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ADVANCED WASTE FORMS FROM SPENT NUCLEAR FUEL[*]

by

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ABSTRACT

More than one hundred spent nuclear fuel types, having an aggregate mass of more than 5000 metric tons (2700 metric tons of heavy metal), are stored by the United States Department of Energy. This paper proposes a method for converting this wide variety of fuel types into two waste forms for geologic disposal. The method is based on a molten salt electrorefining technique that was developed for conditioning the sodium-bonded, metallic fuel from the Experimental Breeder Reactor-II (EBR-II) for geologic disposal. The electrorefining method produces two stable, optionally actinide-free, high-level waste forms: an alloy formed from stainless steel, zirconium, and noble metal fission products, and a ceramic waste form containing the reactive metal fission products. Electrorefining and its accompanying head-end process are briefly described, and methods for isolating fission products and fabricating waste forms are discussed.

INTRODUCTION

More than one hundred spent nuclear fuel types, having an aggregate mass of more than 5000 metric tons (2700 metric tons of heavy metal), are stored by the United States Department of Energy.[1] A method, based on electrotransport in a molten salt medium, is proposed for reducing this wide variety of spent nuclear fuel types to just two stable, actinide-free waste forms for geologic disposal.[2] Figure 1 shows a schematic of the overall electrometallurgical process for treatment of metal and oxide spent fuels. The process was originally developed for recovery of a rare-earth contaminated mixture of uranium and transuranium elements;[3] it has been modified to avoid isolation of transuranium-rich material and to place the transuranium fraction into the ceramic waste.

Seventy-one percent of the fuel mass (81% of actinide mass) is in the form of metallic fuel that can be electrorefined directly. A reduction-electrotransport process has been developed to handle the 13% (11% of actinide mass) that is in the form of oxide; extension of the process to graphite-based fuels and other types is in a very early stage of development. Some of the fuels are considered to be "at risk" in that they (1) have seriously degraded during storage, (2) are highly enriched in fissile isotopes, (3) are chemically reactive or contain reactive materials, or (4) cannot be expected to retain their integrity or remain stable over an extended period of dry storage.

