Dry Processing of Used Nuclear Fuel

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Abstract – *Dry (non-aqueous) separations technologies have been used for treatment of used nuclear fuel since the 1960s, and they are still being developed and demonstrated in many countries. Dry technologies offer potential advantages compared to traditional aqueous separations including: compactness, resistance to radiation effects, criticality control benefits, compatibility with advanced fuel types, and ability to produce low purity products. Within the Department of Energy's Advanced Fuel Cycle Initiative, an electrochemical process employing molten salts is being developed for recycle of fast reactor fuel and treatment of light water reactor oxide fuel to produce a feed for fast reactors. Much of the development of this technology is based on treatment of used Experimental Breeder Reactor II (EBR-II) fuel, which is metallic. Electrochemical treatment of the EBR-II fuel has been ongoing in the Fuel Conditioning Facility, located at the Materials and Fuel Complex of Idaho National Laboratory since 1996. More than 3.8 metric tons of heavy metal of metallic fast reactor fuel have been treated using this technology. This paper will summarize the status of electrochemical development and demonstration activities with used nuclear fuel, including high-level waste work. A historic perspective on the background of dry processing will also be provided.*

I. INTRODUCTION

Dry separation technologies have been used for treatment of used nuclear fuel since the 1960s, and they are still being developed and demonstrated in many countries including the United States, Russia, Japan, Korea, France, United Kingdom, Czech Republic, China, and India. Dry processes typically employ salts or metals in either a molten or gaseous phase. Differences in thermodynamic stabilities or vapor pressures at elevated temperatures are used to facilitate chemical separations. In the United States, work on dry technologies is being pursued as part of the Department of Energy's Advanced Fuel Cycle Initiative (AFCI).

Dry technologies offer potential advantages compared to traditional aqueous separation technologies like PUREX. Solvents (molten salts and liquid metals) used in dry technologies typically are not subject to radiation damage, so relatively short-cooled fuel can be processed. Used fuel does not need to be stored several years before recycling.

Dry processes can handle larger quantities of fissile material, since a water moderator is not present. Nuclear criticality concerns are reduced significantly without the presence of moderator material. These technologies are potentially more compact than aqueous technologies, so the option exists to co-deploy separations facilities with reactor complexes to lessen shipment of used nuclear fuel and special nuclear material.

Non-aqueous technologies typically result in incomplete separation of fissile material from fission products and transuranic elements. Early in the development of nuclear separations technologies, this characteristic was considered a disadvantage, since incomplete separation meant that the recovered materials still had to be processed in shielded hot cells.[1] The recycled spent fuel would have a significant radiation field and would be subject to remote fabrication instead of either hands-on or glovebox fabrication. With the increased focus on non-proliferation, this feature is now considered a benefit. The recovered material is less attractive with respect to proliferation. Work is now focused on developing and demonstrating aqueous technologies that result in incomplete separation. Because of this inherent characteristic of incomplete separations with dry processes, technologies have been developed and demonstrated for remote fabrication of recycled fuel from dry processes. There are now more than 40 years of experience with remote fabrication of fuel from materials recovered from non-aqueous technologies.

All of these advantages make dry processing technologies ideal candidates to recycle fast reactor fuels. Fast reactor fuels generally have higher radiation fields due to increased burnups, so solvent radiation damage is a concern in aqueous systems. Fast reactor fuels have significantly higher fissile material concentrations than light water reactor fuels, so criticality control can be limiting. In general, dry technologies are not suitable as separation technologies for recycle of fuel to thermal reactors because they do not remove enough of the fission products that are neutron poisons in a thermal neutron spectrum. These same fission products are not neutron poisons in a fast neutron spectrum. Because of the focus on fast reactors, the technology has been assessed or used for many of the fuel types considered for advanced reactor technologies including metals, nitrides, and oxides.

