ABSTRACT

The disposal of DOE sodium bonded spent fuel in a geologic repository is a problem of national scope. There exists 60 metric tons of this fuel, which under current regulations cannot be safely placed in the proposed underground repository. The primary issue in the safe disposal of this fuel is treating the elemental sodium present in such a manner as to make it inert. The electrometallurgical treatment process treats the fuel and neutralizes the elemental sodium by reacting it to form sodium chloride. This process also recovers the uranium from the fuel and produces two high level waste forms, a metal waste form and a ceramic waste form. The process utilizes molten salt electrorefining technology to separate the uranium from the active fission products, such as Cs, Sr, I, and the rare earths, and residual actinides, such as Np, Pu and Am, which remain in the molten salt electrolyte. The cladding hulls are also separated and remain in the anode basket, which originally contained the fuel to be processed. Elements that are noble to the potential applied in the electrorefiner remain with the cladding hull remnants, this includes Zr, Tc, Ru, Rh, Pd and Ag. The cladding hulls and “noble” metals are consolidated into a metal waste ingot, which is primarily stainless steel in composition but also contains 15 weight % zirconium. The salt from the electrorefiner is periodically removed and mixed with zeolite at an elevated temperature, which results in the salt being occluded in the zeolite. A small quantity of glass frit is then mixed with the salt occluded zeolite and the resulting material is then processed at high temperature or high temperature and pressure to produce a glass-bonded sodalite ceramic waste form. This paper will discuss the demonstration phase of this project where over 100 subassemblies of irradiated fuel were treated and several waste forms of both types were produced. Tests and analyses are being conducted to evaluate the physical, radiological and chemical properties of the two high-level waste forms with regard to three sets of information needs: 1) requirements specified for waste form acceptance into the DOE disposal system in the Waste Acceptance System Requirements Document, 2) issues related to Total System Performance Assessment and 3) issues related to process control for manufacture of the waste forms. This paper will discuss the status of the two high-level waste forms with respect to those needs.

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 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 [1-3]. 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 production of waste forms for stabilizing the fission products and transuranics was part of this demonstration. For the purposes of this paper, the demonstration operations are divided into two areas, treatment operations and high-level waste operations.

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

**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 then 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.

The cathode products from electrorefining operations are further processed to remove adhering salt and to recover uranium. These operations are performed in the cathode processor and casting furnace, respectively. The solid cathode from processing driver fuel 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 the literature [4-7].

DEMONSTRATION RESULTS

Two types of sodium-bonded fuel, driver and blanket, were treated in the demonstration. The driver fuel (67% 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 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 Fig. 1. These dendritic deposits were consolidated at the cathode processor (where any salt carry-over is distilled away), and downblended at the casting furnace to yield 40 low-enriched (less than 20% U-235) uranium ingots (1111 kg total).
The majority of the driver assemblies was 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 were further processed in the cathode processor and sampled at the casting furnace.

During blanket treatment operations, a throughput demonstration was conducted for the blanket fuel, which began on July 17, 1999. 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.

HIGH-LEVEL WASTE OPERATIONS

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 such as 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 radioactive and non-radioactive 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.

Ceramic Waste Form

Background and Process Equipment Qualification

The reference ceramic waste form is a glass-bonded sodalite produced from the thermal conversion of zeolite. Zeolites are crystalline aluminosilicates containing 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 open structures 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 occluded with halite salts and processed at elevated temperatures, it converts to the mineral sodalite, Na$_6$[(AlO$_2$)$_6$(SiO$_2$)$_6$]$\cdot$2NaCl. Zeolite consists of a large $\alpha$ cage (11.4 angstroms in diameter) surrounded by smaller $\beta$ cages (6.6 angstroms in diameter). Sodalite only has $\beta$ 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 radioactive 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 non-radioactive 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 with a dryer operating temperature of 550 °C. 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 the 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 at temperature for 15 hours in order to occlude the salt into the zeolite structure.

When the salt-loaded zeolite is cooled, approximately 15 kg of glass frit is mixed with it in the V-mixer yielding a material that is 25 weight percent glass frit. The V-mixer vessel is not heated for glass mixing. This blended material is then transferred from the V-mixer into fill containers using vibrators to aid with powder flow. Next the blended material is loaded into cans that will be used to process the material through a hot isostatic press (HIP), manufactured by ABB Autoclave, Inc. Prior to 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 operating cycle includes a maximum temperature of 850°C and a maximum pressure of 100 MPa.

The testing program has focused on the most complex operations of this process, the V-mixer and the HIP. The V-mixer was installed in HFEF hot cell in June 1999. Two batches of radioactive salt have been processed in this equipment at this time with more batches awaiting processing. The first batch resulted in 50 kg of blended material, salt occluded zeolite and glass frit. For the second batch the size was increased to 112 kg of total blended material. 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 successfully performed with the blended materials from the V-mixer. The first demonstration-scale radioactive ceramic waste form sample and the HIP are pictured in Figure 2.
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 (principally zirconium), 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.

