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PYROPROCESSING PROGRESS AT IDAHO NATIONAL LABORATORY

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At the end of May 2007, 830 and 2600 kilograms of EBR-II driver and blanket metal fuel have been treated by a pyroprocess since spent fuel operations began in June 1996. A new metal waste furnace has completed out-of-cell testing and is being installed in the Hot Fuel Examination Facility. Also, ceramic waste process development and qualification is progressing so integrated nuclear fuel separations and high level waste processes will exist at Idaho National Laboratory. These operations have provided important scale-up and performance data on engineering scale operations. Idaho National Laboratory is also increasing their laboratory scale capabilities so new process improvements and new concepts can be tested before implementation at engineering scale. This paper provides an overview of recent achievements and provides the interested reader references for more details.

I. INTRODUCTION

Since June 1996, uranium has been recovered from Experimental Breeder Reactor-II (EBR-II) spent metal fuel by new non-aqueous separations process. Idaho National Laboratory (INL) has a long history of developing and demonstrating pyrochemical separations processes for spent nuclear fuel. Melt refining of fuel was performed from September 1964 to 1969, and approximately 5 metric tons (35,000 metal fuel pins) of spent fuel was processed.¹ Operations included remote fuel fabrication with the recycled fuel being used in EBR-II reactor. The cessation of fuel processing and fabrication was not due to separations technology or equipment problems but was simply a change in EBR-II mission to an irradiation facility for the national fast reactor development program.

After the U.S. government decided to stop pursuing separations of pure plutonium for

civilian nuclear power, Argonne National Laboratory (ANL) began developing the Integral Fast Reactor that included a new improved pyrochemical process that included fuel recycle.² Separations are performed by an electrorefining process which has been described in numerous articles.^{3,4} Actinides are recovered as a group so that pure plutonium never occurs in the operations. This new pyrochemical process integrated the waste processes closely with the separations processes.⁵ While the process was being developed at bench scale in laboratories in Illinois, the Fuel Conditioning Facility (FCF) at the EBR-II site on INL was being modified to demonstrate the technology with irradiated metal fuel. This demonstration was initially designed to include spent fuel separations, uranium-plutonium-zirconium metal fuel fabrication, and high level waste processes.⁶ After EBR-II was shutdown in 1994, fuel fabrication was no longer a program objective but the technical feasibility of pyrochemical separations and waste processes remained. The entire process became operational in 1996 and its success was reviewed and verified by a special subcommittee of the National Research Council.^{7, 8} Since the completion of this demonstration, INL pyroprocessing has been focused on understanding and developing engineering scale separations equipment performance and completing process scale-up of high level waste processes. Since 2002, the Advanced Fuel Cycle Initiative within the U.S. Department of Energy's Office of Nuclear Energy has funded additional pyroprocessing research and development including two new front end processes: voloxidation and spent oxide fuel reduction which allows oxide fuel in addition to metal to be pyroprocessed. Many other countries are pursuing pyroprocessing, and INL is involved with collaborative programs with Japan's Central Research Institute of Electric Power Industry (CRIEPI) and Korea Atomic Energy Research Institute.

II. BACKGROUND

The facilities at INL have typically been focused on engineering scale demonstrations and laboratory scale work with radioactive materials. The new separations technology are being tested in FCF which is a large hot cell facility that contains two processing lines. The Mk-IV electrorefiner has been treating EBR-II driver fuel which is highly enriched uranium and zirconium alloy with a typical burn-up of 80,000 GWd per MT HM. However, uranium-plutonium-zirconium alloy and higher burn-up (up to 180,000 GWd per MT HM) experimental fuels are available for testing to address transuranic dissolution efficiency and effects of burn-up on process operations. Another 2 MT of an earlier generation of EBR-II fuel is available that has a highly enriched uranium and unique alloy mixture containing 2.36% molybdenum, 1.96% ruthenium, 0.28% rhodium, 0.19% palladium; 0.1% zirconium and 0.1% niobium. This special EBR-II fuel is particularly suited to study the behavior and recovery of noble metals. The results of early tests and detailed description of the MK-IV electrorefiner have been provided in various references.^{8,9,10} The highly enriched uranium product from the electrorefiner is processed through a cathode processor which recovers electrorefiner salt and consolidates the uranium product. This uranium ingot is taken to a casting furnace that is used to mix depleted uranium with highly enriched uranium to make a low enriched uranium product. The early successful results from these unit operations have been described.^{11,12}