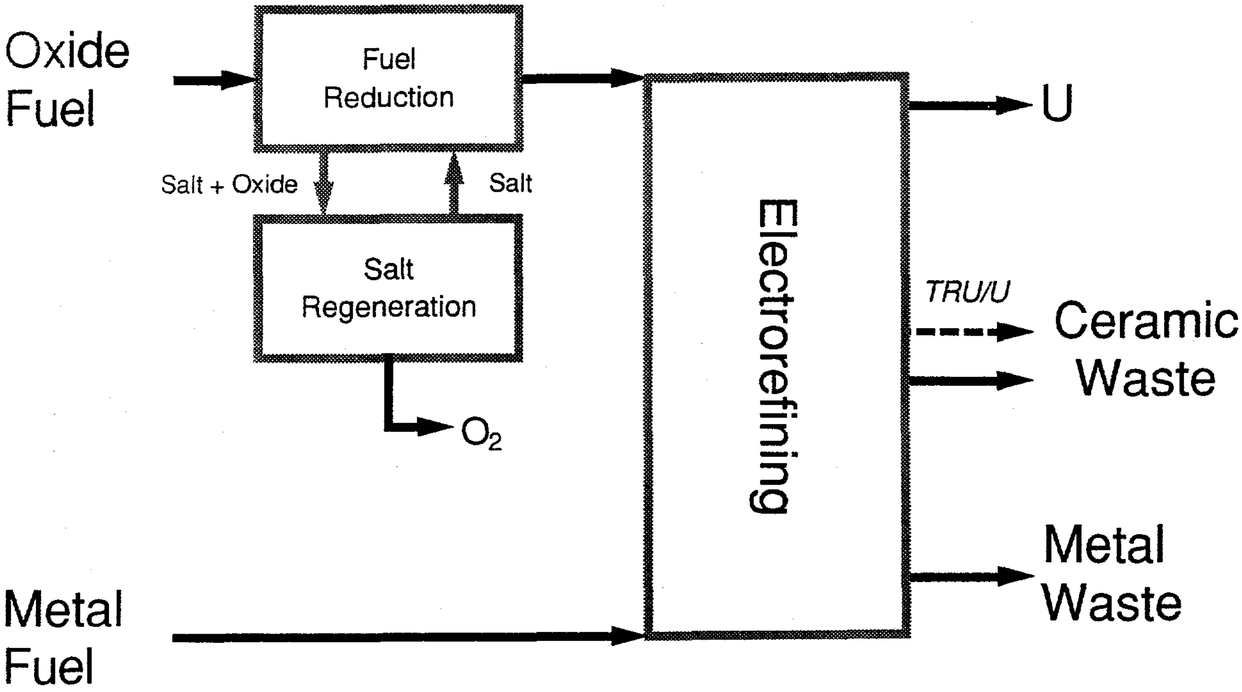

Fig. 1. Electrometallurgical Process for Treatment of Spent Nuclear Fuel

Modification of an inert-gas hot-cell facility for electrometallurgical treatment of the first at-risk spent fuel (EBR-II stainless-steel clad, sodium-bonded metal fuel) is nearly complete. Essentially the same kind of facility and process can handle the other types of metal fuels. A reduction process is being developed to extend the concept to most oxide fuels.

PROCESS DESCRIPTION AND TEST RESULTS

Reduction of Oxide Fuels. Metal fuels may be introduced directly into the electrorefiner, but oxide fuels must first be converted to metal. Oxides are reduced to metals by using lithium reductant in a lithium chloride medium at 925 K. The resulting lithium oxide solution in lithium chloride is subjected to electrolysis to remove oxygen as a gas, and to regenerate the lithium reductant so that the lithium chloride can be recycled. The metals are separated from the molten salt and physically transferred to an electrorefiner, as described in the next section. The important features of the oxide reduction process include the reduction step and the behavior of fission products and fuel components during reduction, and the salt electrolysis to regenerate lithium from the Li_2O. These features are discussed in the following paragraphs.

Reduction Step. Reduction of oxides by lithium in the molten LiCl system proceeds according to the reaction

$$MO_x\,(s) + 2xLi(l) \leftrightarrow xLi_2O(salt) + M(s) \tag{1}$$

where M is the metal to be reduced. The free energies of formation of the actinide elements are fairly close to that of Li_2O; therefore, it is not immediately apparent that lithium would be a good reductant for these oxides. In particular, the free energies of formation of Pu_2O_3 and Am_2O_3 are quite close to, or even slightly more negative than that of Li_2O. Both experiments and calculations indicated that it is important to keep the activity of Li_2O in the molten LiCl low (about 1/4 to 1/3 of saturation) to ensure that the reductions of these actinide elements are driven to completion. Under conditions of low Li_2O activity, complete (>99.9) reductions at 925 K have been consistently achieved.

Fission product behavior in the reduction step may also be determined by thermodynamic calculations. Obvious conclusions from such calculations are that the alkali and alkaline-earth fission products are converted to chlorides that are soluble in the molten LiCl, and that anions such as iodine, tellurium, and selenium form soluble compounds with lithium. Less obvious is the behavior of the rare-earth fission products. Our studies found that the more stable oxides (such a d Ce_2O_3 and Nd_2O_3) partially react with Li_2O according to the equation

$$Nd_2O_3\,(s) + Li_2O(soln) \leftrightarrow 2LiNdO_2(soln) \tag{2}$$

forming a complex oxide, which is much more soluble in the LiCl than is the simple oxide. In these molten salt systems, the rare-earth elements, europium and samarium, behave more like alkaline-earth elements than like the other rare earths, in that they form stable divalent chlorides that are fairly soluble in the LiCl. Thus, they are expected to stay with the reduction salt. That portion of the stable rare-earth oxides (such as Ce_2O_3) that remain unreacted must be removed from the LiCl for disposal by filtration.

Salt Electrolysis. To recycle the LiCl reduction salt, it is necessary to electrolytically reduce the Li_2O to lithium metal, while discarding oxygen gas from the system. Commercial production of lithium metal from LiCl is a fairly routine process; however, in the commercial process, the chloride salt decomposes, evolving chlorine at a carbon anode. Carbon is inert to chlorine, but reacts readily with oxygen to form CO/CO_2 mixtures. In our experiments with carbon (graphite) anodes, the carbon appeared to be preferentially reacted along the grain boundaries. Carbon grains were thus set free into the molten salt, forming carbon "dust" that tended to short the cell and could react with actinides in subsequent process steps. Two solutions were found to the carbon "dust" problem: (1) use of a porous shroud around the anode compartment to contain the dust and (2) use of inert anode materials that evolve oxygen gas directly without reaction.

