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Electrometallurgical Treatment Demonstration At ANL-West

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ABSTRACT

Electrometallurgical treatment (EMT) was developed by Argonne National Laboratory* (ANL) to ready sodium-bonded spent nuclear fuel for geological disposal.[1] A demonstration of this technology was successfully completed in August 1999. EMT was used to condition irradiated EBR-II driver and blanket fuel at ANL-West. The results of this demonstration, including the production of radioactive high-level waste forms, are presented.

I. INTRODUCTION

Within the Department of Energy, there is a quantity of spent nuclear fuel containing elemental sodium that was used within the fuel elements to provide a thermal bond between the fuel matrix and cladding. This fuel was generated during operation of the Experimental Breeder Reactor II (EBR-II) at ANL-West in Idaho and of Fermi I in Michigan. Both were fast reactors using metallic fuel and sodium coolant. Some experimental fuel was also produced as part of testing in the Fast Flux Test Facility (FFTF) at Hanford. Table 1 gives an account of all such fuel. The driver fuel is highly enriched uranium, and the blanket fuel is depleted uranium.

The sodium metal within the fuel matrix is highly reactive. Because of its presence, the fuel is generally believed to not be suitable for direct disposal in a geological repository and to require treatment.[2,3] Argonne National Laboratory has demonstrated the electrometallurgical treatment technology to prepare these fuel types for eventual disposal. During the demonstration, which ran from June 1996 through August 1999, 100 EBR-II driver fuel and 13 EBR-II blanket assemblies were treated. The demonstration of waste forms for stabilizing the fission products and transuranics was part of this project. For the purposes of this paper, the demonstration operations are divided into two areas, treatment operations and high-level waste operations.

Table 1. Sodium-Bonded Spent Nuclear Fuel

Fuel Type	Mass of Heavy Metal (MT)	Storage Location
EBR-II Driver (alloyed w/zirconium)	1.1	ANL-West
EBR-II Driver (Fissium alloy)	2.0	Idaho Nuclear Technology and Engineering Center (INTEC)
EBR-II Blanket	22	ANL-West
Fermi Blanket (alloyed with molybdenum)	34	INTEC
FFTF Test Assemblies	0.25	Hanford

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II. TREATMENT OPERATIONS

A. Process Description

The fuel treatment operations are performed in the Fuel Conditioning Facility (FCF) hot-cell complex at ANL-West. FCF consists of two operating hot cells. Spent fuel is first transferred into a rectangular-shaped, air-filled hot cell where the fuel elements are separated from the fuel assembly hardware using the vertical assembly dismantler (VAD). Intact fuel elements are transferred into the adjacent, annular-shaped, argon-filled hot cell.

In the argon cell, fuel elements are first chopped into segments with an element chopper. These segments are then transferred to the electrorefiners in steel baskets (anode baskets).

Fuel treatment operations in the electrorefiners are based on a process that uses molten salts and liquid metals in an electrochemical operation. The molten salt medium is a solution of LiCl-KCl eutectic and dissolved actinide chlorides, such as UCl_3. For both electrorefining and fuel chopping, separate equipment is used for blanket and driver fuel.

In the electrorefiners, the spent fuel is electrochemically dissolved from the anode baskets, and an equivalent amount of uranium is deposited on a steel cathode. The uranium is separated from the bulk of the fission products and transuranics. Most of the fission products (alkali, alkaline earth, rare earth, and halides) and transuranics accumulate in the salt. The sodium is neutralized by forming non-hazardous NaCl.

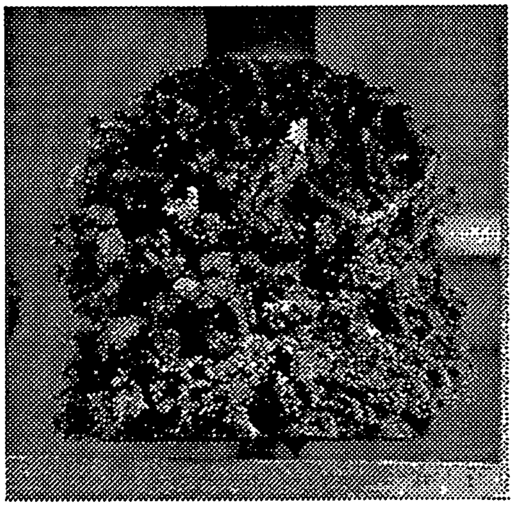

Figure 1. Deposit No. 48 (9.7 kg) from the Treatment of EBR-II Driver Fuel in the Mark IV Electrorefiner

The cathode products from electrorefining operations are further processed to distill adhering salt and to recover uranium. These operations are performed in the cathode processor and casting furnace, respectively. As part of the driver fuel processing, the solid cathode contains highly enriched uranium. Therefore, the recovered uranium metal is blended with depleted uranium to produce a product that is less than 20 percent enriched. The low-enriched uranium product is formed into ingots and placed in interim storage in canisters on the ANL-West site pending a DOE decision on final disposition.