In order to commercialize pyroprocessing, a larger throughput electrorefiner and process scale-up parameters are needed to show technical feasibility. For this reason, a next generation electrorefiner (Mk-V ER) was constructed and has been operating in FCF since 1998. The Mk-V ER processes EBR-II blanket fuel (23 MT available) which is depleted uranium that contains approximately 1 weight percent plutonium when removed from the reactor. This electrorefiner has an improved anode cathode arrangement and continuously removes the uranium from the cathode surfaces. The Mk-V electrorefiner has been operated with four anode cathode modules with a current capacity of 600 amps per module and the uranium throughput has been increased by a factor of 20 over that of

the Mk-IV ER.¹³ The Mk-V product is also run through the same cathode processor equipment that processes the Mk-IV ER product. During cathode processor operations, the Mk-V product batch size can be larger due to the difference in criticality safety limits between the depleted uranium, and highly enriched uranium product. In addition, the need for casting furnace operations has been eliminated because uranium enrichment is low enough and final product composition can be measured on drill samples of the ingots. Recent electrorefining and cathode processing data are discussed in Section III.

INL pyroprocessing results in two high level waste streams, metal and ceramic. The metal stream made up of cladding hulls covered with electrorefiner salts are processed in a high temperature furnace that distills the salt for recycle and consolidates the cladding into an eighty five weight percent stainless steel – fifteen weight percent zirconium alloy. This process has been scaled from tenths of kilograms to 90-kilogram ingots.¹⁴ The equipment and recent results will be discussed in Section III. Scaled-up ceramic waste process equipment is still in surrogate testing because in cell engineering scale equipment is not yet needed. The composition of ER salt has not reached any processing limits that would require its removal and immobilization in the ceramic waste. Electrorefiner salts will need to be immobilized when one of the following three limits are reached: 1) the heat load from the accumulated fission products exceeds the cooling power available to maintain the ER operating temperature within its limit, 2) the sodium buildup in the salts increases the eutectic salt solidification point close to the ER operating temperature, or 3) plutonium inventory reaches the 50 kilograms total plutonium limit in one electrorefiner due to the criticality hazards control strategy.¹⁵

Although some ceramic waste equipment has been installed in the Hot Fuel Examination Facility (HFEF), a new engineering scale ceramic waste furnace¹⁴ will be needed to handle the existing quantities of salt in the two electrorefiners. Significant process development needs to be completed before this new furnace can be installed. This development is being driven by process development needs rather than one of the operational limits mentioned above which would force ER salt withdrawal and immobilization.

In addition to the engineering scale developments, more emphasis has been placed on laboratory scale equipment and data to support modeling efforts. Several glovebox furnaces are available to investigate morphology of electrorefiner deposits and test different process control schemes. In addition, a remote laboratory scale electrochemical cell called the Hot Fuel Dissolution Apparatus has been used to support both electrolytic reduction of spent light water reactor fuel¹⁶ and electrorefining of single segment fuel samples or small baskets (50 grams). In HFEF, a new capability has been added to study the voloxidation process and capture of the volatile fission products.¹⁷

Another electrochemical cell capability and equipment for studying sodium removal from metal fuel at high temperature and vacuum have been added to a glovebox in the Fuels and Applied Science Building. This electrochemical apparatus, shown in Figure 1, can be configured as either an electrolytic reduction vessel to study oxide fuel reduction or as an electrorefiner. Initially, this apparatus will test some specialized fuel configurations but its capabilities will support new processing concepts and on-line monitoring.