II. CLASSES OF DRY PROCESSES

A number of technologies and flowsheets have been examined using non-aqueous systems. At present, most work is directed to electrochemical technologies. A few of the other technologies will first be noted.

Volatilization is one type of dry process. It takes advantage of the different vapor pressures of the elements or compounds in used nuclear fuel. In general, the fuel can be heated to release gaseous fission products (noble gases, iodine, and tritium). These elements can be released around 500°C. If higher temperatures are employed (750°C to 1100°C), more volatile fission products like cesium and technetium can also be removed. In some applications, spent oxide fuel is converted from UO_2 to U_3O_8 that is less dense. As the fuel is oxidized, the pellets are fragmented, and the resulting material is powder, shown in Fig. 1. This particular process is referred to as voloxidation. Pulverization of the fuel pellet facilitates removal of volatile fission products. The remaining fission products and transuranic elements remain in the used fuel.

Fig. 1. Resulting powder from voloxidation of used oxide fuel.

Application of volatilization has focused in two areas: a head-end operation for another separation process or a recycle option to specialized reactors like the CANDU design. For the CANDU option, referred to as DUPIC (direct use of PWR fuel in CANDU), pressurized or boiling water reactor fuel can be treated by voloxidation to remove a fraction of the fission products.[2] For this recycle option, used oxide fuel is first oxidized to U_3O_8 and then reduced back to UO_2 in a cycle called OREOX (Oxidation and Reduction of Oxide Fuel). The resulting powder material can be converted remotely into new fuel for a CANDU reactor that can operate with the enrichment values of uranium in used fuel from either pressurized or boiling water reactors. Approximately 50% more energy can be derived from recycle of the LWR fuel as CANDU fuel.[3]

Voloxidation technologies are also being assessed as front-end operations for both aqueous and dry process technologies. For aqueous technologies, the addition of voloxidation has the potential to remove some of the more problematic fission products before fuel dissolution. For other dry technologies, voloxidation may serve as a means to reduce the size of the used fuel in order to enhance the dissolution of the uranium oxide.

Halide volatility is another class of dry separation technology. Halides (fluorides or chlorides) can form volatile compounds of the actinides, most notably UF_6. By converting spent fuel into halides, the actinide halides can be separated from the bulk of the fission products as gases. Of the various dry processes, halide volatility does offer the best potential for a high degree of separation. Because of the challenge to convert some of the transuranic elements to halides, this technology works best in systems that are primarily uranium based.[1]

One of the first non-aqueous technologies deployed was a partial oxidation process called melt refining or skull refining. In this process, a portion of the fission products are again separated from the spent fuel. The fission products are chemically oxidized to separate them from the actinides in the spent fuel. Melt refining was used to recycle fuel from the Experimental Breeder Reactor II (EBR-II) from 1964 through 1969.[4] EBR-II was a sodium-cooled fast reactor that operated with a uranium-alloy metallic fuel. The spent fuel was disassembled, chopped, placed into a Zr_2O crucible, and heated to 1400°C. Chemically reactive fission products (alkali, alkaline earth, and rare earths) reacted with the crucible to form oxides. The uranium and noble metals remained in the metallic state and were recovered from the melt. This recovered material was remotely fabricated into metallic fuel for recycle into EBR-II, a fast reactor. The fuel was fabricated by injection casting. This technology was used to fabricate fuel for EBR-II both remotely and later in gloveboxes for the reactor's entire thirty years of operation. An injection-casting furnace is pictured in Fig. 2.

Fig. 2. Hot Cell Injection Casting Furnace

More than 700 EBR-II fuel assemblies were recycled using melt refining. Some of the fuel alloy was recycled as many as four times. From this recycled fuel, more than 34,000 fuel elements were remotely fabricated.[4] This demonstration program proved the feasibility of co-location of a fuel cycle facility with a fast reactor. EBR-II and its connected Fuel Conditioning Facility (FCF) are pictured in Fig. 3.

