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**RECENT ADVANCES DURING THE TREATMENT
OF
SPENT EBR-II FUEL**

By

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ABSTRACT

Several recent advances have been achieved for the electrometallurgical treatment of spent nuclear fuel. In anticipation of production operations at Argonne National Laboratory-West, development of both electrorefining and metal processing has been ongoing in the post-demonstration phase in order to further optimize the process. These development activities show considerable promise. This paper discusses the results of recent experiments as well as plans for future investigations.

I. BACKGROUND

The electrometallurgical treatment of Experimental Breeder Reactor-II (EBR-II) spent nuclear fuel comprises a set of operations designed to neutralize the bond sodium and produce a low enriched uranium product.¹⁻³ The reactive sodium, essential for heat transfer purposes during reactor operations, is easily incorporated into the process chemistry of the treatment technology. Metallic uranium fuel is initially separated from radioactive fission products by an electrorefining operation although additional recoveries are realized by further processing.⁴⁻⁷ The fission products are segregated into two waste forms during treatment operations: a glass-bonded sodalite ceramic waste form and a stainless steel-based metallic waste form.⁸ A limited demonstration of the electrometallurgical treatment process was initiated in June 1996 and concluded recently.

Spent fuel treatment commences with the dismantling of fuel assemblies into individual elements. Elements are chopped into segments by either a solenoid-driven or pneumatic press (Fig. 1) depending on the fuel type, driver or blanket, respectively. The segments are then loaded into an anode assembly which

contains up to nine perforated baskets depending again on the fuel type. The anode assembly is installed into the electrorefiner (Fig. 1) commensurate with the fuel type; Mark-IV for driver and Mark-V for blanket. Although the two electrorefiner vessels are identical in design, the electrode configurations, liquid contents, and process conditions for the two are different.

In the Mark-IV electrorefiner, the anode assembly includes four rectangular fuel dissolution baskets, arranged in a cruciform geometry, to electrochemically dissolve uranium from the chopped fuel segments. The cathode assembly uses a solid steel rod (mandrel) to electrochemically deposit uranium in the form of dendrites. Each electrode, anode or cathode, occupies an individual port. As a consequence, a complete electrochemical cell requires the use of two ports when electrorefining from the fuel dissolution baskets to the mandrel (direct transport mode).

The Mark-IV electrorefiner contains two process liquids, a molten cadmium pool and molten LiCl-KCl electrolyte resting on top of it. During electrorefining with the chopped fuel segments in the fuel dissolution baskets, a fraction of the uranium dendrites are dislodged from the deposit on the mandrel, drop to the cadmium pool, and dissolve. This uranium is retrieved by making the cadmium pool the anode and collecting the uranium on the cathode mandrel (deposition mode).

In the Mark-V electrorefiner, the anode and cathode are collocated in a single module (Fig. 2) so that each of the four ports can contain a complete electrochemical cell. This design was developed to improve the electrorefining rate. The anode-cathode modules (ACMs) consist of curved fuel dissolution baskets concentrically positioned in annular spaces between cathode cylinders. Three concentric cathode cylinders

