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TREATMENT OF OXIDE SPENT FUEL USING THE LITHIUM REDUCTION PROCESS*

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ABSTRACT

The wide variety in the composition of DOE spent nuclear fuel complicates its long-term disposition because of the potential requirement to individually qualify each type of fuel for repository disposal. Argonne National Laboratory (ANL) has developed the electrometallurgical treatment technique to convert all of these spent fuel types into a single set of disposal forms, simplifying the qualification process. While metallic fuels can be directly processed using the electrometallurgical treatment technique, oxide fuels must first be reduced to the metallic form. The lithium reduction process accomplishes this pretreatment. In the lithium process the oxide components of the fuel are reduced using lithium at 650°C in the presence of molten LiCl, yielding the corresponding metals and Li_2O. The reduced metal components are then separated from the LiCl salt phase and become the feed material for electrometallurgical treatment. A demonstration test of the lithium reduction process was successfully conducted using a 10-kg batch of simulated oxide spent fuel and engineering-scale equipment specifically constructed for that purpose. This paper describes the lithium process, the equipment used in the demonstration test, and the results of the demonstration test.

I. INTRODUCTION

Approximately 2700 metric tons of spent nuclear fuel, collected over a 40-year period of reactor research and development, has accumulated within the DOE complex. This fuel reflects the varied purposes of DOE reactors and varies widely in composition, enrichment, cladding, and chemical reactivity.[1] The varied nature of these fuels complicates their long term disposal, and attempting to individually qualify each type for disposal in a repository would be prohibitively expensive. Argonne National Laboratory (ANL) has developed the electrometallurgical treatment technique to convert the different spent fuel types into a uniform set of three product streams.[2] One stream is pure uranium, which is collected separately and will 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 mineral.[3] Both of these waste forms are being designed for ultimate repository disposal. The transuranic elements will be incorporated in one of these waste streams, depending on the results of current research.

There are six main categories of fuel composition: metal, carbide, hydride, cermet, uranium-aluminum alloy, and oxide fuels.[1] The treatment of uranium-aluminum alloy fuel is the subject of current research at ANL.[4] The other metal fuels require no pretreatment other than mechanical disassembly prior to being processed using the electrometallurgical technique. Oxide fuels, such as the TMI-2 core debris, must first undergo a reduction step to convert the oxide compounds of the actinides to the metallic state. Carbide, hydride, and cermet fuels can also be treated by the electrometallurgical process. By making provisions for pretreating nonmetallic fuel, ANL's electrometallurgical process becomes applicable to the complete inventory of DOE fuel currently held in storage.

Argonne National Laboratory has developed a process that uses metallic lithium to reduce oxide fuel materials. In the lithium reduction process, lithium dissolved in molten LiCl reduces the oxide components of the fuel, yielding the corresponding metals and Li_2O. The lithium is recovered for reuse in subsequent reductions by electrolytically decomposing the Li_2O to form Li and O_2. This process was successfully demonstrated using a 10-kg batch of simulated oxide fuel and engineering-scale equipment specifically constructed for that purpose. This paper describes the lithium reduction process, the

equipment used in the demonstration test, and the results of the test.

II. DESCRIPTION OF LITHIUM PROCESS

In the lithium reduction process. the oxide fuel elements are chopped into segments. and the resultant mixture of oxide fuel and cladding is loaded into baskets. The baskets are charged to a reduction vessel, where the fuel is reduced with lithium dissolved in molten LiCl at 650°C. A layer of molten lithium floating on the surface of the salt maintains the lithium activity at unity.[5] The different components of the fuel (actinides, cladding, and fission products) react with the lithium in various ways, depending on their composition.

The actinide oxides. designated generically as MO_2, are reduced to metal according to this reaction:

$$MO_{2\,(s)} + 4\ Li_{(LiCl)} \rightarrow M_{(s)} + 2\ Li_2O_{(LiCl)} \qquad (1)$$

The reduced metal remains in the basket. The cladding, whether stainless steel or Zircaloy, is unaffected and also remains in the basket.