Fig. 3. EBR-II and Co-Located FCF

The ability to process short-cooled fuel was also demonstrated. As part of this demonstration, used fuel was removed from the reactor core, processed by melt refining, remotely fabricated into new fuel, and recycled back to the reactor routinely in four to six weeks.[4] Still, limitations to this recycle technology (separations of noble metals and process losses) eventually led to the development of a non-aqueous electrochemical separation technology that is the topic of the remainder of this paper.

III. ELECTROCHEMICAL PROCESSING

In the mid-1980s, the U.S. Department of Energy's Office of Nuclear Energy resumed work on a dry process for recycle of used fast reactor fuel. Initial technology development activities focused on recycle of metallic fast reactor fuel, specifically an actinide-zirconium alloy. Electrochemical processes employing molten salts and liquid metals were pursued.

This work was initiated at Argonne National Laboratory (ANL) and is now performed at both Idaho National Laboratory (INL) and ANL. Development of this technology was performed as part of the Integral Fast Reactor Program that was eventually terminated in 1994. After 1994, the general technology was applied to the treatment for disposition of used fuel from EBR-II. Before being applied to this fuel management application, the technology underwent a three-year demonstration program from 1996 through 1999. The National Research Council reviewed the demonstration. Three of the main findings or recommendations from that review were:

> "Finding: The committee finds that ANL has met all of the criteria developed for judging the success of its electrometallurgical demonstration project.

> Finding: The committee finds no technical barriers to the use of electrometallurgical technology to process the remainder of the EBR-II fuel."

> "Recommendation: If DOE wants an additional option besides PUREX for treating uranium oxide spent nuclear fuel, it should consider continued development and implementation of the lithium reduction step as a head-end process to EMT."[5]

After the successful demonstration, DOE prepared an environmental impact statement, independent cost assessment, and non-proliferation assessment.[6,7,8] Based on the results of these assessments, DOE moved forward with application of the technology to the treatment of sodium-bonded spent fuel in 2000. Worked has focused on treatment of the EBR-II sodium-bonded fuel, but there is also sodium-bonded fuel from tests performed in the Fast Flux Test Facility (FFTF) at Hanford and from safety tests performed at Sandia National Laboratory (SNL). Both the FFTF sodium-bonded fuel and SNL material were transferred to INL in 2008.

With the formation of AFCI in 2002, application of electrochemical technology expanded beyond treatment to again address recycle of fast reactor fuel. Research and development work has included experiments with simulants, transuranics, and actual spent nuclear fuel. Integral to this work are activities focused on developing and implementing process improvements and qualifying resulting high-level waste forms.

Much of the development work associated with electrochemical technology is focused on treatment of fuel from fast-spectrum nuclear reactors, like the EBR-II in Idaho. Such reactor systems are also currently a focus of the Generation IV Nuclear Energy Systems, an international nuclear program. A limited amount of work has also been focused on treatment of LWR fuel to produce a feed for fast reactors. LWR oxide fuel can be reduced to metal and then fed directly to the electrochemical fuel cycle for metallic fast reactor fuel.

Outside the United States a dry electrochemical process has also been developed for recycle of oxide fast reactor fuel without conversion of the actinides to metal. Development of this alternative has been centered at the Russian Institute of Atomic Research (RIAR). The RIAR process is an oxide electro-winning technology. Remote fuel fabrication is performed by viborcompaction.[9, 10]

The remainder of this paper will focus on the electrochemical process for treatment of metallic fuel. The flowsheet for treatment of metallic spent fuel starts with chopping. The stainless-steel cladded fuel pins are chopped into 0.6 to 1.3 cm segments that are loaded into steel baskets. The steel baskets are transferred into an electrorefiner where they serve as an anode. The electrorefiner contains a solution of molten LiCl-KCl eutectic and dissolved actinide chlorides, such as UCl_3 and $PuCl_3$. The electrorefiners are typically operated at 500°C.