During the demonstration, 6 metal waste form ingots were produced from the cladding hulls of EBR-II driver fuel. An additional 3 ingots were produced from blanket cladding hulls. A typical ingot is featured in figure 3.

**Waste Form Qualification Issues**

Tests and analyses are being conducted to evaluate the physical, radiological and chemical properties of the two high-level waste forms with regard to three sets of information needs: 1) requirements specified for waste form acceptance into the DOE disposal system in the Waste Acceptance System Requirements Document (WASRD) [10], 2) issues related to Total System Performance Assessment (TSPA) for the proposed disposal system at Yucca Mountain on the Nevada Test Site, and 3) issues related to process control for manufacture of the waste forms. The testing program is organized to follow the approach outlined for data
collection and analysis for predicting long-term behavior in a disposal system [11]. For the ceramic waste form, tests and analyses have been conducted with surrogate waste forms made with different mass ratios of glass, zeolite, and salt and with various salt compositions containing nonradioactive chemical surrogates, salts doped with selected radionuclides (U, Pu), and waste forms made with actual radioactive waste salts. For the metal waste form, test and analyses have been conducted on surrogate waste forms made with varying chemical composition, surrogate alloys containing selected radionuclides (Tc, Pu, Np, U) and waste forms produced from actual irradiated cladding hulls.

The WASRD provides interface to the regulatory requirements, the repository design, and the waste inventory and includes both general and specific requirements for commercial spent fuel and vitrified high-level waste. Examples of some of the specific requirements in the WASRD would be: 1) the exclusion of any HLW regulated as a hazardous waste according to the Resource Conservation and Recovery Act, 2) reporting the projected chemical composition and crystalline phases, and 3) demonstrating process control via a product consistency test. An example of a general requirement found in the WASRD would be the interfacing of transportation with waste acceptance and interim storage. Vitrified HLW is defined in the WASRD as either a borosilicate or a ceramic material that has long-term durability greater than or equal to that of borosilicate glass. This definition of HLW in the WASRD will have to be broadened to include the metal waste form from the EMT process. This activity is currently being pursued.

There are no specific performance criteria for waste forms in the disposal system. Instead, the capacity of the overall disposal system to retain the radionuclides is regulated. The TSPA is being conducted by the DOE Office of Civilian Radioactive Waste Management (OCRWM) to represent and simulate the systems, components, and processes that impact the performance of the disposal system. The calculation is done using sub-models designed to take into account key processes and interactions that affect the containment of radionuclides. Process models based on mechanistic understandings are used when possible. A TSPA has been conducted for viability assessment (TSPA-VA) [12] to assess the probable behavior of the disposal system. Separate TSPAs will be conducted for site recommendation (TSPA-SR), to support proceeding to preparation of license application, and for license application (TSPA-LA) to provide reasonable assurance that the repository will comply with applicable regulatory limits. The impact of the high-level waste forms from the electrometallurgical treatment process will not be included in either the TSPA-VA or the TSPA-SR. A possible strategy for including the impact of these two waste forms in the TSPA-LA will be to demonstrate that an upper bound to the impact of the waste forms on the TSPA is provided by the model for the HLW glass. We note that the HLW glass degradation is not currently viewed as a primary factor for system performance and a bounding model for the glass degradation rate (which is itself used as a upper bound for the release rate of radionuclides) will be used for the TSPA-SR.

To provide the data required for all three information needs (WASRD, TSPA and process control) Argonne National Laboratory has planned and conducted extensive matrices of tests for both high-level waste forms. These tests have resulted in preliminary degradation models for both ceramic and metal waste forms [13]. These preliminary models show that the degradation behavior of the EMT high-level waste forms are bounded by the dissolution of the borosilicate high-level waste form [13]. Refinements to these models are underway and confirmation tests are planned. The specific issues raised by the WASRD are being addressed such as the proof of non-hazardous character of the waste forms [14]. Extensive testing for the purpose of demonstrating a well-controlled process is underway for both waste forms [6, 9, 14-18].
PROGRAM STATUS AND PATH FORWARD

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, a set of success criteria for the demonstration were established [19]. 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 Record of Decision for the EIS was issued in September of 2000. The EMT process was chosen as the preferred alternative for treating the sodium-bonded spent fuel from EBR-II. A decision on the treatment process for the sodium-bonded spent fuel from the Fermi-I reactor was deferred for a time period of four years. The extensive process of waste form qualification is well underway at Argonne and should yield the appropriate and complete documentation required for interment of the waste forms in a geologic repository.

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