

# ELECTROMETALLURGICAL TREATMENT OF OXIDE SPENT FUELS<sup>1</sup>

by

E. J. Karell, K. V. Gourishankar, L. S. Chow, and R. E. Everhart

Argonne National Laboratory  
Chemical Technology Division  
9700 S. Cass Ave.  
Argonne, IL 60439

Phone: (630) 252-9328  
Fax: (630) 252-9917  
e-mail: karell@cmt.anl.gov

RECEIVED  
SEP 28 1999  
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To be Presented at the GLOBAL '99 Conference  
August 30-September 2, 1999  
Jackson Hole, Wyoming

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<sup>1</sup>Work supported by the U.S. Department of Energy, Nuclear Energy Research & Development Program, under Contract W-31-109-Eng-38

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Argonne National Laboratory  
Chemical Technology Division  
9700 S. Cass Avenue  
Argonne, IL 60439-4837  
(630) 252-9328

## ABSTRACT

The Department of Energy (DOE) inventory of spent nuclear fuel contains a wide variety of oxide fuel types that may be unsuitable for direct repository disposal in their current form. The molten-salt electrometallurgical treatment technique developed by Argonne National Laboratory (ANL) has the potential to simplify preparing and qualifying these fuels for disposal by converting them into three uniform product streams: uranium metal, a metal waste form, and a ceramic waste form. This paper describes the major steps in the electrometallurgical treatment process for oxide fuels and provides the results of recent experiments performed to develop and scale up the process.

## I. INTRODUCTION

Approximately 200 tonnes<sup>a</sup> of various types of oxide fuel is currently stored at DOE sites. These oxide fuels exhibit a wide variety in their physical condition, chemical stability, burnup, and enrichment, complicating their long-term storage and disposal.<sup>1</sup> The electrometallurgical treatment technique developed at ANL can be used to convert the different spent fuel types into a uniform set of three product streams, simplifying their long-term disposition.<sup>2</sup> One stream is pure uranium, which is collected separately and can be held in interim storage until its ultimate disposition is decided. The other two product streams lead to stable high-level waste forms, one metal and the other ceramic. Both of these waste forms are being designed for ultimate repository disposal.<sup>3</sup>

The electrometallurgical treatment of oxide spent fuels consists of two stages. The first stage is the reduction of the oxides to the metallic state. The actinide oxides are reduced using lithium dissolved in molten LiCl at 650°C, yielding the corresponding metals and

Li<sub>2</sub>O. The metallic product from the reduction step becomes the feed material for the second stage of the process, known as electrorefining. In the electrorefining step, the principal components of the fuel (uranium, cladding, transuranics, and fission products) are separated electrochemically to produce the three product streams described above.

A significant amount of work has already been done to investigate the basic chemistry of the lithium reduction process and to demonstrate its applicability to the treatment of light-water reactor (LWR) spent fuel.<sup>4</sup> The success of this work has led to conceptual plans to construct a pilot-scale oxide reduction facility at ANL's Idaho site.<sup>5</sup> In support of the design effort, a series of laboratory- and engineering-scale experiments is being conducted using unirradiated oxide fuel. These experiments have focused on investigating the engineering issues associated with scaling up the process and proving that the individual process steps are compatible. This paper summarizes the results of these experiments and outlines plans for future work.

## II. PROCESS DESCRIPTION

### A. Overview

The major steps in the electrometallurgical (EM) treatment process are (1) a head-end step in which the fuel assemblies are chopped into segments, (2) a reduction step in which the actinide oxides are converted to the metallic form, (3) a salt-recovery step that allows for recycling of the process salt and reductant from the reduction step, and (4) an electrorefining step in which the U, transuranics (TRUs), and fission products are separated by selective electrotransport of the uranium in a molten salt electrolyte. Figure 1 is a simplified flowsheet that illustrates the major process steps in the EM treatment of oxide spent fuels.

<sup>a</sup> Reported mass corresponds to the heavy metal content of fuel. Thoria-based fuels are not included.

