injected into closed-end molds, which are rapidly cooled. The fuel-bearing molds are then sent to the fuel pin processing step; there, the molds are removed, then the fuel slugs are cut to length, inspected, and inserted into fresh fuel pin cladding that also contains a small amount of sodium for thermal bonding. The top end caps for the new fuel rods are then welded closed, and the bond sodium is distributed along the length of the fuel slug. Another inspection step follows, and the accepted fuel pins are loaded into bundles and installed in new fuel subassembly hardware for insertion into the reactor.

All of these operations are performed remotely, in a highly shielded hot cell facility, because the decontamination factor for fission products in the fuel product is purposely kept low to provide self-protection for the fuel and thus afford a high degree of diversion resistance to the nuclear materials contained therein. Details of the pyroprocess equipment and the plans for demonstration of this process in the Fuel Cycle Facility at the Argonne-Idaho site have been reported previously by Battles and colleagues.[2] This demonstration is planned to begin in September, 1993 and extend for several years. The purpose is to verify the technical and economic feasibility of the IFR fuel cycle.

III. THE ELECTROREFINING STEP

Electrorefining is the key step in the pyroprocess, because it is at this point that the actinides are recovered and separated from the fission products present in the spent fuel. The process is shown schematically in Figure 1. Electrorefining is carried out in a steel vessel, with the current engineering-scale units being about 100-cm in diameter and 100 cm high. A 15-cm thick layer of cadmium (melting point 321°C) is placed at the bottom of the electorefiner. Overlying this cadmium layer is a 30-cm layer of the electrolyte salt, a eutectic mixture of LiCl and KCl (melting point 350°C). The cell is operated at a temperature of 500°C. The chopped spent fuel segments are placed in perforated steel anode baskets and lowered into the electrolyte salt. For startup operations, $CdCl_2$ is added to the electrolyte and oxidizes a certain quantity of the elements in the spent fuel to their chlorides, with typical reactions being

$$2U + 3CdCl_2 = 2UCl_3 + 3Cd$$
$$2Pu + 3CdCl_2 = 2PuCl_3 + 3Cd$$
$$Sr + CdCl_2 = SrCl_2 + Cd$$
$$2Y + 3CdCl_2 = 2YCl_3 + 3Cd.$$

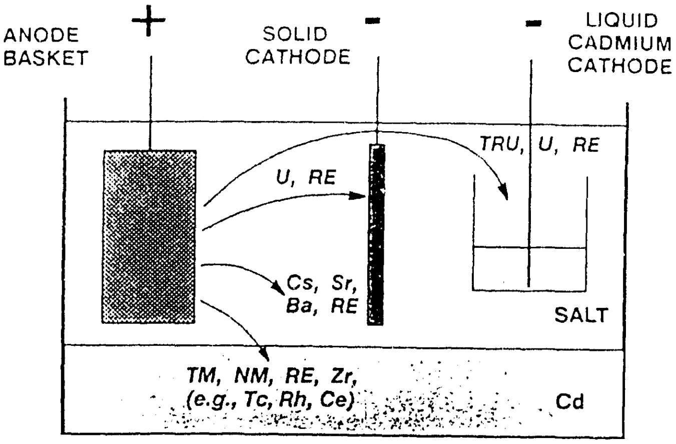

Figure 1. Schematic representation of the IFR electrorefining process. TRU: transuranic elements; RE: rare earth fission products; TM, NM: transition metal and noble metal fission products.

The chloride electrolyte system was selected for the reason that the stabilities of chloride compounds of interest are arranged in a particularly convenient manner. As seen in Table I, the free energies of formation of the various chlorides of interest can be separated into three groupings: high, intermediate, and low stabilities. The chlorides of the alkaline earth and alkali metal fission products, as well as most of the rare earth fission products, are highly stable and tend to remain in the salt phase. The chlorides of the transition metals are relatively unstable, so that these fission products tend to favor the cadmium phase. The actinide elements and zirconium are in a range of intermediate stability, which means that they can be partitioned between the salt and metal phases and thus subjected to electrotransport.