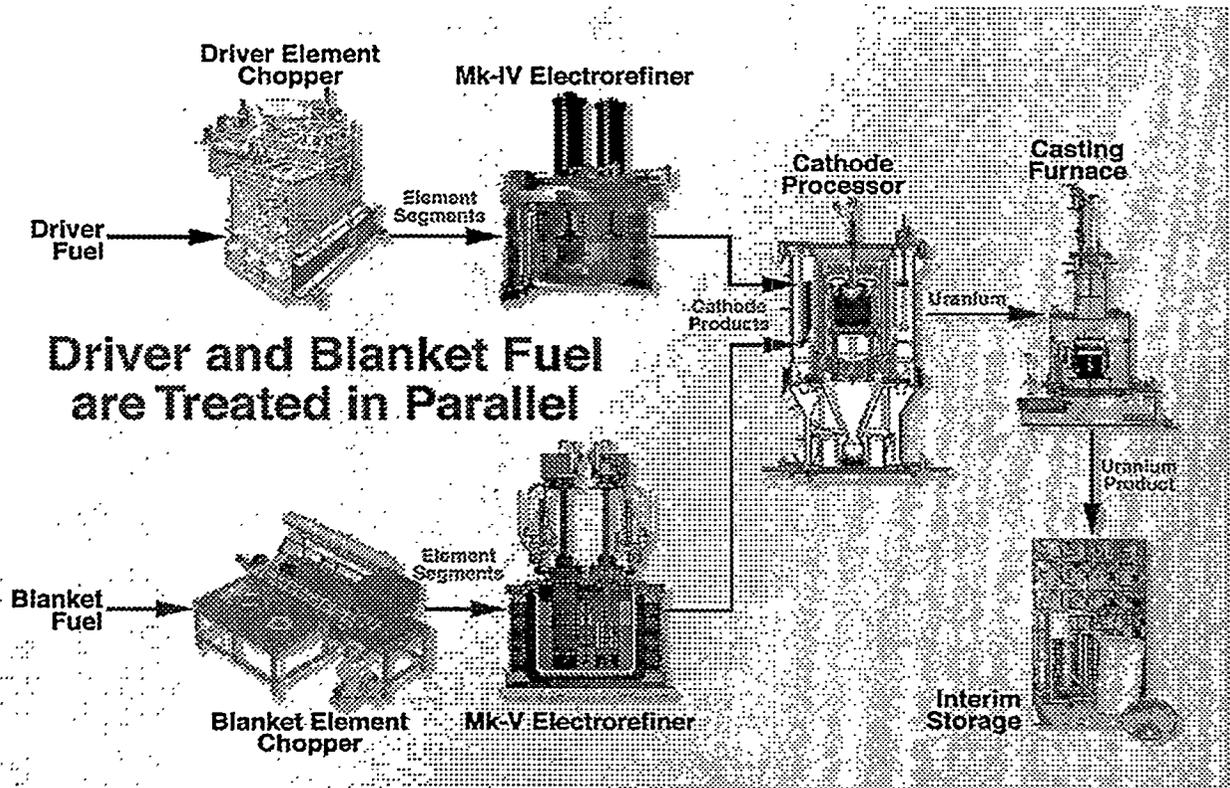


Fig. 1. Process Flowsheet for Electrometallurgical Treatment of Spent Fuel

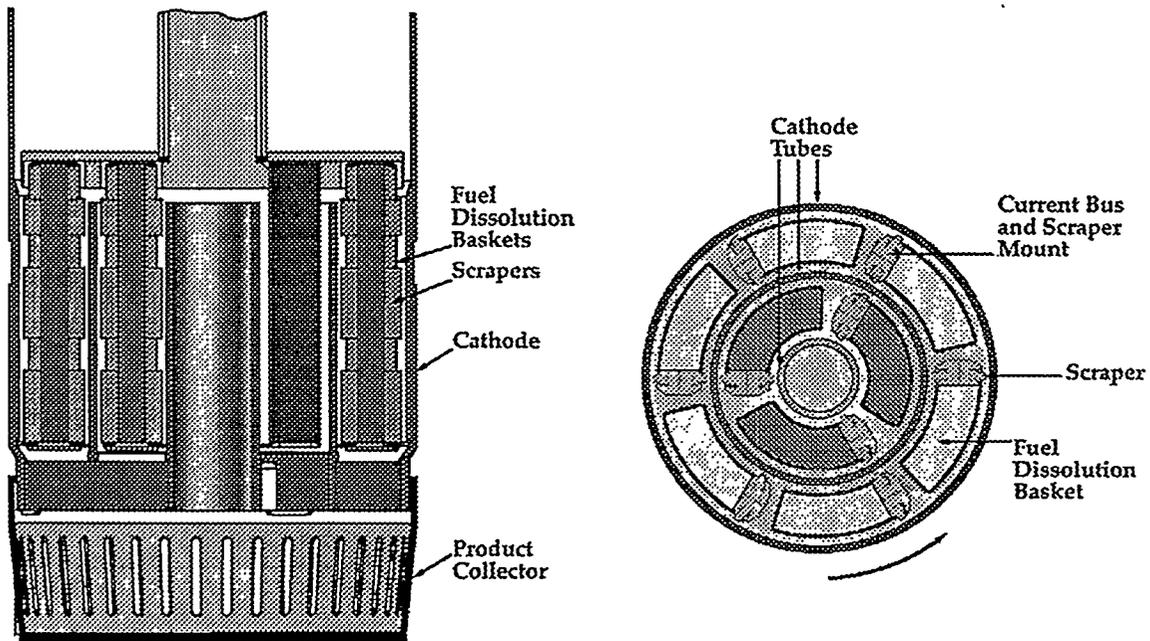


Fig. 2. Anode-Cathode Module with Product Collector for the Mark-V Electrorefiner

are used to form two annular spaces which are occupied by the fuel dissolution baskets. In the inner annulus, there are three baskets while in the outer annulus, there are six. During electrorefining, the fuel dissolution baskets are rotated such that scrapers will shear the depositing uranium off the cathode cylinder surfaces. The sheared deposit falls into a product collector residing directly below the ACM. The Mark-V electrorefiner does not contain a cadmium pool, since the material falls from the cathode cylinder surfaces into the product collector.

The cathode products from both the Mark-IV and Mark-V electrorefiners are primarily uranium metal coated with adhering salt. Final recovery of the uranium is achieved by distilling the chloride salts in a cathode processor by vacuum retort. The cathode processor is an induction-heated furnace capable of temperatures to 1400°C and vacuums to 0.1 Torr. The furnace region contains a passively cooled induction coil and a graphite furnace liner that acts as the susceptor to heat the process materials. Ordinary operation of the cathode processor includes reducing the internal pressure of the vessel to less than 1 Torr and heating to 1200°C. Slight variations to this sequence are employed to maximize the effectiveness of the cathode processor operation.

Upon completion of the cathode processor operation, which includes an adequate cooldown period, the resultant uranium ingot is further processed in a casting operation at 1300°C for sampling purposes. The casting furnace also utilizes a passively cooled induction coil. For the driver stream, depleted uranium is blended with the uranium product during casting to lower the enrichment to less than 20 wt. %. Besides uranium processing, the casting furnace has also been used for the production of irradiated metal waste forms.