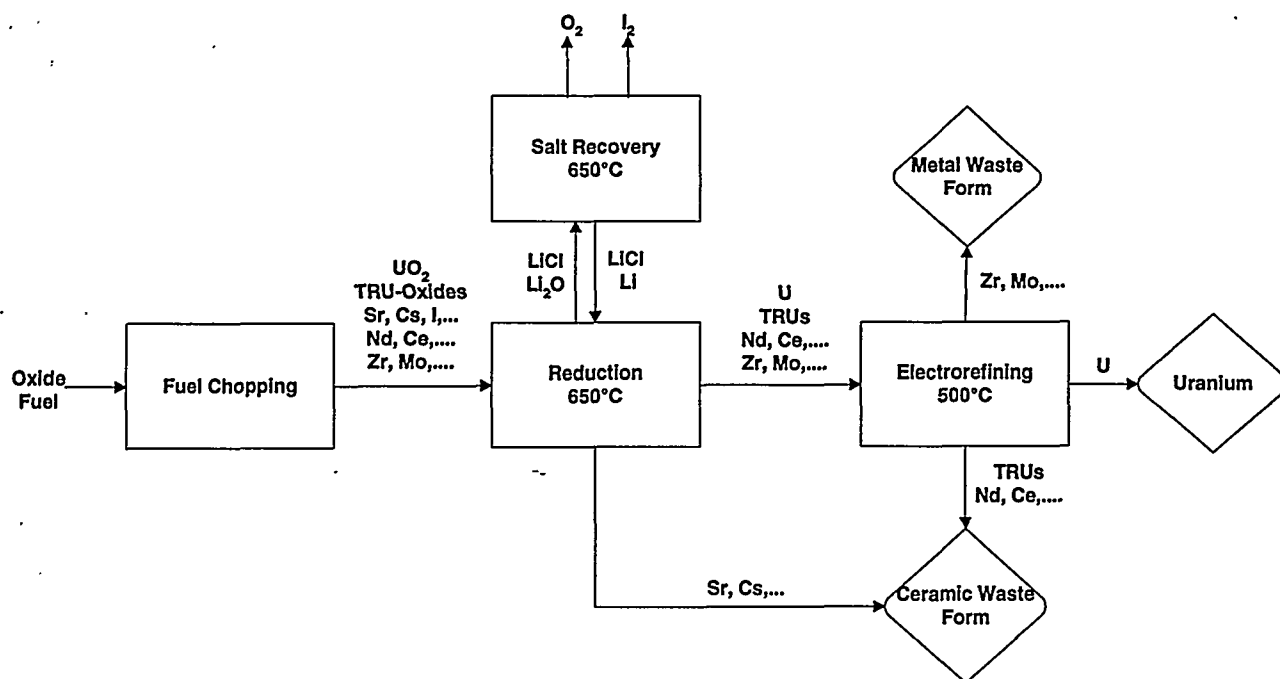


Fig. 1. Process Flowsheet for the Electrometallurgical Treatment of Oxide Spent Fuel

## B. Fuel Chopping Step

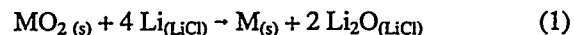
The first step in the EM treatment of oxide fuel is a head-end step in which the fuel assemblies are chopped into small segments to expose the fuel to the molten salt. The resultant mixture of oxide fuel and cladding is then loaded into baskets. The method of fuel assembly chopping currently used in commercial reprocessing plants was chosen as the reference process. Studies performed at Oak Ridge National Laboratory on shearing fuel bundles provided a basis for estimating the size distribution of the material that would be obtained.<sup>6</sup> The size of the fuel fragments produced in a chopping process is an important design parameter. The largest particle size determines the minimum time for the reduction to be completed, while the smallest requires that the fuel basket hold the fuel fragments and still allow free access of salt and lithium to the fuel.

## C. Reduction Step

The reduction step is a necessary first step in the electrometallurgical treatment of oxide spent fuel as the electrorefining process requires a metallic feed. In addition, the reduction step separates certain fission

products from the spent fuel as salt-soluble chlorides or lithium compounds.

In the reduction step, the actinide oxide components of the fuel are reduced to the metallic form using lithium dissolved in molten LiCl at 650°C. The net reaction is shown in Equation (1), where the actinide oxides are designated generically as MO<sub>2</sub>:



The reduced metal remains in the basket along with the cladding, which is unaffected by the lithium. The Li<sub>2</sub>O produced is soluble in the salt.

The fission products can be divided into four groups, depending on their chemical behavior in the reduction step. These four groups are designated "FPA," "FPB," the rare earth (RE) fission products, and the nobler metal (NM) fission products.

The "FPA" fission products consist of the alkali and alkaline earth elements (e.g., Sr and Cs) and Eu. These elements form stable chlorides in the reduction system and become soluble in the LiCl. The "FPB" fission products consist of Se, Br, Te, I, and Sb. These elements

react with lithium to form lithium compounds, such as  $\text{LiI}$  and  $\text{Li}_2\text{Te}$ . As with the "FPA" fission products, the "FPB" fission products also become soluble in the salt.