The fission product oxides can be divided into four groups based on their reaction with lithium. Fission products that form chlorides are classified as the "FPA" group. The alkali and alkaline earth elements are in this category. They dissolve in the salt after converting to their chlorides according to these reactions:

$$Cs_2O_{(s)} + 2\ LiCl \rightarrow 2\ CsCl_{(LiCl)} + Li_2O_{(LiCl)} \qquad (2)$$

$$SrO_{(s)} + 2\ LiCl \rightarrow SrCl_{2\,(LiCl)} + Li_2O_{(LiCl)} \qquad (3)$$

Also in the FPA group is europium, which behaves like the alkaline earth metals and forms $EuCl_2$. The rare-earth (RE) elements other than europium are not reduced and remain as oxides. These rare-earth oxides interact with Li_2O according to the following typical equilibrium:

$$Nd_2O_{3(s)} + Li_2O_{(LiCl)} \rightleftharpoons 2\ LiNdO_{2(s)} \qquad (4)$$

The $LiNdO_2$ has limited solubility in the salt, but Nd_2O_3 is virtually insoluble. Thus. elements in the RE group are distributed between the basket and the salt. Fission products that react with lithium to form salt-soluble compounds, such as LiI and Li_2Te, are designated as the "FPB" group. This group includes I. Te, Sb, Se, and Br. The balance of the fission products. the noble metal (NM) group, are reduced to metal along with the actinides and remain in the fuel basket.

The reduction conditions chosen for the demonstration test were based on laboratory-scale investigations of the effects of salt composition, temperature, and Li_2O concentration. [5] Effective reductions are possible at temperatures as low as 450°C when lower melting point eutectics such as LiCl-KCl or LiCl-LiF are used. However, the LiCl-LiF combination proved incompatible with the mineral waste form and the LiCl- KCl combination was undesirable because of potassium vaporization. Also, the solubility of Li_2O in LiCl-KCl is easily exceeded at the lower temperatures. These considerations lead to the selection of LiCl as the process salt and 650°C as the process temperature. While the solubility of Li_2O in LiCl at 650°C is 8.7 wt %, we found that to obtain efficient plutonium reductions the Li_2O concentration must be kept below 3 wt %. The reason is apparently the equilibrium reaction:

$$2\ Pu_{(s)} + 3\ Li_2O_{(LiCl)} \rightleftharpoons Pu_2O_{3(s)} + 6\ Li_{(LiCl)} \qquad (5)$$

To keep the Li_2O concentration at an acceptable value and to recover the lithium for reuse after the reduction step, the Li_2O is electrochemically decomposed to liberate oxygen and lithium:

$$Li_2O_{(LiCl)} \rightarrow 2\ Li_{(l)} + \tfrac{1}{2}\ O_2\uparrow \qquad (6)$$

This process is known as electrowinning. Equation (6) is the net result of the following two reactions, one taking place at the anode and the other at the cathode:

$$O^{-2}_{(LiCl)} \rightarrow \tfrac{1}{2}\ O_{2\,(g)} + 2\ e^- \qquad \text{(anode)} \qquad (7)$$

$$2\ Li^+_{(LiCl)} + 2\ e^- \rightarrow 2\ Li_{(l)} \qquad \text{(cathode)} \qquad (8)$$

The electrowinning step also serves to reduce the concentration of FPB and RE fission products dissolved in the salt. The rare-earth oxides that dissolve in the salt during the reduction step precipitate as the Li_2O concentration is reduced. These precipitated oxides are filtered from the salt before the recovered salt is returned for use in another reduction step. The FPA group fission products are unaffected and remain with recycled salt. The concentration of these fission products is controlled when it reaches the design limit by discarding a small portion of the salt as part of the mineral waste form.

III. EXPERIMENTAL

A. Equipment

The engineering-scale 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 electrowinning stage: and the casting station provides a means to cast the salt into ingots for recovery and reuse. The molten salt and lithium are transferred among these three components through heated transfer lines. All of the equipment is enclosed in an inert atmosphere glovebox; the facility is qualified to handle limited quantities of plutonium and other transuranics. Figure 1 is a cutaway view of the engineering scale equipment.

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 surrounded by a set of resistance heaters and insulating material, all of which are inside the vessel. The outside of the vessels is covered by a water cooling jacket. 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. Each vessel is approximately 1.2 meters tall and 1 meter in diameter; the inner crucible is 0.4 m in diameter and 0.7 m tall.