The performance of the carbon and inert anode materials in the electrolysis step was measured in many small-scale experiments, the results which are summarized in Table I. All of the experiments were performed at 650°C, for both carbon and Pt-Rh anodes. The cathode was initially a steel rod, but as the electrolysis progressed, lithium metal deposited on the steel, and the cathode became a pool of liquid lithium that floated on the surface of the LiCl molten salt. A higher current density was achieved with the carbon anode, because the chemical reaction of oxygen with carbon helps drive the overall reaction. The current efficiency was determined by comparing the amount of lithium metal produced to the integrated current passed. Very high current efficiencies were achieved with the inert anode, probably because of a lower tendency for chemical short-circuit reactions. With the carbon anode, it is possible that some of the evolved CO_2 will react with Li_2O to form soluble Li_2CO_3, which can then diffuse to the cathode compartment and react with some of the lithium. The carbon anode was expected to corrode fairly rapidly because it is consumed in the reaction; however, the consumption rate was even more rapid than the reaction rate because some of the carbon was released into the molten salt in the form of "dust", as mentioned above. The Pt-Rh anode was not significantly corroded, but this material is too expensive for a production process. Other inert materials are being explored, and several have been identified for further study.

Table I. Summary of Small-scale Electrolysis Experiments

Experimental Parameter	Carbon Anode	Inert Anode
Temperature, °C	650	650
Anode material	Carbon	Pt-Rh
Cathode material	Liquid lithium	Liquid lithium
Current density, mA/cm^2	540	280
Current efficiency, %	91	~100
Anode corrosion	Consumable anode	Very low

Electrorefining. Spent fuel in metallic form is obtained either from the reduction process or by chopping metal fuel. It is placed in a metallic basket, and introduced into the molten salt electrolyte of an electrorefiner that is maintained at 775 K. The electrolyte is a LiCl-KCl eutectic, containing about 2 mole % of actinide chlorides; it melts at 635 K. Any highly reactive metals (alkali, alkaline-earth, rare-earth) are oxidized to their chlorides by the actinide chlorides;[4] additional oxidant, such as uranium chloride, is added from time to time to restore the level of actinide chloride to about 2 mole % and sustain the electrotransport step. The oxidizing condition in the electrorefiner is, thus, adjusted so that reactive metals, including nearly all the rare earths in the fuel, are found in the electrolyte. Noble metal fission products and cladding materials remain in the basket as metals, and actinides are in the salt and (primarily) the metal phase. A schematic diagram of the electrorefiner is shown in Fig. 2.