The two high-level waste forms, ceramic and metal, incorporate active and noble fission products, respectively. Active fission products are those oxidized to the salt electrolyte while those that do not are considered noble. Once accumulated in the salt electrolyte, the active metals are immobilized in the ceramic waste by occlusion in a zeolite structure. Consolidation of the zeolite with a glass frit is performed using elevated temperatures and/or pressures. The zeolite, upon processing, is converted to the mineral sodalite.

The metal waste form consists of noble fission products, stainless steel cladding hulls, remnant fuel constituents, and additional zirconium alloyed into a cast

ingot. The stainless steel cladding, which encases the spent fuel during reactor operations, is left behind after electrorefining in the anode baskets. Due to the incomplete dissolution of the fuel constituents in the cladding hulls during electrorefining, the metallic waste also contains minor amounts of uranium and other noble fuel alloying agents, such as zirconium and molybdenum. Supplemental zirconium is added to form phase intermetallics that act as a sink for the noble metal fission products.

II. EXPERIMENTAL RESULTS

Following the conclusion of the demonstration activities for spent fuel treatment operations, several recent experimental programs are yielding results worth noting. These results are preliminary and thus subject to further analysis. Following are the recent experimental results for both the electrorefining and metal processing activities.

A. Electrorefining

Experiments involving both the Mark-IV and Mark-V electrorefiners have been continuing through the end of the demonstration. The scope of the demonstration program was to process 100 driver assemblies (~4 kg uranium/assembly) and up to 25 blanket assemblies (~47 kg uranium/assembly). Driver processing in the Mark-IV ceased in June 1999 upon completion of the 100 assemblies. For the Mark-V electrorefiner, sixteen blanket assemblies were treated between November 1998 and January 2000. In addition, two blanket assemblies have been processed in the Mark-IV electrorefiner to augment the Mark-V operations.