The cladding material is not dissolved in these operations. It is processed into a high-level waste. The fission products which form halides in the electrorefiner salt will be stabilized into a second high-level waste form. The electrorefiner, cathode processor, and waste operations are described in more detail in earlier papers.[4,5,6,7]

C. Demonstration Results

Two types of sodium-bonded fuel, driver and blanket, were treated in the demonstration. The driver fuel (63% U-235) was irradiated to a relatively high burnup (approximately 8 atom percent). The irradiated blanket fuel was depleted uranium with a low burnup (approximately 0.2 atom percent). Results from driver fuel treatment demonstrated the reproducibility of the electrometallurgical process and provided data on fission product behavior. Results from blanket fuel demonstrated high-throughput operations.

Two electrorefiners were used to treat the fuel, the Mark-IV ER for driver fuel and the Mark-V for blanket fuel. The electrorefiner vessels are identical in design. Each has a cover with four 25-cm diameter ports that were used for inserting electrode assemblies. However, the electrode configurations, electrorefiner liquid contents, and process conditions differ for these two electrorefiners. The Mark-V component designs were developed to improve the electrorefining rate since the inventory of blanket fuel is significantly larger than the inventory of driver.

The treatment demonstration with driver fuel began in June 1996. In slightly less than three years, 100 driver assemblies (approximately 410 kg heavy metal) were treated. Ninety deposits of uranium were obtained from the Mark-IV electrorefiner. One of these deposits is pictured in Figure 1. These dendritic deposits were consolidated at the cathode processor and downblended at the casting furnace to yield 40 low-enriched (less than 20% U-235) uranium ingots (1111 kg total).

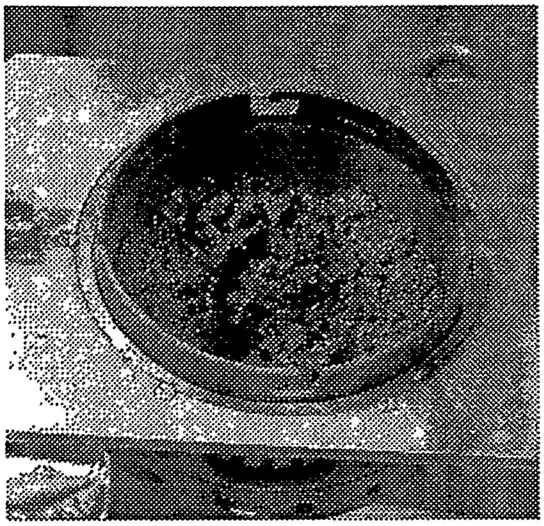

Figure 2. Product Collector from the Treatment of EBR-II Blanket in the Mark V Electrorefiner (4.2 kg)

The majority of the driver assemblies were treated in experiments to characterize the process and to develop unit process conditions that would meet specific success criteria. Process conditions were selected for driver fuel in a three-month repeatability demonstration that began in mid-November 1998. A major goal was to show that the driver fuel could be treated with fixed process conditions at a rate of four assemblies per month (approximately 16-kg heavy metal per month) for three months. The rate obtained was approximately 24-kg heavy metal (HM) per month. The highest driver treatment rate obtained thus far was 33 kg HM per month.

Blanket treatment began in August 1998. At the end of February 2000, eighteen irradiated blanket assemblies (approximately 855-kg heavy metal) were electrorefined. The uranium deposits obtained from the Mark-V electrorefiner, pictured in Figure 2, were further processed in the cathode processor and sampled at the casting furnace.

During blanket treatment operations, a throughput demonstration, which began on July 17, 1999, was conducted for the blanket fuel. The goal was to treat 150 kg HM, at each unit operation, in one month. During the throughput demonstration, heavy metal throughputs at the blanket element chopper, Mark-V electrorefiner, cathode processor, and casting furnace were 164 kg, 205 kg, 207 kg, and 177 kg, respectively.