The cadmium chloride oxidation process establishes a sufficient concentration of actinide ions in the salt that electrotransport can be sustained, and a potential of about one volt is then applied between the solid cathode (a simple steel rod) and the anode. Uranium is electrotransported to the solid cathode at a rate of about 3 g per ampere-hour and collected in the form of a dendritic deposit containing a small amount of occluded electrolyte salt. Any dendrites which break off fall into the cadmium pool at the bottom of the electrorefiner, from which they can be recovered simply by making the cadmium pool anodic and transporting the uranium from the pool to the solid cathode. Plutonium cannot be deposited on the solid cathode, because the chlorides of plutonium and uranium are in equilibrium according to the reaction,

$$UCl_3 + Pu = U + PuCl_3 .$$

Because the chloride of plutonium, per Table I, is more stable than the chloride of uranium, and because both chlorides of uranium and plutonium are present in the electrolyte salt, any plutonium metal which tends to deposit

Table I. Free Energies of Formation of Chlorides at 500°C, kcal/g-equivalent chlorine; shaded area indicates elements that are amenable to electrotransport in the IFR electrorefining process.

Compound	$-\Delta G_f^o$	*Compound*	$-\Delta G_f^o$
$BaCl_2$	87.9	$CmCl_3$	64.0
CsCl	87.8	$PuCl_3$	62.4
RbCl	87.0	$NpCl_3$	58.1
KCl	86.7	UCl_3	55.2
$SrCl_2$	84.7	$ZrCl_2$	46.6
LiCl	82.5	$CdCl_2$	32.3
NaCl	81.2	$FeCl_2$	29.2
$CaCl_2$	80.7	$NbCl_5$	26.7
$LaCl_3$	70.2	$MoCl_4$	16.8
$PrCl_3$	69.0	$TcCl_4$	11.0
$CeCl_3$	68.6	$RhCl_3$	10.0
$NdCl_3$	67.9	$PdCl_2$	9.0
YCl_3	65.1	$RuCl_4$	6.0

on the solid cathode immediately reacts with UCl_3 and the reaction is driven strongly to the right. In order to make the reverse reaction operate and enable the collection of plutonium (and the minor actinides Am, Np, and Cm, which behave like plutonium), it is necessary to reduce the activity of Pu. This is done by increasing the Pu:U concentration ratio in the salt to a value greater than 2-3, and then electrotransporting Pu and the minor actinides to a liquid cadmium cathode where they form intermetallic compounds with cadmium. This cathode consists of a ceramic crucible suspended in the salt phase, containing a small amount of liquid cadmium at the bottom, to which electrical contact is made. The Pu, Am, Np and Cm deposit as intermetallic compounds (such as $PuCd_6$) at the interface between the cadmium and salt in the ceramic crucible. Collection efficiencies close to 100% have been achieved in laboratory-scale tests of the liquid cadmium cathode. A typical liquid cadmium cathode deposit contains approximately 3 kg Pu and minor actinides, together with a small quantity (several hundred ppm) of the rare earth fission products. In the present electrorefiner design configuration, a solid cathode deposit of 10 kg uranium per electrode is obtained in a period of about 24 hours. Efforts are underway to optimize the anode/cathode geometry, so that the deposition rates can be increased by factors between five and ten. This is considered to be an essential step in the commercialization of this technology.

IV. A SYMBIOTIC LWR-IFR SYSTEM

The spent fuel discharged from currently operating light water reactors (LWRs) represents a valuable resource for use in future power generation. By the year 2010, there will be over 40,000 metric tons of LWR spent fuel in storage at reactor sites or in monitored retrievable storage. If the decision is made to proceed with the direct disposal of LWR spent fuel in a geologic repository, and if the current reactors continue to operate for the duration of their licenses, and if the first repository is opened by the scheduled date of 2010, the legislated capacity of the first repository will be exceeded before the projected end of spent fuel emplacement. Thus, the preparation of a second repository, possibly with similar costs and similar siting problems, would be required shortly after the first repository goes into operation. At issue is the advisability of a policy based on the disposal of all LWR spent fuel. If the nuclear generating capacity in the U.S. is to increase in accordance with Department of Energy projections, then the fuel resources available in spent LWR fuel could make a significant contribution to the realization of these projections. This fuel contains about 1% transuranic elements that can be used effectively as fuel material in the IFR, where the fast neutron energy spectrum promotes the efficient fissioning of these elements. The spent fuel also contains about 96% uranium, having a ^{235}U content slightly greater than that in natural uranium; this uranium could be re-enriched and recycled to LWRs, and a portion of it could be used as makeup feed to the IFR, either as a blanket material or as makeup core fuel material. Actinide recycle permits sustained growth in nuclear generating capacity without severe environmental penalties from increased uranium mining and milling, and without economic penalties if the process proves to be as inexpensive as expected. The transuranic content of the current annual U.S. output of LWR spent fuel, for example, is sufficient to provide adequate fuel to support the startup of about 1,500 MWe IFR generating capacity yearly.