The RE group of fission products consists primarily of the Lanthanides (except for Eu) and Y. The oxides of these elements are not reduced by lithium; however, they do interact with  $\text{Li}_2\text{O}$  according to the following typical equilibrium:

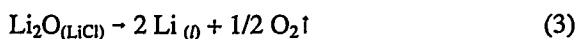


The  $\text{LiNdO}_2$  has limited solubility in the salt, but  $\text{Nd}_2\text{O}_3$  is virtually insoluble. Thus, elements in the RE group are distributed between the basket and the salt. The balance of the fission products, the NM group, is reduced to metal along with the actinides and remains in the fuel basket.

When the concentration of fission products in the reduction salt reaches a certain level, a feed-and-bleed process is used to reduce it. A  $\text{LiCl}$  salt with a high concentration of fission products is removed from the reduction vessel and replaced with fresh salt. The spent salt is blended with glass and zeolite to produce the ceramic waste form.

#### D. Salt-Recovery Step

To keep the  $\text{Li}_2\text{O}$  concentration in the salt at an acceptable value and to recover the lithium for reuse after the reduction step, the  $\text{Li}_2\text{O}$  is electrochemically decomposed by liberating oxygen at an inert anode and collecting lithium at the cathode:

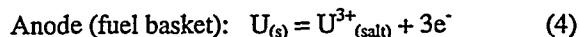


This electrowinning process is called the salt-recovery step. The recovered lithium and the treated salt are then reused in the reduction of subsequent batches of fuel. Because the FPB-lithium compounds decompose at a lower voltage than  $\text{Li}_2\text{O}$ , the electrowinning process also reduces the concentration of FPB elements in the salt.

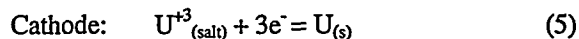
#### E. Electrorefining

The product from the reduction step consists of the reduced U, TRUs, and NM fission products, the cladding hulls, and a portion of the RE fission product oxides. In the electrorefiner, the fuel basket containing this product is made the anode and a steel rod or tube acts as a cathode. The anode and cathode are held in an electrolyte consisting of a  $\text{LiCl-KCl}$  eutectic salt with a

small amount of dissolved  $\text{UCl}_3$ . When a voltage is applied, the uranium and TRUs from the fuel basket dissolve into the electrolyte as the chloride according to the following reaction:



By proper selection of the operating parameters of the electrorefiner the uranium can be selectively deposited at the cathode as the metal according to the reaction:



The greater stability of the TRU chlorides forces the TRU-chlorides to remain dissolved in the eutectic salt. The RE fission product oxides are also expected to form stable, soluble chlorides. Thus, after all the uranium has been transported, the TRUs and REs remain in the salt and only the NM fission products and the cladding hulls remain in the fuel basket.

When the concentration of TRUs and fission products in the electrolyte reaches a certain level, the feed-and-bleed process described earlier is used to reduce it. Thus, the TRUs and fission products in the spent salt are incorporated into the ceramic waste form while the NM fission products and cladding hulls are converted into the metal waste form.

### III. EXPERIMENTAL

#### A. Laboratory-Scale Equipment

Laboratory-scale equipment was built to support testing of process chemistry and scale-up issues related to the electrometallurgical treatment process. All the laboratory-scale experiments were performed in a high-purity helium ( $\text{H}_2\text{O} < 5 \text{ ppm}$ ) atmosphere glovebox. The reduction and electrorefining experiments were performed in 25.4-cm dia furnace wells. The primary crucible used in these experiments was made of 304 stainless steel, with a volume of 7500 cc. A stainless steel stirrer was used in some of the experiments. The mass of fuel used in these experiments varied from 100 to 300 g. Fuel baskets were built of stainless steel screening to hold the fuel in the reduction vessel.

#### B. Engineering-Scale Equipment

The engineering-scale facility was designed to support testing of all the process steps at fuel loadings up to 20 kg per batch. The facility consists of three major components: the reduction vessel, the electrochemical vessel, and the casting station. The reduction vessel holds the salt, fuel, and lithium during the reduction step;

the electrochemical vessel holds the molten salt during the salt-recovery stage; and the casting station provides a means to cast the salt into ingots for recovery and reuse. The molten salt is transferred among these three components through heated transfer lines. All of the equipment is enclosed in an argon atmosphere glovebox; the facility is qualified to handle limited quantities of plutonium and other transuranics. Figure 2 is a photograph of the engineering-scale glovebox.