In the electrorefiners, spent fuel is electrochemically dissolved from anode baskets, and an equivalent amount of uranium is deposited on a steel cathode, Fig. 4. The uranium is consequently separated from the bulk of the fission products and transuranics. Most of the active metal fission products (alkali, alkaline earth, and rare earth), halides, and transuranics accumulate in the salt because their chlorides are chemically more stable than UCl_3.

Fig. 4. Uranium cathode deposit.

The electrorefiners operate in a batch mode. When cathodes are removed from the heated electrorefiner, adhering salt freezes to the surface of the recovered uranium. This salt is separated from the uranium in a 1200°C distillation operation, and the uranium is melted into an ingot. The distillate salt is recycled back to the electrorefiners.

Electrochemical treatment of spent nuclear fuel results in two high-level waste (HLW) forms, the ceramic waste form and the metal waste form. The ceramic waste form, which stabilizes electrorefiner salts containing the aforementioned active metal and halide fission products, is a glass-bonded sodalite produced from thermal conversion of zeolite A. Salts are occluded into the zeolite structure in a V-mixer heated to 500°C. After the salt is occluded in the V-mixer, the salt–loaded zeolite is mixed with 25% glass frit. This mixture is loaded into a steel canister and then consolidated into a monolithic waste form in a furnace at 915°C. During the consolidation process, salt-loaded zeolite is converted to sodalite, a naturally occurring mineral.

The metal waste form consists of metallic ingots that are used to stabilize noble metal fission products, undissolved actinides, the non-actinide fuel matrix, and cladding materials. Zirconium metal, one of the non-actinide fuel matrix materials, is needed to improve performance properties and to produce a lower melting point alloy. The typical composition is stainless steel and 15 weight percent zirconium. It is produced in a casting operation at 1600°C.

III.A. Fuel Processing

Much of the development and demonstration work associated with the electrochemical fuel cycle makes use of used fuel from EBR-II. Work with this fuel is performed in FCF, the same facility that was used to demonstrate melt refining in the 1960s. FCF underwent a

major upgrade in the 1990s. This facility consists of two shielded hot cells for handling highly radioactive material. The first of these cells is filled with air and is used for storage of fuel pending treatment. Process testing and treatment are performed in a hot cell filled with argon gas. An inert gas is needed because of the hygroscopic nature of the molten salts and the pyrophoric and reactive characteristics of the actinide metals and bond sodium used in the fuel pins. The moisture and oxygen content are kept low in the cell to minimize these reactions.

Two electrorefiners are employed in FCF. The first, Fig. 5, was installed in 1994 and the second in 1998. Both electrorefiners are one meter in diameter. They contain between 430 and 650 kg of molten salt. Four to seven weight percent of this mixture is actinides as actinide tri-chlorides to facilitate electrotransport of spent fuel. The base salt is high purity LiCl-KCl. After treating spent nuclear fuel, the salt also contains chlorides of fission products that are more stable than actinide chlorides. This includes $CsCl$, $SrCl_2$, $LaCl_3$, $NdCl_3$, etc. An increasing concentration of NaCl that forms from the reaction of bond sodium is found in the salt as well. The electrorefiners now contain between 9 and 13 kg of sodium as NaCl.

Fig. 5. FCF electrorefiner.

In 1996, spent fuel was first processed in FCF as part of the demonstration program that was reviewed by the National Research Council. For development testing and demonstration operations, more than 3.8 metric tons of heavy metal (MTHM), including both EBR-II driver fuel and blanket fuel, have been processed in these systems. Because of the resistance of these salts to radiolysis effects, the same salt solvent has been used throughout these operations, and it will not require change out during treatment of all EBR-II spent fuel, more than 25 MTHM.

In the electrochemical process, stainless steel fuel clad is not dissolved. More noble fission products like technetium, rhodium, ruthenium, and molybdenum are also not oxidized. They remain with the clad in elemental form.