Ion exchange is being investigated as a means of concentrating fission products in zeolite to reduce ceramic waste volume. Also, small scale heated mixers and various furnaces have helped to evaluate new glass formulations, cooling rates and range of particle sizes. This experimental equipment should enable the discovery of a robust range of operating parameters.

III. FUEL SEPARATIONS RESULTS

At the end of May 2007, 830 and 2600 kilograms of driver and blanket fuel respectively have been processed since spent fuel operations began in June 1996.

III.A. Electrorefining

Electrorefiner operations have enabled a better understanding of the process and equipment performance. Process enhancements such as larger anode baskets (which hold more fuel to improve throughput) and modifications

which have improved equipment reliability have been tested. Also, new reference electrodes have been built to provide better process monitoring.

As mentioned previously, the electrorefiner salts have not degraded and process limits appear to be less stringent than initial estimates. Since EBR-II fuel is over 13 years old, fission products accumulating in electrorefiner are contributing only seven kilowatts of the eleven kilowatts needed to heat the electrorefiner vessel, so the heat limit will not be reached with our present fuel inventory. Initially 30 mole percent sodium chloride concentration was estimated to cause the salt eutectic solidification point to be above 400C which could stop electrorefiner operation. However, tests with 38 mole percent sodium in the ER salt laden with fission products have shown the melting point actually decreases from 356C to 347C so the sodium limit appears to be even higher than 38 percent. Since heat load and sodium concentration are not limiting, the plutonium limit becomes central. With the current Mk-V electrolyte plutonium inventory of approximately nineteen kilograms, experiments have verified the performance of the electrochemical operations and the product

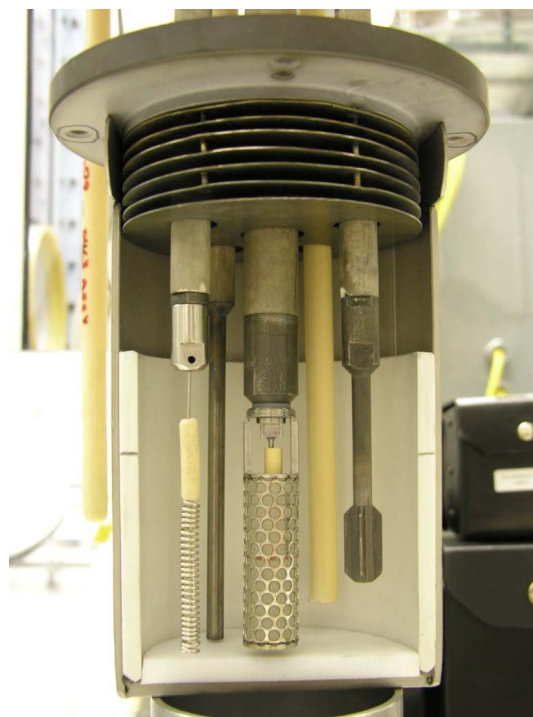


Figure 1. Sectional view of new glovebox electrochemical apparatus.

specification that were used to develop our criticality control limits.

The electrorefiner process model is able to predict the mass and composition of the electrorefiner inventory. Using the known mass of the input and output streams, the ER process model predicts the salt and cadmium volume. The percent deviation of the predicted salt volume relative to measured averaged 0.18% and -0.04% for the Mark-IV and Mark-V electrorefiners, respectively. For the Mark-IV ER cadmium pool, the average was 2.42%. This data provides a measure of confidence in the ER process model to predict the inventory volumes.

During electrorefining, typically the dissolution of the fuel at the anode is the rate limiting step. Two experiments were run to see the effect on mass transfer characteristics when smaller diameter fuel was chopped (same length segments as our typical fuel). Figure 2 shows a comparison of anode voltage between Mk-IIICS and Mk-III fuels. Both of these fuels had the same uranium-10 weight percent zirconium initial alloy. The anode resistance of the Mk-IIICS was higher than that of the Mk-III fuel the

resistance was higher, the dissolution efficiency because the length to diameter ratio of the sheared fuel elements is 0.52 and 0.69 for the Mk-IIICS and Mk-III fuel, respectively. Although was similar to our typical operations with 99.8% uranium and greater than 99% plutonium dissolution. These results are important because 2 MT of EBR-II driver fuel has the smaller diameter.