The reduction and electrochemical vessels are similar in size and construction. Inside each vessel is a 304 stainless-steel crucible that holds the molten salt and lithium at the process temperature of 650°C. This inner crucible is 0.4 m in diameter and 0.7 m tall and is surrounded by a set of resistance heaters and insulating material. The lids on both vessels contain penetrations for transfer lines, melt sampling, and salt addition. In addition, the reduction vessel lid has a penetration for a

variable speed mixer, and the electrochemical vessel lid contains a penetration for the anode assembly. Figure 3 is a cutaway view of the engineering-scale equipment.

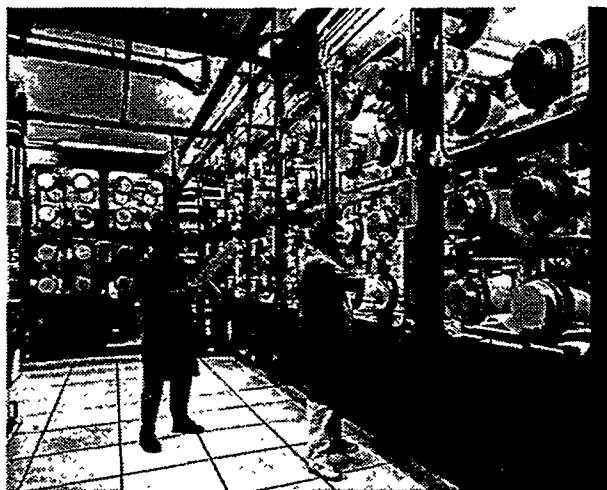


Fig. 2. Engineering-Scale Test Facility Glovebox

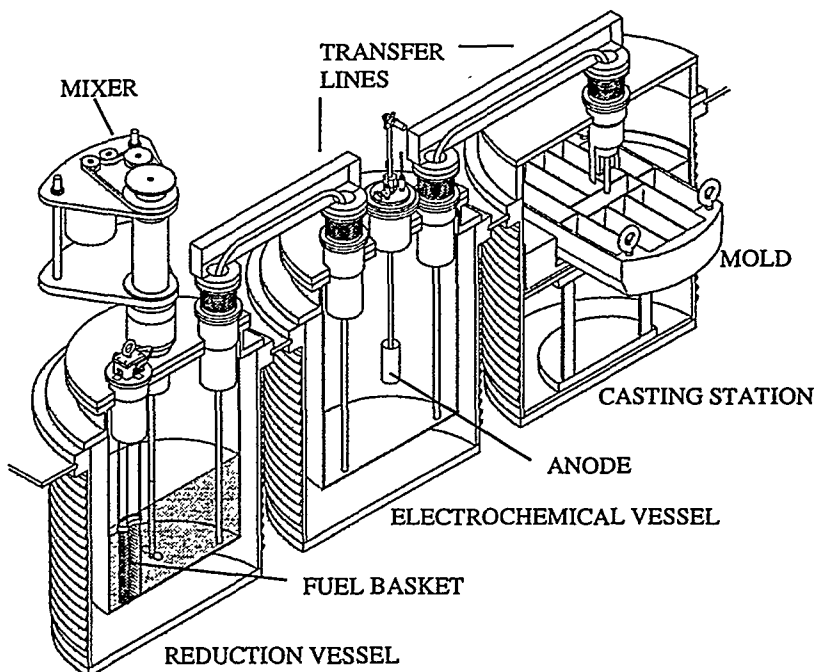


Fig. 3. Cutaway View of Engineering-Scale Process Vessels

### C. Simulated Fuel

The fuel material used in these experiments was selected to simulate that which might result from chopping spent oxide fuel assemblies into segments. Unirradiated stainless steel-clad fuel rods, 0.95 cm O.D., were sheared into nominal 1-cm-long segments using steel dies and a hydraulic press. The resulting mixture simulated the expected particle size distribution. The largest segments in the chopped fuel mixture were no longer than 1 cm in length, while the dislodged particles ranged in size from several millimeters down to 45  $\mu\text{m}$ . Figure 4 shows the typical material obtained from shearing the clad fuel rods.