V. RECOVERY OF ACTINIDES FROM SPENT LWR FUEL

In a symbiotic LWR-IFR fuel cycle system, it is desirable that the processes for treating the spent fuel from both reactor types be compatible. The commonality of equipment and processes, as well as the production of a similar high-level waste form, would all serve to improve the economic posture of the system. Argonne National Laboratory has been working to develop a method for processing LWR spent fuel that is fully compatible with the IFR system. A summary of the progress to that end has recently been reported by Pierce *et al.*[3] and Laidler.[4] Basically, the process for recovering actinides from spent LWR fuel involves the reduction of the LWR oxide fuel to metallic form, followed by the separation of fissior products and the separation of the bulk of uranium from the transuranic elements. More details are provided in the paper by McPheeters *et al.* [5] at this conference. A combined IFR-LWR pyroprocessing flowsheet can then have the general form shown in Figure 2.

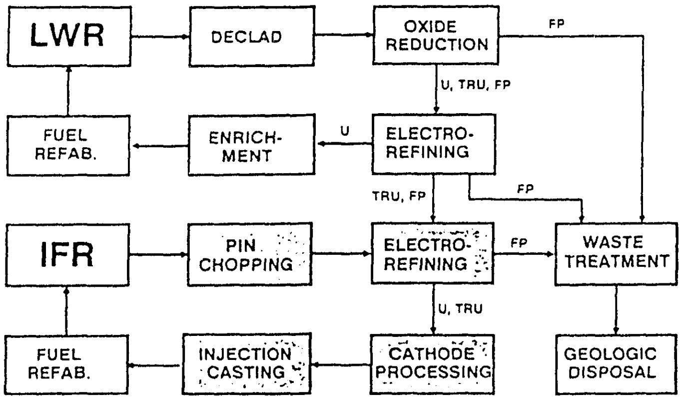

Figure 2. Combined IFR/LWR flowsheet. TRU: transuranic elements; FP: fission products.

VI. TREATMENT OF DOE SPENT FUEL

The U.S. Department of Energy currently holds a large inventory of unprocessed spent fuel, arising from decades of operation of special test reactors, research reactors, and defense materials production reactors. The spent fuel inventory includes about 100 distinct fuel types, with enrichment levels from natural to highly enriched uranium. Licensing of this wide variety of spent fuel for direct repository disposal could prove to be prohibitively expensive, should it be necessary to qualify each individual fuel type for repository acceptance.

The IFR-LWR pyroprocess can be applied with great effect to the problem of DOE spent fuel disposition. Because the process has been developed for use with metal or oxide fuel, it can be easily adapted for the processing of virtually all of the DOE spent fuel types: metal, oxide, graphite, cermet, matrix, etc. At this time, pyroprocessing appears to be practical for all fuel types except aluminum-based fuels. The latter are perhaps better treated by conventional aqueous methods, because the aluminum tends to form stable intermetallic compounds with the actinide elements and makes their removal more difficult. Pyroprocessing is eminently suited for treatment of all other fuel types, requiring only a modification to the head end of the process to adapt it to each broad fuel class.

The use of pyroprocessing for DOE spent fuel management has a number of benefits: (1) the recovery of actinide elements, such as highly-enriched uranium, for subsequent re-use in power generation; (2) a substantial reduction in packaged waste volume for ultimate disposal; and (3) the production of a common waste form regardless of starting fuel type. Processing can be done with a common basic process, with common equipment and procedures. This would result in greatly-improved economics of waste management. The actinides recovered in the course of pyroprocessing, as in the case of the IFR fuel cycle, are co-deposited so that a separate stream of weapons-usable material is not generated.

VII. WASTE MANAGEMENT

An integral part of IFR pyroprocess development is the treatment and packaging of high-level waste materials arising from the pyroprocess operations, along with the qualification of these wastes for disposal in a geologic repository. This is the first time that a reactor technology development program has had as a major program element the development of high-level waste management operations before the wastes were actually produced.