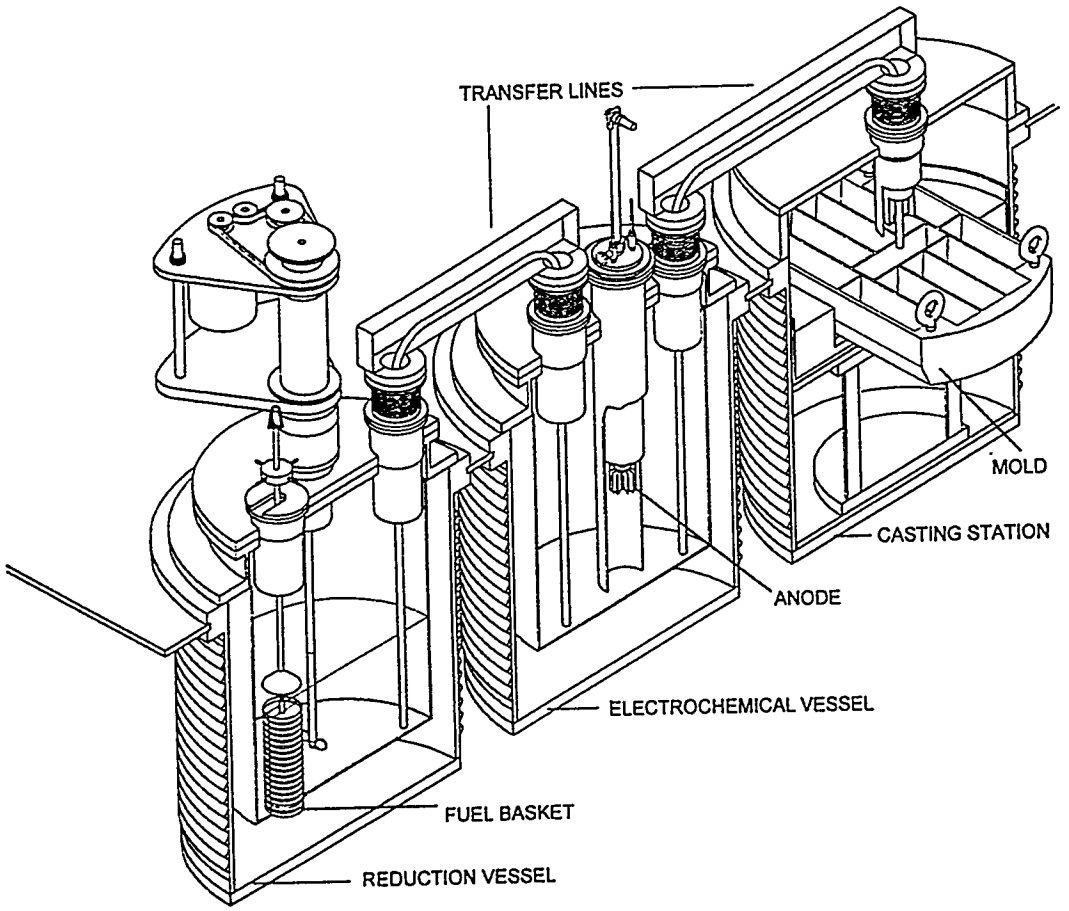

Fig. 1. Cutaway View of Components

Molten salt and lithium are transferred between the process vessels through two transfer lines. These stainless steel tubes are capable of being heated to 800°C. One transfer line connects the reduction and electrochemical vessels. the other connects the electrochemical vessel with the casting station. Salt transfer is performed by reducing pressure in one vessel relative to the other. The transfer can be stopped by equalizing pressure between the two vessels.

The anode used in the demonstration test consisted of 36 radial fins, each 0.025-cm (0.010-in.) thick and 6.3-cm (2.5-in.) high mounted at one end of a 0.5-in.-O.D. tube. The area of the exposed surface of the finned assembly was ~1600 cm^2. The tube and anode fins were constructed of a platinum-rhodium alloy to provide chemical resistance to the oxygen produced on the anode surface. The anode was surrounded by an alumina shroud designed to guide oxygen evolved at the anode surface up and out of the vessel. The inner wall of the stainless steel crucible served as the cathode.

The casting station allows for recovery of the salt by casting it into ingots. It holds a stainless steel mold designed to cast up to 22 liters of salt into 11 ingots. The mold rests on a chill block supported on copper rods that conduct heat away from the mold to the water cooling jacket on the outside of the vessel. Once the cast salt has cooled the mold is lifted out of the casting station and the ingots of salt are removed.

B. Fuel Loading

The simulated fuel used in the reduction consisted of a mixture of (1) hard-fired mixed oxide mock spent fuel pellets with a nominal composition of 5 wt % PuO_2, (2) hard-fired mixed oxide mock spent fuel pellets with a nominal composition of 0.5 wt % PuO_2, and (3) hard-fired natural uranium oxide pellets. The mock spent fuel pellets also contained small quantities of Am, formed by the radioactive decay of Pu, and 1 wt % fission product oxides. The pellets were crushed and screened to obtain a feed material with a particle size greater than 60 mesh. Powdered NpO_2 and additional oxides of fission products were added to the crushed fuel pellets to complete the loading. Table 1 provides the net composition of the simulated fuel loaded into the reduction vessel.