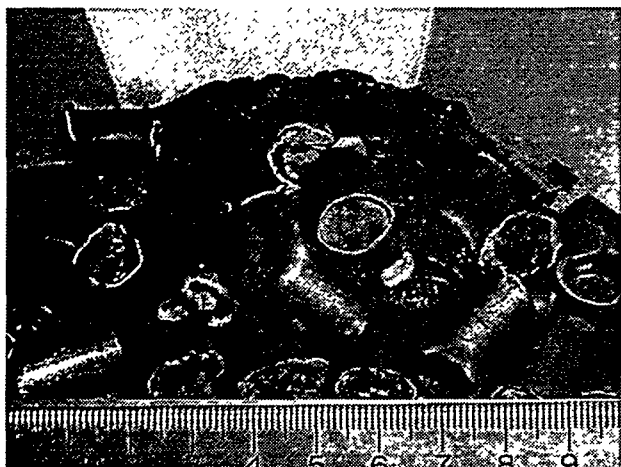


Fig. 4. Photograph of a Typical Sheared Fuel Mixture

### D. Analytical Methods

The primary analytical tools used to monitor the extent and rate of reduction included visual inspection, optical metallography, chemical titration, and X-ray diffraction (XRD). Chemical titrations were performed with 0.1N HCl to determine the  $\text{Li}_2\text{O}$  concentration of salt samples periodically drawn from the reduction salt. This method was useful in monitoring the rate of reduction as it provided almost real-time information. At the end of the reduction, samples of the reduction product were ground, loaded into glass capillaries, and then analyzed by XRD for phase information. In laboratory-scale pellet reductions, reduced pellets were sectioned, metallographically prepared, and examined with an optical microscope.

## IV. RESULTS

### A. Reduction – Salt Recovery Steps

Two engineering-scale experiments were performed to demonstrate the reduction and salt-recovery steps. The reduction experiment, designated ES-6, was performed using a full-scale electrorefiner basket from the Mark V electrorefiner currently used at ANL Idaho site. The Mark V basket consists of a perforated sheet metal shell with a single insert made of 325-mesh stainless steel screening. Figure 5 is an illustration of the outer shell and the insert in a Mark V basket.

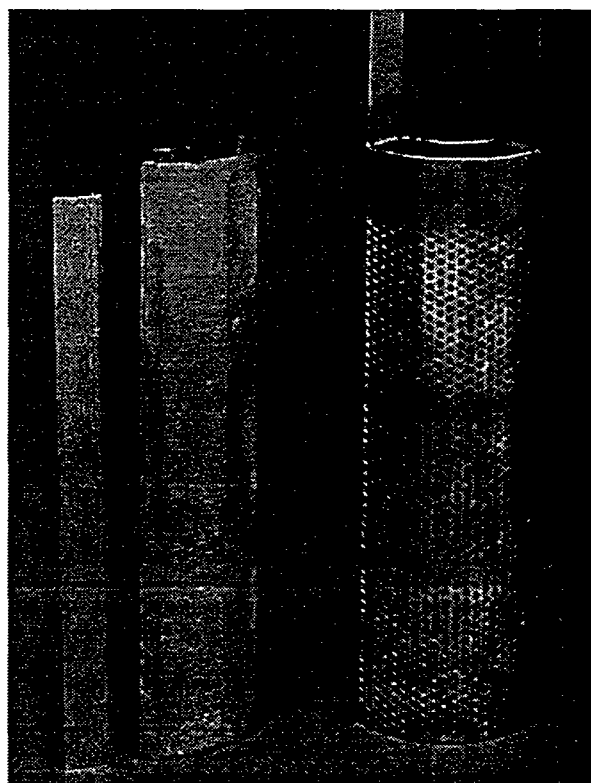


Fig. 5. Photograph of the Mark V Outer Basket (right) and Insert (left) Used in ES-6

The basket was loaded with 3.7 kg of crushed  $\text{UO}_2$ . The fuel was separated into four size fractions: 45-590  $\mu\text{m}$ , 590-1190  $\mu\text{m}$ , 1190-2830  $\mu\text{m}$ , and 2830-4000  $\mu\text{m}$ . A few 1-cm segments of clad fuel rod were also included in the fuel basket. The starting  $\text{Li}_2\text{O}$  concentration of the reduction salt was 2.0 wt%.