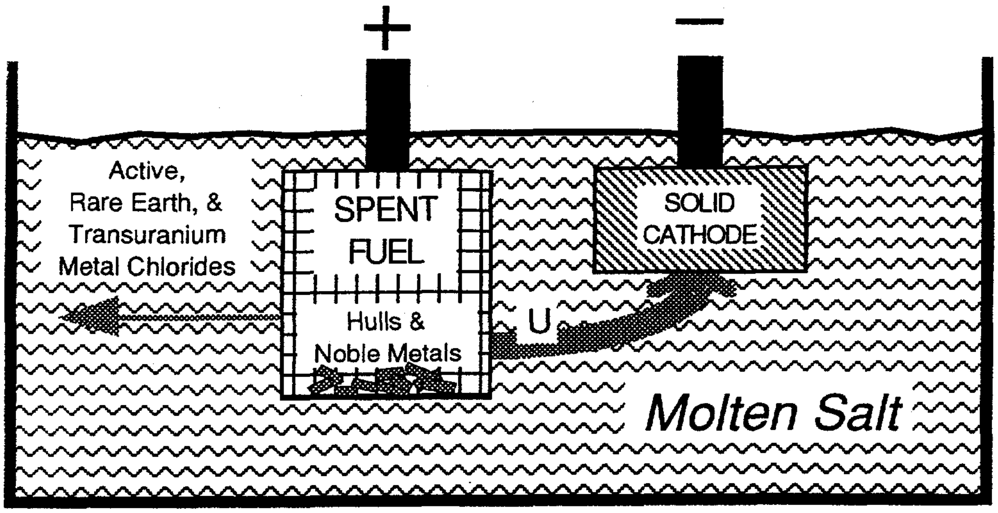

Fig. 2. Schematic of Electrorefiner

The feed baskets are attached to the positive pole of a dc power supply; they will become anodes. Steel mandrels are attached to the negative pole; the mandrels become cathodes. Passage of current results in the electrotransport and deposition of nearly pure uranium on to the steel cathodes. The uranium is removed and, if it is enriched, isotopically diluted to convert it to commercial fuel. Depleted or natural uranium is converted to oxide for storage. This process was previously developed to recycle fuel to a fast reactor; in that case, a liquid cadmium cathode was used to reduce the activity of the transuranium actinide mixture.

The electrorefining process has been in routine operation at engineering scale (10-kg uranium cathode deposits) at Argonne National Laboratory for more than seven years. The process is reliable, reproducible, and efficient, and it has been adapted for hot-cell operation. The process has been modified so as to place the transuranium (TRU) elements into the ceramic waste form, as described in the following paragraphs.

Waste Isolation and Waste Forms

Metal Waste. Particulate matter can enter the electrorefiner as compounds that are formed by reaction with trace amounts of impurities, such as water from the cell atmosphere, or through the loss of noble metals from the anode baskets. These particulates are removed by circulating the salt through stainless-steel filters; the filters and their contents are then combined with the contents of the anode baskets (noble metal fission products and cladding hulls) and melted under a $CaCl_2$ flux that contains an oxidant, such as Cu_2Cl_2. Any residual actinide chlorides will dissolve in the salt; metallic actinides will be oxidized to chlorides. Also, oxides are thought to be preferentially wet by the salt. A similar process was shown to result in a nearly actinide-free ingot.[5] The heat generated by the transition metal fission products dissipates rapidly because of their generally short half lives; thus, decay heat does not affect fission product loading in the metal waste form. After 50 years, the total fission product activity is extremely low - only a few hundred curies per ton, mostly from ^{63}Ni ($t_{1/2}$=100 y) and ^{99}Tc ($t_{1/2}$=2x10^5 y). The composition of the alloy depends on the nature of the fuel cladding. Metal wastes from fuels with stainless-steel cladding contain 15 wt % zirconium and 1 to 5 wt % fission products (balance stainless steel); those from zircaloy-clad fuel contain roughly the same amount of fission products and 8 wt % of stainless steel (balance zirconium). Fission product loading falls naturally in the range of 1 to 5 wt % (depending on burnup and fuel pin design) because this is the ratio of fission products to cladding hulls. Corrosion rates of the waste alloys are low (<20 μm/year in J-13 well water, pH 7, at room temperature); accelerated tests are being devised in which the rates become high enough to distinguish effects of composition variations. The alloys have similar mechanical properties to the stainless steels.

Ceramic Waste. After several dozen batches of fuel have been processed, a temperature control limit is approached in the electrorefiner because of buildup of decay heat in the salt. The salt is then treated to remove fission products, as shown in Fig. 3.

First, the bulk of the actinide chlorides are removed by reduction with a stream of Cd-3 wt % Li alloy; this alloy "stores" the actinides temporarily. Next, the remaining transuranium actinides are removed by multistage countercurrent extraction of the salt with a nearly saturated alloy of uranium in cadmium. This cadmium is combined with the reductant cadmium. Fission product chlorides are then removed from the salt by ion exchange into beds of salt-loaded zeolite A. Cadmium chloride oxidant is added to the purified salt, and the oxidizing salt is contacted with the combined cadmium stream to return the actinides to the salt. The salt is replaced in the electrorefiner, and the process resumes. The cadmium is recycled.

The fission product-loaded zeolite bed is combined with salt-free zeolite, to incorporate the liquid salt that wets the surface of the bed particles into the zeolite molecular structure; this combined material is blended with glass frit bonding agent and densified by hot-pressing to make a uniform, monolithic waste form. When the reduction step is used with oxide fuels, the lithium chloride reduction salt eventually becomes excessively contaminated with active metal fission products as well. It is then diluted with KCl to a melting point of 775 K and mixed with salt-free zeolite to make the ceramic waste form, as described above.