III. High-Level Waste Operations

A. Introduction

The treatment of spent nuclear fuel for dispositioning by the electrometallurgical technique results in two high-level waste forms, the ceramic waste form and the metal waste form. The ceramic waste form stabilizes the active fission products (alkali, alkaline earths, and rare earths) and transuranic elements. The metal waste form consists of stainless steel cladding, non-actinide fuel matrix material like zirconium, and noble metal fission products. Development of both waste forms has been ongoing at Argonne in Illinois since 1985 as part of both the Integral Fast Reactor program and the EBR-II Spent Fuel Demonstration Program. The demonstration of the electrometallurgical technique included production and testing of irradiated and non-irradiated samples of both waste forms.

Waste testing focused on demonstrating that this process will result in acceptable waste forms for disposal in a geological repository. In order to help ensure the acceptability of the waste forms Argonne personnel have had increased interactions with DOE programs associated with the geological repository and waste form. Personnel participated in the preparation of the Yucca Mountain Repository Environmental Impact Statement. They responded to the data call and reviewed the document. Data for the EMT waste forms from treating 60 MTHM of sodium-bonded fuel are included as part of this EIS.[8]

Argonne also participates in regular meetings with personnel of the National Spent Nuclear Fuel Program and the INEEL Spent Nuclear Fuel Program. The purpose of many of these meetings is to determine the activities necessary to best integrate DOE-owned spent nuclear fuel into the repository. Issues addressed include disposal requirements, data needs, interfaces for standardized canisters, material shipments, and quality assurance programs. Many of these meetings also include DOE Office of Civilian Radioactive Waste Management (RW) personnel.

B. Ceramic Waste Form

The reference ceramic waste form is a glass-bonded sodalite produced from the thermal conversion of zeolite. Zeolites are crystalline aluminosilicates of the group I (alkali) and group II (alkaline earth) elements. Their framework is a network of AlO_4 and SiO_4 tetrahedra linked by the sharing of oxygens. The networks of tetrahedra in the zeolite form cages in which molecules are occluded. The sodium ions in this structure are subject to ion exchange. Both of these properties are taken advantage of with the ceramic waste form. The specific zeolite being used as the base of the ceramic waste form is Zeolite A, $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$. When this material is processed at elevated temperatures, it converts to the mineral sodalite, $Na_6[(AlO_2)_6(SiO_2)_6]\bullet 2NaCl$. Zeolite consists of a large α cage (11.4 angstroms in diameter) surrounded by smaller β cages (6.6 angstroms in diameter). Sodalite only has β cages.

Development of the waste forms on the laboratory scale occurred in the Chemical Technology Division of ANL in Illinois.[9] The work at ANL-West focused on producing larger-scale waste forms and on studying the effects of fission products and transuranics in the ceramic waste.

When treating EBR-II spent fuel in the FCF electrorefiner, the active metal fission products are allowed to build up in the salt as chlorides. The transuranics, including plutonium, also remain in the electrorefiner as salts. After the demonstration quantity of fuel was processed through the electrorefiner, a portion of the electrorefiner salt was processed into irradiated ceramic waste form samples. These operations occurred in the Hot Fuel Examination Facility (HFEF), a hot-cell complex adjacent to FCF at ANL-West. The equipment for producing large-scale samples was first used out-of-cell in gloveboxes or with enclosed atmospheres to produce cold samples. This work has been documented in other papers.[7].

The first piece of ceramic waste equipment is the zeolite dryer. Zeolite A occludes more than 20 weight percent water, which is removed before the zeolite is contacted with salt. Zeolite drying is routinely performed on a 34-kg batch size. The use of an outside vendor, Kemp Development Corporation in Houston, TX, has been employed for most demonstration drying services.

The zeolite used for most of these tests has a particle size distribution between 75 and 150 μm. To increase the efficiency of mixing, the salt to be occluded into the zeolite is milled to a similar particle size using a mill/classifier from Prater Industries, Inc.

The salt is occluded into the zeolite structure in a heated V-mixer. The nominal capacity of this mixer is 50 kg, but a recent test indicated that its performance is not adversely affected with a 112-kg batch. It is rotated at 17 rpm and can be heated to more than 500°C, which is required for the salt occlusion process. The heat is provided from two immersion heaters that enter the vessel from the end plates and from strip heaters attached to the outside shell of the vessel.

For a nominal V-mixer run, approximately 4.1 kg of salt are mixed with 34.7 kg of dried zeolite 4A. This mixture is then rotated, and heat is applied to increase the material temperature to 500°C, where it is held for 15 hours in order to occlude the salt into the zeolite structure.