Table 1. Fuel Loading.

Component	Weight [grams]
UO_2	9480
PuO_2	72
AmO_2	0.4
NpO_2	5.5
Fission Products[1]	290
Total	9850

[1]The total added consisted of a mixture of Sr, Y, Zr, Rh, Ba, La, Ce, Pr, Nd, Sm, Eu, Ru, Mo, as oxides, and Cs as CsCl.

The simulated fuel was loaded into 17 circular trays, each 10 cm in diameter and 1.5 cm deep. A hole in the center of each tray allowed mounting the trays, one on top of the other, along a central rod. The trays were designed to ensure that the bottom of one tray did not touch the top of the tray below it. The trays themselves were formed from 325-mesh stainless steel screens to allow the salt and lithium ready access to the fuel from the sides and below. The completed fuel basket assembly is illustrated in Figure 2.

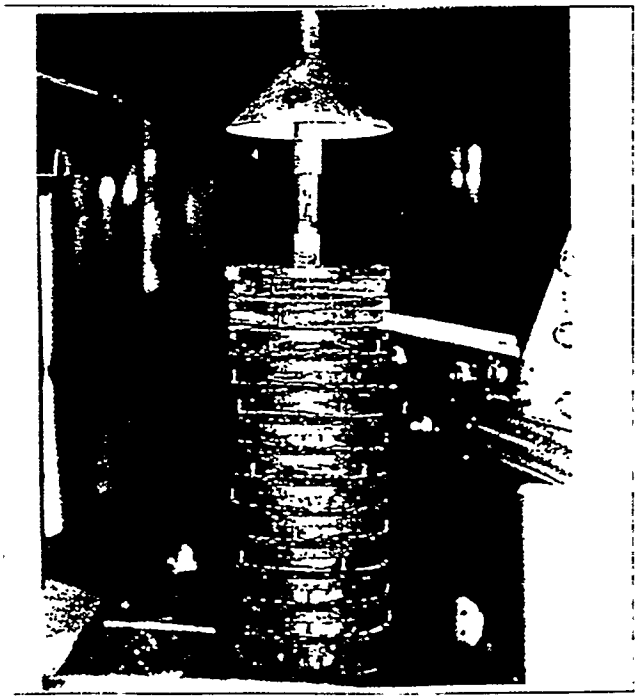

Figure 2. Fuel Basket Assembly.

C. Experimental Sequence

The reduction step began with melting 73 kg of LiCl in the reduction vessel and bringing it to the process temperature of 650°C. This took 13 hours. Once the operation of the heater controllers proved satisfactory at maintaining the temperature. 1.3 kg of lithium metal was added to the melt. The fuel basket assembly was then lowered into the melt and the mixer was energized. It was originally planned to let the reduction step go for 24 hours - a conservative estimate of the time required to totally reduce the larger pieces of fuel pellets. Instead, the step was extended to 47 hours so that the removal of the reduced fuel and transfer of the spent salt to the electrochemical vessel could be done during the day shift. At the end of the 47 hours the fuel basket assembly was removed from the vessel and allowed to cool. The fuel basket assembly was then dismantled, the reduced product was weighed and samples were recovered for analysis. Samples of the salt remaining in the reduction vessel were also obtained for analysis. These samples were obtained by drawing the salt into a stainless steel tube through a tantalum frit, which served to filter the salt.

The melt was then transferred to the electrochemical vessel for the second step of the process. The Pt-Rh anode was lowered into the melt and potentials of up to 3.0 V were established between the anode and the wall of the stainless steel crucible. which served as the cathode. The current and voltage were monitored for 68 h; the integrated current supplied to the melt was 3600 A-h, which was 95% of the integrated current theoretically required for electrowinning all the Li_2O produced in the reduction step. After this period, the current was switched off, the anode was removed from the melt, and a sample of the salt was obtained.

The final step in the demonstration test was to cast the salt and lithium into ingots by transferring the melt from the electrochemical vessel to the casting station. To avoid overfilling the molds, only about a third of the melt was transferred into the casting station at a time. Although only a few minutes were required to complete a transfer, the salt in the molds had to cool, which took about 10 hours, before the ingots could be removed.