The glass-bonded zeolite ceramic waste form appears to have leach rates that are similar to or better than the "environmental" glass that has been used as a standard for defense glass waste forms in the United States. The fission product loading of the ceramic waste form can be quite high (about 5 wt % of radioactive nuclides). For relatively fresh, high-burnup fuels, the ceramic waste material may have to be aged before emplacement in the repository, or formed into relatively small diameter logs, to avoid excessive heating of the repository rock and excessive centerline temperatures in the waste form.

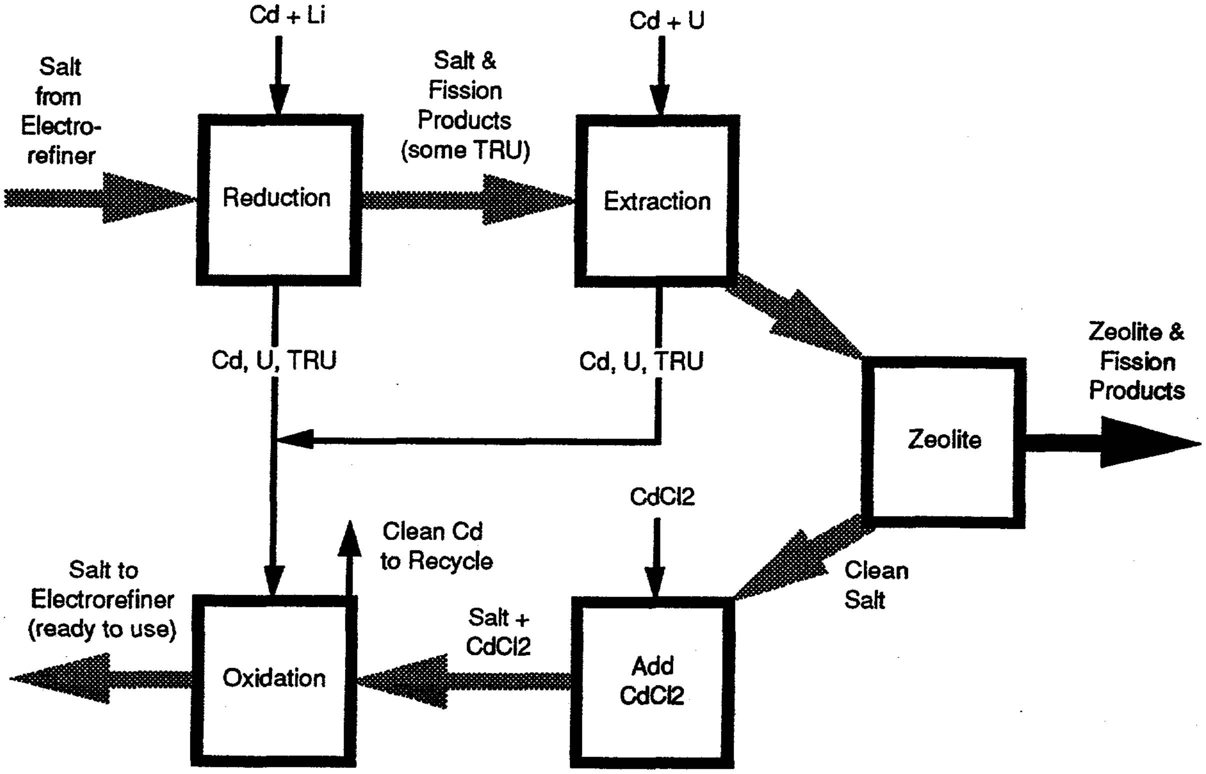

Fig. 3. Removal of Fission Products from Electrorefiner Salt

CONCLUSION

Waste qualification for geologic disposal of the many types of spent nuclear fuel being stored by the United States Department of Energy is a difficult issue. Electrometallurgical treatment of these spent nuclear fuels is a promising concept for solving many of the DOE spent fuel disposal problems, and deserves further consideration. The concept is simple, and the method results in isolation of the wastes in two stable, low-volume waste forms, which should be capable of qualification for geologic disposal. The process steps, including oxide reduction, molten salt electrolysis, electrorefining of metals, waste salt treatment, and waste form production, have been demonstrated to be feasible at engineering scale. Hot demonstration of the electrorefining step by treatment of the EBR-II spent fuel is ready to begin at the Fuel Conditioning Facility in Idaho.

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