After the salt-loaded zeolite is cooled, approximately 15 kg of glass frit are mixed with the material in the V-mixer. The vessel is not heated for glass mixing. This blend is then transferred from the V-mixer into fill containers using vibrators to aid with powder flow.

Next the blend is loaded into cans that will be used to process the material through a hot isostatic press (HIP). These cans, referred to as HIP cans, are loaded through a 2.54 cm fill tube. Before being processed in the HIP, the cans are baked at 500°C and evacuated. The fill tube is then crimped and TIG welded.

The HIP was manufactured by ABB Autoclave, Inc. The HIP operating cycle includes a maximum temperature of 850°C and a maximum pressure of 100 MPa.

Because of the nature of the equipment, much of the testing has focused on the HIP and heated V-mixer. The V-mixer was installed in HFEF in June 1999. Two batches of radioactive salt have been processed in this equipment. The first batch resulted in 50 kg of ceramic material. For the second batch, the size was increased to 112 kg. Both batches resulted in acceptable material for ceramic waste production. The HIP has been operational in HFEF since February 1999, and more than 15 experiments have been performed. The first demonstration-scale radioactive ceramic waste form sample and HIP are pictured in Figure 3. Characterization results of these radioactive waste form samples are provided in other papers.[10] The results of characterization tests indicate that the waste form should be easily acceptable for disposal in a geological repository.

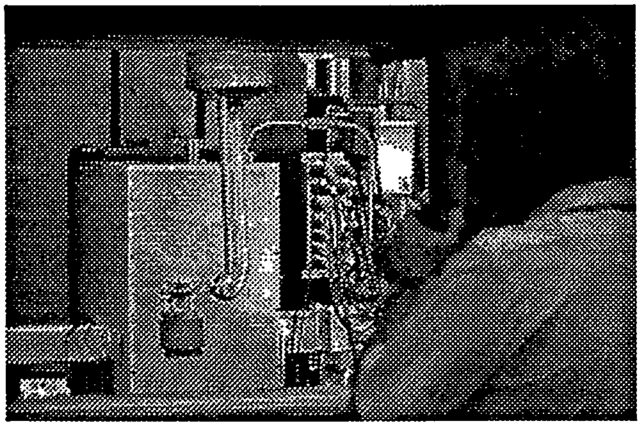

Figure 3. Hot Isostatic Press in the Hot Fuel Examination Facility and the First Irradiatied Ceramic Waste Form Product

ASTM C1285-94, the Product Consistency Test (PCT), is the solution-based test performed on virtually all samples. This test lasts for seven days at 90°C with a surface area to volume leachant ratio of 2000 m^{-1}. The test material was in the -100 to +200 mesh size fraction. The Materials Characterization Center Test 1 (MCC-1) is performed on a portion of the samples. Normalized release rates as determined from the standard PCT are provided in Table 2 for the first radioactive ceramic waste form sample.

Table 2. Normalized Release Rates from a Standard PCT Test on the First Radioactive Ceramic Waste Form Sample

Element	Normalized Release Rate ($g\ m^{-2}\ day^{-1}$)
Lithium	0.1
Sodium	0.04
Potassium	0.02
Silicon	0.01
Aluminum	0.01
Boron	0.1
Chlorine	0.3
Cesium	0.03
Neodymium	0.001
Strontium	0.007
Barium	0.008
Plutonium	0.002
Uranium	0.001

C. Metal Waste Operations

The second high-level waste form resulting from the treatment of spent nuclear fuel for dispositioning by the electrometallurgical technique is the metal waste form. This waste form consists of metallic ingots which are used to stabilize the stainless steel cladding material, non-actinide fuel matrix materials, and noble metal fission products. Minor amounts of actinides that remain in the cladding hulls after dissolution are also present. Zirconium metal is added to improve performance properties and to produce a lower melting point alloy. The typical composition is stainless steel and 15 weight percent zirconium.

The charge for the alloys consists of stainless steel cladding hulls (types 304, 316, and D9), zirconium from the fuel being treated or feedstock zirconium, noble metal fission products (molybdenum, technetium, ruthenium, rhodium, palladium, etc.), and minor amounts of actinides that are present with the cladding hulls. The metal waste form alloy is cast with a target zirconium concentration of 15 weight percent and an allowable range in ingot zirconium concentrations of anywhere from 5 to 20 weight percent. The target is 15 weight percent zirconium based on initial characterization and corrosion data, along with consideration of the alloying temperature. An alloy that contains 15 weight percent zirconium has a lower melting temperature than does a SS-rich alloy with a different zirconium concentration. As a result, lower processing temperatures can be employed to produce homogeneous ingots.