IV. EXPERIMENTAL RESULTS

A. Reduction Step

The performance of the reduction step was evaluated by measuring the Li_2O concentration in the salt at the beginning and end of the step. The relationship between the increase in Li_2O concentration and the amount of metal oxides reduced is given in Equation (1) A total of 1960±200 g of Li_2O was produced during the reduction step, corresponding to the reduction of 8.0 to 9.8 kg of metal oxides. The actual total metal oxide loading of 9.6 kg falls within this range. No unreduced UO_2 was visible in the metal product, indicating that the reduction was complete.

Samples of the reduced metal product and the post-reduction filtered salt samples were analyzed to determine the concentrations of U, Pu, Am, and selected fission products. Inductively coupled plasma spectroscopy was used to determine the concentrations of U and Pu. The concentrations of Am and Np were determined by measuring sample activities. Accuracies of both methods were approximately ± 10 %. The analytical results were used to perform a material balance for the actinides and to determine the distribution of the actinides and selected fission products between the salt and metal phases. The material balance for the actinides was satisfactory: 95% of the U, 80% of the Pu, 54% of the Am and 100% of the Np was accounted for. Shortfalls are attributed to the accuracy of the sampling and analytical techniques and the possibility that some of the fuel material fell to the bottom of the crucible when the fuel basket was lowered into the reduction vessel salt.

The amount of actinides chemically transferred into the salt phase was very low. Of the total initially loaded, < 0.1% of the U, < 1% of the Pu, ≈ 1% of the Am, and ≈ 3 % of the Np were transferred into the salt phase. These values were expected and are acceptable, except for Np, which is higher than expected. The reasons for this behavior are not known at present. Previous laboratory work has indicated that NpO_2 is readily reduced by lithium, and that Np is not appreciably transferred to the salt phase. Table 2 provides the measured concentrations of the actinide elements in the salt phase.

Table 2. Concentrations of Actinides in Post-reduction Salt Samples.

Element	Sample 1	Sample 2
U	< 0.01 wt.%[1]	< 0.01 wt.%[1]
Pu	< 0.001 wt.%[1]	< 0.001 wt.%[1]
Am[2]	0.064 ppm	0.048 ppm
Np[3]	2.09 ppm	1.72 ppm

[1]Analytical detection limits.
[2]Values based on ^{241}Am activity measurements.
[3]Values based on ^{237}Np activity measurements.

The distribution of selected fission products between the salt and metal phase was also determined. The behavior of the FPA group of fission products was checked using Sr and Ba. Both of these were transported into the salt phase. The NM group of fission products was tracked using Mo, Ru, and Zr, all of which remained in the metal product. The FPB group of fission products was tracked using La, Ce, Pr, and Nd. These fission products were distributed between the metal and salt phases in the following ratios: La (3:2), Ce (3:1), Pr (1:1), and Nd (3:1). These ratios are based on samples of material actually recovered and serve only as an indication of material distribution. The indications are, however, that the fission product distribution occurred as expected.

B. Electrowinning Step

The performance of the electrowinning step was evaluated by measuring the Li_2O concentration before and after electrowinning. In this step, the concentration of Li_2O should decrease as lithium metal is produced. As the integrated current supplied was 95% of that theoretically required, the expected concentration of Li_2O in the salt after electrowinning was very low. However, measurements of the Li_2O concentration in salt samples before and after electrowinning indicated a slight increase in Li_2O concentration. Furthermore, a visual examination of the cast salt indicated that there was very little lithium formed. Later analysis indicated that the oxygen evolved at the anode was being transferred back into the melt rather than out of the vessel via the anode shroud. This had the effect of producing Li_2O as quickly as it was electrolytically decomposed.

V. CONCLUSION

The March 1995 test successfully demonstrated the lithium reduction process at the 10-kg scale. Apart from the anode shroud assembly, the equipment functioned extremely well and requires no modifications. Material balances on the actinides were satisfactory, and the chemical behavior of the actinides and fission products was as expected.

In the near-term, work is focused on redesigning the anode assembly. Once laboratory-scale experiments prove the feasibility of this new design, an engineering-scale version will be built, installed in the electrochemical vessel, and tested. Preparations are also being made to run a reduction experiment using simulated core material representing TMI-2 core debris. Longer-term goals include increasing the batch size of the fuel and demonstrating a complete cycle of reduction, electrowinning and reduction. By making provisions for reducing oxide fuel materials, the lithium reduction process makes the electrometallurgical treatment technique applicable to a significant portion of DOE fuel types.

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