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Electrometallurgical Treatment of TMI-2 Fuel Debris

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ABSTRACT

Argonne National Laboratory (ANL) has developed an electrometallurgical treatment process suitable for conditioning DOE oxide spent fuel for long-term storage or disposal. The process consists of an initial oxide reduction step that converts the actinide oxides to a metallic form, followed by an electrochemical separation of uranium from the other fuel constituents. The final product of the process is a uniform set of stable waste forms suitable for long-term storage or disposal. The suitability of the process for treating core debris from the Three Mile Island-2 (TMI-2) reactor is being evaluated. This paper reviews the results of preliminary experimental work performed using simulated TMI-2 fuel debris.

INTRODUCTION

Approximately 200 metric tons<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> This paper presents preliminary experimental results concerning the application of the electrometallurgical treatment technique to TMI-2 fuel debris, which constitutes 80 metric tons of the oxide fuel inventory.

The electrometallurgical treatment technique consists of two distinct stages. The first of these is the reduction of the oxide compounds of the actinides 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, and fission products) are separated electrochemically to become the three product streams described above.

The ability of the lithium reduction process to reduce the principal components of oxide fuel has been demonstrated at the engineering scale,<sup>4</sup> as has the ability of the electrorefiner to separate the components of reduced Zircaloy-clad oxide fuel.<sup>5</sup> However, the unique characteristics of the TMI-2 debris require additional testing of the reduction step. A significant portion of the debris consists of a ceramic mixture of (U,Zr)O<sub>2</sub> combined with iron and chromium from melted structural components and small amounts of cadmium and silver from melted control rods. In addition, there are partial fuel assemblies from relatively undamaged peripheral sections of the core. Specific issues identified for testing include the conditions required to reduce the (U,Zr)O<sub>2</sub> ceramic, the effect of cladding on the reduction rate of UO<sub>2</sub> pellets, and the engineering questions associated with transferring the reduced product to the electrorefiner. The ultimate goal of the current work is the reduction of TMI-2 core debris to produce a product suitable for electrorefining.

EXPERIMENTAL

In the current series of experiments, material from the melted central region of the TMI-2 core was represented using synthetic "corium" -- a mixture of (U,Zr)O<sub>2</sub>, Zr, Fe, and Cr. Partially intact fuel rods from peripheral regions of the TMI-2 core were represented by clad UO<sub>2</sub> fuel rods. Laboratory-scale

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

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experiments were performed using samples of synthetic corium, clad  $\text{UO}_2$  fuel pellets, and pure  $\text{ZrO}_2$  to obtain information on the extent and rate of the lithium reduction reaction. Information was obtained using X-ray diffraction (XRD) studies of the reduced corium, and visual inspection of sectioned fuel rods after reduction. The  $\text{Li}_2\text{O}$  concentration in the bulk salt was used to make quantitative estimates of the extent of the reduction for both materials. Samples of reduced corium and fuel pellets were also subjected to metallographic examination, including scanning electron microscopy (SEM) and X-ray fluorescence techniques.

The initial engineering-scale reduction of simulated TMI-2 debris was performed in September 1996. The first part of the experiment was the reduction of 4 kg of synthetic corium for 30 hours in 77 kg of  $\text{LiCl}$ . The corium reduction was followed by the reduction of the clad fuel pellets. For this part of the experiment, 2.5 kg of stainless-steel clad  $\text{UO}_2$  fuel rods was cut into 1-cm segments and reduced for 47 hours. The same salt was used for both reductions, although lithium was added to the molten salt for the reduction of the fuel rod segments. Both the corium and fuel pellets were contained in a prototypical fuel basket assembly being considered for use in future electrorefiner designs.

## RESULTS

The results of the laboratory-scale reduction experiments indicated that the complete reduction of corium was possible provided that the concentration of  $\text{Li}_2\text{O}$  in the salt did not exceed 1.3 wt%. Exceeding this value led to the production of lithium zirconate ( $\text{Li}_2\text{ZrO}_3$ ) through a reaction between zirconium metal and  $\text{Li}_2\text{O}$ . This reaction, however, was only of significance with finely divided Zr metal. Zircaloy cladding was essentially unaffected. The reduction rate of the corium was relatively rapid, being complete in most cases after 20 hours. Experiments with various lengths of clad pellets indicated that the reduction of clad pellets 1 cm in length would require 48 hours.

The information from the laboratory-scale tests was used to establish the duration of the engineering-scale experiment. However, it was found that the results of the laboratory-scale experiments under-predicted the reduction times required using the engineering-scale equipment. The reasons for this appear to be related to the surface area to volume ratio for the fuel basket used in the engineering-scale experiment. This ratio could not be accurately

duplicated in the laboratory-scale experiments. Modifications to the fuel basket are being made that will improve the access of  $\text{LiCl}$  and  $\text{Li}$  to the fuel. A second engineering-scale experiment using this new design is scheduled for completion in February 1997.

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