Electrorefining process improvements are a major focus of AFCI technology development. Three electrorefiners are remotely operated in hot cells at INL. Those operating in FCF are the largest and newest. The first electrorefiner used for tests with spent fuel was the Hot Fuel Dissolution Apparatus (HFDA). It is a laboratory-scale system used to demonstrate feasibility of the technology. It has been operating in the Hot Fuel Examination Facility (HFEF) at INL since 1990. It is sized for less than one kilogram of salt. From this first device to the FCF units, the current capacities were increased from 3.5 to 2400 amps. Overall collection efficiencies have also improved, resulting in a three orders of magnitude increase in throughput.

The two FCF electrorefiners are identical in size. They differ in anode-cathode configuration and the presence or absence of a molten cadmium pool. A cadmium pool was placed in the first FCF electrorefiner. It was eliminated in the second design. Both electrorefiners have four ports in which electrodes are inserted into the molten salt. In the first of these electrorefiners, an individual anode or cathode is placed into each port, so two anode-cathode configurations can be operated simultaneously with two independent power supplies. For the second electrorefiner, the anode and cathode are combined into a concentric module. Four anode-cathode modules can be operated simultaneously in the second electrorefiner, and the capacity of each anode is twice that of the anode configuration for the first electrorefiner. Additionally, the current capacity of this design is approximately a factor of six higher. In total, the throughput increase between the first FCF electrorefiner and the later design is a factor of 20 in an identically sized vessel.

Establishing performance data is also a focus of electrorefining work with spent fuel. One key performance aspect is dissolution of spent fuel, specifically the actinides. Tests have been performed at laboratory scale with uranium-plutonium fuels and in FCF with uranium fuels. The results of both tests indicated the ability to dissolve at least 99.7% of the actinides.[11] High dissolution of actinides results in significant positive benefits for geological disposal of resulting high-level wastes.

Tests have also been performed to demonstrate electrochemical recovery of zirconium. Some of the EBR-II fuel is alloyed with ten percent zirconium, and advanced metallic fuels will likely use a zirconium alloy. Tests have been performed to demonstrate that zirconium rich

cathodes can be recovered so the potential exists to recycle it with new fuel. A zirconium-rich cathode is pictured in Fig. 6. Zirconium is also needed for the metal high-level waste that stabilizes the cladding and noble metal fission products. Electrorefining experience has also demonstrated that zirconium can be left with the cladding materials to support waste operations.

Fig. 6. Zirconium-rich cathode with uranium.

One of the key focus areas for development of electrochemical treatment of spent fuel is recovery of uranium and transuranics as a group. A group actinide recovery technology using a cathode of liquid cadmium was demonstrated at laboratory-scale in the HFDA and in a FCF electrorefiner. [12, 13] The work in the FCF electrorefiner was at the kilogram-scale for transuranics. Fig. 7 depicts a FCF liquid-cadmium cathode.
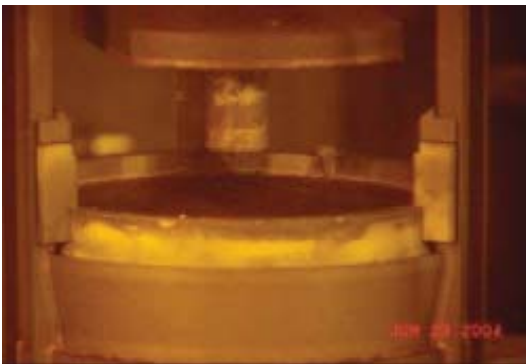

Fig. 7. Liquid-cadmium cathode for group recovery of actinides.

Because of the chemical similarity of the rare earth fission products and the transuranics, a portion of these and some uranium are also recovered with the transuranics. This transuranic product will have a radiation field associated with it so that fabrication of fuel for recycle will

have to be performed remotely in a hot cell. This aspect of the technology provides a potential nonproliferation benefit.