As part of the blanket processing demonstration, a one-month throughput of 205 kg uranium was achieved for the Mark-V from mid-July to mid-August 1999. For the month, individual anode processing rates of up to 260 g uranium per hour were accomplished in the Mark-V. The simultaneous operation of up to four ACMs was also demonstrated.

Following the one-month throughput period at the Mark-V electrorefiner, significant improvements to the processing rates were realized as a result of anode agitation experiments. From November 1998 through August 1999, rotation of the anode during electrorefining was unidirectional at about 20 rpm. After August 1999, experiments were performed rotating the anodes both clockwise and counter-clockwise in

rapid succession. This mode of operation, termed anode agitation, yielded processing rates of up to 660 g uranium per hour - an increase of 150%. In addition, the agitation mode reduced the stalling frequency of the anode considerably.

Another dramatic improvement to the Mark-V electrorefiner operations occurred during November 1999. Although processing rates as high as 660 g uranium per hour had been achieved, the product collector container volume limits the mass of product collected. Thus, a higher packing density of the cathode product in the collector is desired to reduce the handling operations. The effective product density in the collector was increased by over 100% (from about 1.1 to 2.4 g/cc) by increasing the current density (mA/cm²) and reducing the uranium concentration in the salt.

For the Mark-IV electrorefiner, the most noticeable improvements in processing rates during the driver campaign were recognized by implementing a dual anode/serial cathode operation. Since multiple ports are available for electrorefining, two anode assemblies (2 ports) can be connected in parallel for a direct transport operation to a single cathode mandrel (1 port). Following the first direct transport and removal of the deposit on the mandrel, a second mandrel is installed to complete the serial operation. Operation in the dual anode/serial cathode mode permitted higher average currents and more efficient workstation utilization.

Recent experiments in the Mark-IV with blanket material have yielded several improvements. The presence and rotation of the anode baskets during deposition runs contributed favorably to the collection efficiency by improving the electrical potential field within the electrorefiner and the convective conditions in the salt, respectively. Experiments have also been performed to minimize electrical shorting of the anode by the addition of scrapers to the anode baskets, which improved detection of the endpoint for fuel dissolution.

B. Metal Processing

In addition to the electrorefining experiments, several metal processing-related test programs have been performed involving both the uranium and metal waste streams. For uranium processing, the programs focused on reducing the ingot radiation readings (R/hr) for the driver product, minimizing graphite crucible failures during cathode processing, and reducing the plutonium content of the blanket product. Two metal waste experiments were performed to simulate a molybdenum-

rich metal waste form that would result from a uranium-molybdenum fuel alloy.

Tests revealed that the top surface of the driver products was enriched in fission product chlorides, particularly Cs-137, due to incomplete distillation of the salt at the cathode processor. The high Cs-137 concentration resulted in elevated radiation readings (>300 R/hr in the storage container) for the ingots. A hold period at 1100°C was initiated near the end of driver program in the cathode processor to enhance the distillation prior to the melting of uranium. Holding prior to the uranium melting point (1132°C) is important to minimize the reaction of the salt with molten uranium. After implementing the 1100°C hold, radiation readings of the driver ingots dropped to less than 2 R/hr in their storage containers.

For the driver program, a single coating of zirconia (ZrO₂) on the graphite cathode processor crucible was sufficient to minimize the reaction of graphite with uranium thus easing removal of the ingot from the crucible.⁷ With the larger cathode processor loads (30-40 kg) experienced during initial blanket processing, the single coating was not adequate as evidenced by coating failures for the first seven batches. Multiple zirconia coatings were applied to the crucible prior to loading of the blanket material in an attempt to reduce the crucible failures. The additional coatings increased the overall quantity of zirconia applied to the crucible from approximately 80 g to more than 200 g. Crucible failures were then reduced significantly (from 100% to about 20% failure rate) throughout the remainder of the blanket program.