Group actinide recovery (Pu, Am, Cm, Np and U) is necessary for fuel recycle. Four operations have been completed using an engineering scale liquid-cadmium cathode. Over four kilograms of transuranics were recovered over a wide range of electrolyte uranium concentrations resulting in 25 to 60% uranium in the transuranic product. Successful operation over this concentration range shows robustness of the operation. This product was returned to the electrorefiner to allow higher electrolyte concentrations to be investigated. If the transuranic products were used for new experimental fuels, the ceramic waste volumes would be decreased because the plutonium inventory limit would not be reached so fission products could build up to higher concentration before the electrolyte would have to be removed for immobilization in the CWF.

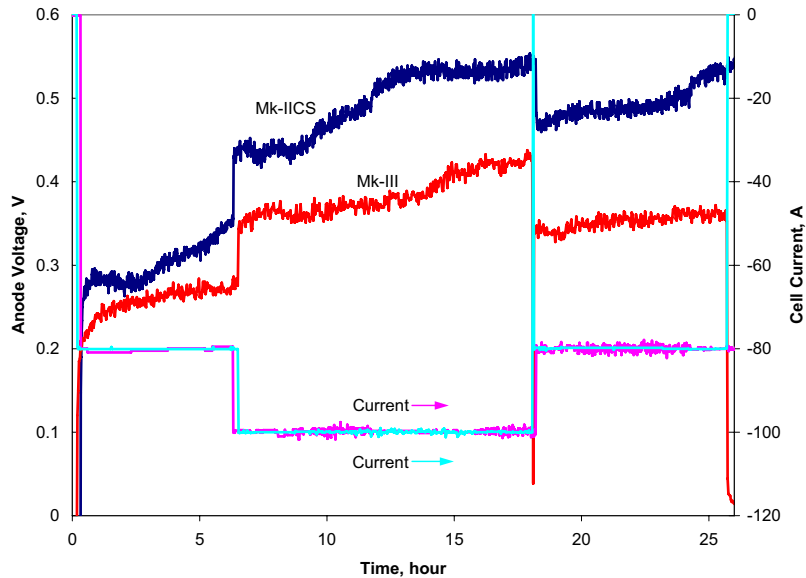


Figure 2. Anode voltage and current during Mk-IIICS and Mk-III fuel electrorefining.

For many of the proposed advanced AFCI metal fuels for fast reactors, zirconium is used in the fuel alloy. Since the final composition of the zirconium needed for the most stable fuel has not been determined and may vary, methods to recover zirconium have been tested using the normal steel mandrel. The recovered cathode product has a different morphology than our uranium product

III.B. Metal Processing

One challenge with high temperature metal processing is limiting the interaction of the pure metals with the processing equipment. Historically, the cathode processor has utilized graphite crucibles with zirconia coating. After each run this coating has to be removed and a new coating applied. This action is labor intensive and limits the throughput of the equipment. The coating also can react with the uranium to form dross which is primarily uranium oxide. This uranium oxide can be reduced and recycled to the process.

Three different new crucibles are being tested so the throughput can be increased and dross formation minimized. A six liter niobium crucible with hafnium nitride coating has been run five times and has shown very little dross formation and no need to reapply coatings. A full size (17 liter) niobium crucible is currently being procured. Two other alternative crucibles are ceramic-lined graphite crucibles where the ceramic is vibrocast into a graphite shell. The first crucible (8 liter) was run six times but showed high dross formation between 1.5 and 5 percent. By improving the fabrication techniques, a second crucible (14 liters) (Figure 3) has been run four times with dross formation between 0 and 1 percent. With these promising results, both types of crucibles will continue to be tested.