Separation factor data obtained from testing indicate that the transuranics, including plutonium, are recovered together along with some of the rare earth fission products. The quantities of fission products recovered are at levels not expected to affect fuel performance in fast reactors.

Electrochemical technology with molten salts is also being assessed for treatment of fuel types other than metallic. Most commercial spent nuclear fuel is oxide. Laboratory-scale and kilogram-scale tests with oxide materials have been performed. To treat these fuel types, the oxides are first electrochemically reduced from oxides to metals. Oxygen gas is evolved in the process. The reduced metal is then processed using the flowsheet discussed earlier. Reduction occurs in a separate vessel from the uranium electrorefiners. The base salt for oxide reduction is LiCl with 1 wt% Li_2O, and the operating temperature is 650°C.

Laboratory-scale tests with used oxide fuels have been performed. These laboratory-scale tests were completed with 50-gram loadings of irradiated oxide fuel. Reduction values as high as 99.7% have been obtained.[14] Electrorefining of the reduced metal in a standard LiCl-KCl electrorefiner was also demonstrated.

III.B High-Level Waste Processing

Demonstration and qualification of the two high-level wastes from electrochemical treatment were performed in parallel with development of the electrorefining processes. The waste forms were tailored to the process. Activities are underway to support both qualification of waste forms and qualification of production processes. Extensive characterization activities were performed on both waste forms, and degradation models were developed to simulate performance in a geological repository. Work performed on these waste forms demonstrates that they should be acceptable for disposal in a geological repository.[5, 15]

High-level waste operations for electrochemical treatment of spent nuclear fuel are performed in HFEF. The furnace for metal waste form production is pictured in Figure 8. This vacuum furnace is used to separate adhering salt from spent fuel cladding by distillation and then to melt the remaining metals into an ingot for disposal. It operates at 1600°C. The furnace was installed in 2008, and process testing is ongoing.
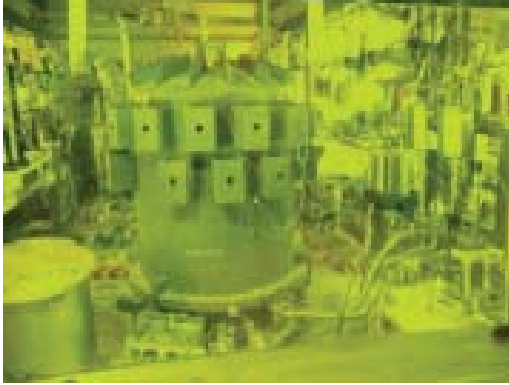
Fig. 8. Metal Waste Production Furnace in HFEF

A consolidation furnace for production of full-scale ceramic waste was procured, installed, and is ready for operation and process testing out of cell. Process testing will first be performed with waste form surrogates before installation in a hot cell. This furnace is capable of producing 400-kg waste forms. Other equipment used for the production of the ceramic waste form, including a large heated V-mixer and a mill/classifier, are already installed and operational in HFEF.

IV. CONCLUSIONS

Dry processes for treatment of used nuclear fuel have been developed and deployed to a limited extent over the last forty years. Significant advancements have been made in the past twenty years with an electrochemical technology for the treatment and recycle of used fuel. Development testing and demonstration operations for aspects of the flowsheet have been performed with spent fuel. During this period, electrorefining testing was scaled by three orders of magnitude in remote hot cells. Critical process goals like high fuel dissolution were achieved. Work is currently underway to demonstrate additional key aspects of the technology including both group recovery of transuranics and application of the technology to commercial oxide fuels. In parallel with work on fuel treatment processes, HLW production processes are being designed, tested, and implemented. This technology may provide benefits over conventional aqueous options for treating used nuclear fuel and may enable the deployment of the next generation of nuclear power systems.

ACKNOWLEDGMENTS

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