The ES-6 reduction was stopped after about 78 hours when it was apparent that the reduction was essentially complete. Visual examination of the reduced product at the end of the reduction showed no evidence



product at the end of the reduction showed no evidence of unreduced  $\text{UO}_2$ . The clad pellets in the fuel basket were sectioned at the end of the run; visual examination showed that they too were completely reduced. The cross sections of these reduced pellets had the same characteristic appearance as the completely reduced clad pellets in earlier laboratory-scale experiments. The bulk of the reduction appears to have been completed in about 50-60 hours.

The salt from ES-6 was then used as the starting material for the salt-recovery experiment, ES-8. In this experiment the  $\text{Li}_2\text{O}$  concentration was reduced from 3 wt % to slightly less than the starting value of 2 wt%. Figure 6 shows the change in  $\text{Li}_2\text{O}$  concentration in the bulk salt as a function of time for both the reduction and salt-recovery steps. The total time required for the salt-recovery step was approximately 45 hours, with approximately 4400 Ah of charge passed. The lithium was recovered in a form suitable for use in future reductions. The cell ran in a reliable, trouble-free manner, but the calculated 30% current efficiency was significantly lower than the 50-80% current efficiencies obtained in the laboratory-scale cells.

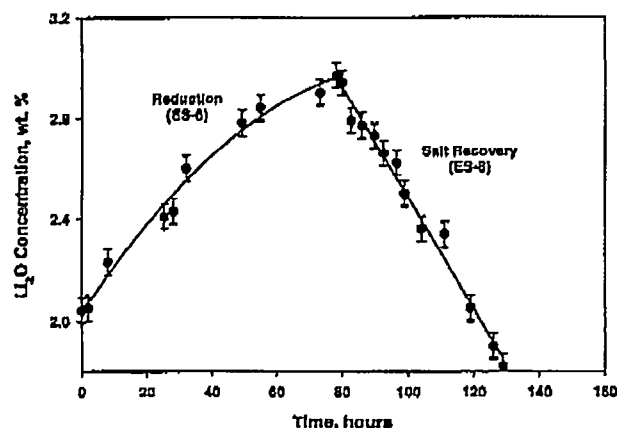


Fig. 6. The  $\text{Li}_2\text{O}$  Concentration of the Salt as a Function of Time for the Reduction (ES-6) and the Salt Recovery (ES-8) Steps

### B. Electrorefining Step

The electrorefining of reduced oxide fuel material has not yet been demonstrated at the engineering scale, although this is planned in the near term. A series of laboratory-scale experiments has, however, been performed in preparation for the planned engineering-scale experiment. These experiments have served to verify that the product from the reduction step can be

electrorefined and to provide initial estimates of current density and efficiency.

The fuel material for the lab-scale electrorefining experiments was first subjected to the reduction step; the reduced product was then transferred to the electrorefiner where the uranium was extracted as a cathode deposit. The experiments have been performed with various fuel morphologies, including clad-fuel fragments and crushed, dislodged fuel in various particle sizes. The cathode deposit and the empty cladding hulls at the end of a typical electrorefining experiment are illustrated in Figs. 7 and 8, respectively.



Fig. 7. Photograph of a Cathode Deposit Containing a Mixture of Uranium Metal and Electrorefiner Salt



Fig. 8. Photograph of Empty Cladding Hulls at the End of the Electrorefining Step (ruler marked in cm)

Typical current densities of the order of  $0.02 \text{ A/cm}^2$  have been observed in the electrorefining experiments. Current efficiencies of about 90% have been obtained. More than 90% of the reduced uranium in the anode basket has been recovered as a cathode product in these experiments. Even though these results are preliminary, they provide important confirmation that the reduced fuel can support current densities of the same order of magnitude as observed in the electrorefining of metal fuels.

## V. CONCLUSIONS

The experiments described in this paper provided valuable information concerning the key parameters governing scale-up of the reduction and salt-recovery steps. In addition, the major steps were shown to be compatible with one another. These results should provide valuable input to the basic design of a pilot-scale oxide reduction facility.

The near-term work planned includes an engineering-scale reduction experiment with a new fuel basket designed to improve reduction rates and an engineering-scale electrorefining experiment to verify the results obtained in the laboratory scale. Longer-term goals include conducting tests with actual irradiated fuel and improving the efficiency of the engineering-scale salt-recovery system.

## ACKNOWLEDGMENTS

We would like to acknowledge the contributions of the following people as having special significance in ensuring the success of the development effort: E. J. Wesolowski for his part in running the experiments, A. C. Alamillo for her help in preparation of the manuscripts of this paper, and D. L. Bowers of the ANL Analytical Chemistry Laboratory for analytical chemistry support.

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