As spent fuel batches are processed in the electrorefiner, fission products accumulate in the vessel. Fission products of the alkaline earth, alkali metal, and rare earth groups build up in the electrolyte salt phase. The transition metals (more electrochemically noble metals) tend to concentrate in the cadmium pool, remain as a sludge in the anode basket, or remain with the cladding hulls. As these fission products accumulate, the heat load due to their radioactive decay processes increases until it exceeds facility or equipment design limits. At that point, it is necessary to remove the heat-generating elements. First, the heavy metals present in the salt phase are recovered in a form suitable for subsequent reintroduction to the electrorefiner, by a process known as "drawdown." After the drawdown operation, which reduces the heavy metal content in the salt to less than 0.01 weight percent, the salt and metal phases are removed for treatment to recover the remaining TRU elements and remove a sufficient quantity of fission products that the salt and cadmium can be recycled.

The spent salt (the salt phase after drawdown), containing fission products such as Cs, Sr, I, and the rare earth elements, all in the form of chlorides, is first sent to a salt extraction step, where the molten salt is reacted with a liquid U-Cd alloy. The extraction of the TRU elements is carried out in a multi-stage centrifugal contactor at a temperature of 500°C. The (depleted) uranium reduces the chlorides of the transuranic elements, which are present at low concentrations in the salt, with the TRU elements partitioning into the metal phase in metallic form. The TRU-bearing cadmium is returned to the electrorefiner, where the TRU elements are subsequently recovered by electrotransport from the cadmium pool. Initial experiments to characterize the separation efficiency of a single-stage contactor are to commence in the near future.

After extraction of the transuranics, the spent salt is sent to a stripping operation in which the salt is reacted with a liquid Cd-Li alloy, again at a temperature of 500°C. The lithium is a strong reductant and acts to reduce all of the rare earth chlorides present in the salt; the rare earths concentrate in the cadmium phase, which becomes a waste material, and most of the salt can be recycled to the electrorefiner until the decay heat load builds up to such a level that the alkaline earth and alkali metal fission products must also be removed. The removal of the rare earth elements from the salt is necessary to reduce the heat load in the electrorefiner; because the rare earths can be electrotransported with the actinide elements, it is also necessary to keep the rare earth concentration in the salt at comparatively low levels to avoid excessive contamination of the heavy metal product. Experiments with the salt stripper have been recently initiated.

The stripped salt is next sent to an immobilization step, where the molten salt is infiltrated through a zeolite column. The zeolite sorbs the fission products by two processes: ion exchange and occlusion of salt molecules in the molecular cage of the zeolite structure. The effluent salt is virtually free of fission products and can be recycled to the electrorefiner. Initial measurements have shown that high fission product loadings in the zeolite can be obtained. The release of fission products from the zeolite-based waste under conditions of groundwater impingement appears to be acceptably small.

The spent cadmium from the electrorefiner and from the salt stripping step is also treated in the IFR pyroprocess, with these two streams combined in a partitioning process where the fission product-bearing cadmium is contacted with a molten aluminum-copper alloy having little solubility for cadmium. The fission products tend to precipitate in the Al-Cu phase as intermetallic compounds, leaving the cadmium phase virtually free of fission products. The cadmium is recovered by retorting and then recycled to the electrorefiner. The Al-Cu alloy, now containing the transition metal, rare earth, and noble metal fission products, can be cast directly into a waste container for repository disposal.

An alternative version of the metal waste form, also under active development at this time, incorporates the cladding hulls as the matrix material. Depending on starting fuel type, this material can be either stainless steel or zirconium alloy. With this approach, a substantial fraction of the original fuel assembly hardware can also be included in the waste form while the packaged waste volume for disposal is minimized.

Although the IFR waste treatment and packaging processes are at a relatively early stage of development, they appear to be technically feasible and fully amenable to waste volume minimization. These processes will be developed and demonstrated at a large scale with simulated fission products, with confirmation of the processes carried out on a somewhat smaller scale as part of the IFR Fuel Cycle Demonstration.

VIII. CONCLUSIONS

Development of the method for pyroprocessing of spent fuel from the Integral Fast Reactor (or Advanced Liquid Metal Reactor) is progressing well and is approaching the technology demonstration phase, in which recycle will be demonstrated with irradiated fuel from the EBR-II reactor. Methods for recovering actinides from spent LWR fuel are at an earlier stage of development but appear to be technically feasible. The utilization of fully compatible processes for recycling valuable spent fuel materials promises to provide substantial economic incentives for future applications of the pyroprocessing technology, perhaps including the treatment of DOE spent fuel for disposal.

IX. ACKNOWLEDGMENT

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