The use of a liquid-cadmium cathode in the pyroprocess to collect transuranics and uranium, requires cadmium distillation from the actinide product for its use in fuel recycle. Four experiments (approximately 25 kg cadmium each) have been performed in the cathode processor. A cadmium distillation rate of 0.41 g/min/cm² was achieved and greater than 99 wt% of the cadmium was collected for recycle. This successful separation of cadmium from actinide products supports our further research in group actinide recovery.

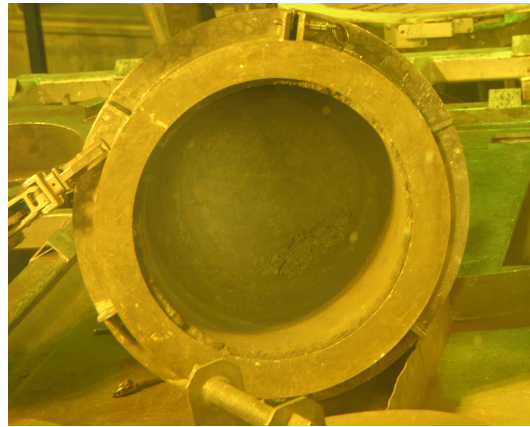


Figure 3. Fourteen liter zirconia-lined graphite crucible after FCF cathode processor test.

The cathode processor has had over 300 batches, and the recovered salts have been recycled to the electrorefiners. No impurities have been detected in the electrorefiners as a result of this recycling.

III.C High Level Waste Processes

In support of installation of an engineering scale metal waste furnace in cell, five ingots were made with this remote operated equipment out of cell to verify that it could produce a product of the same quality as the prototype equipment in a glovebox. These ingots were sampled to show homogeneity in the compositions and characterized with scanning electron microscopy to show that a similar phase structure was produced as our waste qualification work. In addition, the Environmental Protection Agency's toxic characteristic leaching procedure was performed to verify the chromium was adequately immobilized so the material would not be considered a hazardous waste. The results showed good homogeneity, phase composition, and no hazardous characteristics. With these results, the equipment is currently being installed in our Hot Fuel Examination Facility hot cell and operations should begin within a year to recover and recycle the electrorefiner salts on our cladding hulls.

For ceramic waste process development, new commercial glasses were tested because the glass that was previously used in our development program is no longer manufactured. Recent tests have shown ceramic waste forms produced using three commercial glass meet

performance criteria. In addition, tests have been run to verify the glass particle size distributions can be increased. This change in glasses and particle size distribution should enable a more robust process as the engineering scale equipment is tested to determine the range of acceptable operating parameters.

IV. FUTURE PLANNED EXPERIMENTS

As the pyroprocess development continues, experiments will continue to focus on equipment improvements and increased throughput. In electrorefining, major challenges will be optimizing group actinide extraction parameters and the control of impurities in our products. Different equipment configurations, process control schemes and better process modeling is planned to address these issues. In metal processing, continuation of improvements in the crucibles is needed for both increasing throughput and minimizing wastes.

Positive results have been obtained from engineering scale operations with spent metal fuel, front end processing to handle oxide fuel, and possible enhancements such as voloxidation. These are areas for fruitful future research. The laboratory scale oxide electrolytic reduction is very promising but more work on electrochemical cell design and scale-up fundamentals is needed. New equipment will enable more efficient experiments to supplement the irradiated fuel database.

Testing of the new remote metal waste furnace with cladding hulls from electrorefiner operations will provide valuable information on our high level waste processes. For the ceramic waste processes, engineering scale operating parameters need to be determined and new processes such as ion exchange are needed to minimize our waste volumes.

V. CONCLUSIONS

Separations of EBR-II spent nuclear fuel for the past eleven years have successfully demonstrated the feasibility of the pyroprocess for fast reactor fuel recycle. The engineering scale equipment is providing valuable information on the process robustness and overall performance. The data provide a solid technical basis to adapt this technology to different fuels and guide our future experimental work to areas where improvements are needed.

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