The noble metal concentrations in the metal waste form are expected to be between 2 and 4 weight percent when driver fuel is treated, depending on fuel burnup, and to be near 0.5 weight percent when blankets are treated. The actinides will be present in the alloy in concentrations up to 10 weight percent.

The metal waste form ingots that will be generated from EBR-II driver fuel elements will contain primarily components from Type 316 and D9 stainless steels. When EBR-II blankets are treated, Type 304 stainless steel cladding will be consolidated. If Fermi blanket material is treated, Type 304 stainless steel will be consolidated; and the final ingot will be enriched in molybdenum, from the molybdenum that is present in the U-2.7 Mo alloy that is being electrorefined.

The general steps for producing the metal waste form during the demonstration were: (1) cladding hulls are removed from the FCF electrorefiners after dissolution, (2) cladding hulls are unloaded from fuel dissolution baskets, (3) cladding hulls are processed in the cathode processor to remove adhering salt, and (4) cladding hulls are cast into an ingot in an induction-heated furnace. All of these operations occurred in FCF. For production operations beyond the demonstration, the last two steps would be combined into one operation in a single furnace in HFEF. For the distillation operation, the furnace chamber is sealed and evacuated to approximately 1 torr and heated to approximately 1100°C. This vaporizes the salt and transports it to the condenser where it is collected as an annular ingot. After the run, the solidified salt ingot is returned to the electrorefiners or sent to the ceramic waste form. After completion of the distillation phase, the crucible temperature will be increased to approximately 1600°C, consolidating the cladding hulls into an ingot.

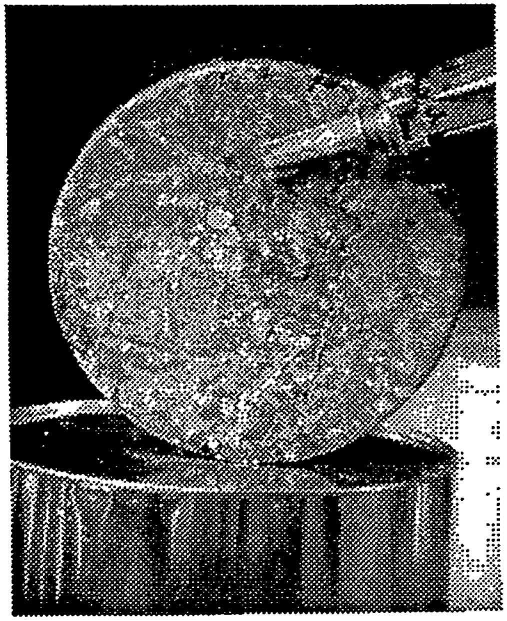

Figure 4. Metal Waste Form Ingot

During the demonstration, 6 metal waste form ingots were produced from the cladding hulls of EBR-II driver fuel. From blanket cladding hulls, an additional 3 ingots were produced. One of these is pictured in Figure 4. Again, characterization results indicated that the waste form should be easily acceptable for disposal in a geological repository.

The baseline HLW form in the nuclear industry is borosilicate glass. The typical method of comparison between waste forms is to examine the different release rates for matrix constituents, fission products, or actinides. Because of the differences between glass and the metal waste, only comparisons between select fission products and actinides may be made. For a key long-lived fission product of concern for the repository, technetium, the estimated forward release rate from the metal waste as determined from a variety of samples is less than or equal to 1×10^{-3} g m^{-2} $day,^{-1}$ which is roughly three orders of magnitude lower than that for glass.[11, 12] The forward release rate for uranium in the metal waste form is approximately 1×10^{-3} g m^{-2} $day,^{-1}$ which is comparable to HLW glasses.[12, 13, 14]

IV. CONCLUSIONS AND SCHEDULES

The three-year demonstration program showed that electrometallurgical treatment could be effectively used to condition sodium-bonded spent nuclear fuel for disposal in a geological repository. An independent committee was established by the National Research Council to review the progress and results of the demonstration. This committee typically reviewed progress twice a year. With the committee's input success criteria for the demonstration were established.[15] All of these criteria were met or exceeded during the demonstration. In July 1999, DOE completed a draft environmental impact statement to assess the treatment of the sodium-bonded spent fuel. The electrometallurgical treatment is one of the alternatives considered. The final EIS and naming of a preferred alternative is expected by April 2000. If EMT is selected treatment operations on additional fuel would begin in September 2000.

ACKNOWLEDGMENTS

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