In order for more definitive disposition options to be realized for the blanket product, reduction of the plutonium contamination is necessary. A series of experiments were investigated in the cathode processor to reduce the plutonium levels (50-150 ppm) in the blanket product assuming that the plutonium was either metal or chloride. Operating conditions of the cathode processor were adjusted to allow for longer hold times at 1100°C and increased power levels assuming plutonium was a chloride. Little effect on the plutonium concentration was observed for either adjustment. For the plutonium metal assumption, the cathode processor was operated such that the following fluxing reaction could be exploited:



Unfortunately, the plutonium levels for these tests were higher than normal and may be explained by adverse operating conditions for the reaction.

The purpose of recent irradiated testing on the metal waste form was to simulate a molybdenum content (10 to 20 wt. %) equal to that expected from the Fermi blanket fuel, a uranium-molybdenum alloy fuel. Additions of pure molybdenum were made to irradiated blanket cladding hulls to achieve the desired concentrations (10 and 20 wt. %). Both the processing conditions and waste form microstructure were of concern for the molybdenum-rich metal waste castings. Based on chemical analyses of the metal waste ingots, dissolution of the molybdenum into the charge was sufficient for both castings at the reference operating temperature of 1600°C. Although a similar microstructure (Fig. 3) was observed for the 10 wt. % molybdenum metal waste form in terms of major alloy phases, the appearance of a minor phase rich in molybdenum is being investigated further.

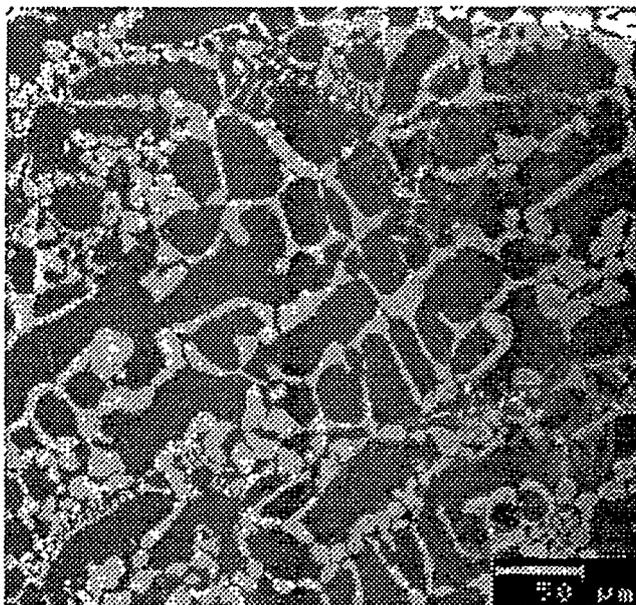


Fig. 3. Micrograph of Molybdenum Metal Waste Form

III. FURTHER INVESTIGATIONS

A limited number of tests have been performed in the Mark-IV electrorefiner recently to assess the variability of cathode mandrel materials. Four different substrates (mild steel, smooth stainless steel, grooved stainless steel, and molybdenum-coated stainless steel) are being studied in terms of collection efficiency. The

reference material through driver processing had been mild steel. Initial results indicate that the stainless steel mandrels show promise although further testing is necessary.

Experiments have been performed to distinguish the influence of the Mark-V electrorefiner and cathode processor on the mechanism of plutonium carry-over to the blanket products. The experiments focused on the processing of plutonium-free materials through equipment previously used for plutonium operations. Unfortunately, the results are not yet available but the degree of plutonium contamination of these products is expected to indicate the location and mechanism of plutonium carry-over.

A high-temperature (1350°C) test has been completed in the cathode processor as a continuation of adjustments to the operating conditions. Results are pending for this experiment. Further testing is planned in the cathode processor to fully investigate the fluxing reaction with the remaining blanket products.

ACKNOWLEDGMENTS

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