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Electrometallurgical Treatment of Oxide Spent Fuel — Engineering-Scale Development

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Abstract

Argonne National Laboratory (ANL) has developed the electrometallurgical treatment process for conditioning various Department of Energy (DOE) spent fuel types for long-term storage or disposal. This process uses electrorefining to separate the constituents of spent fuel into three product streams: metallic uranium, a metal waste form containing the cladding and noble metal fission products, and a ceramic waste form containing the transuranics, and rare earth, alkali, and alkaline earth fission products. While metallic fuels can be directly introduced into the electrorefiner, the actinide components of oxide fuels must first be reduced to the metallic form. The Chemical Technology Division of ANL has developed a process to reduce the actinide oxides that uses lithium at 650°C in the presence of molten LiCl, yielding the actinide metals and Li_2O. A significant amount of work has already been accomplished to investigate the basic chemistry of the lithium reduction process and to demonstrate its applicability to the treatment of light-water reactor- (LWR-) type spent fuel. The success of this work has led to conceptual plans to construct a pilot-scale oxide reduction facility at ANL's Idaho site. In support of the design effort, a series of laboratory- and engineering-scale experiments is being conducted using simulated fuel. These experiments have focused on the engineering issues associated with scaling-up the process and proving compatibility between the reduction and electrorefining steps. Specific areas of investigation included reduction reaction kinetics, evaluation of various fuel basket designs, and issues related to electrorefining the reduced product. This paper summarizes the results of these experiments and outlines plans for future work.

I. INTRODUCTION

The Department of Energy (DOE) inventory of spent nuclear fuel contains a wide variety of fuel types that are unsuitable for direct repository disposal in their current form. Concerns about the enrichment, chemical stability, and physical condition of these fuel types complicate the task of preparing and qualifying them for repository disposal. The electrometallurgical (EM) treatment technique developed by Argonne National Laboratory (ANL) has the potential to simplify preparing and qualifying these fuels for disposal by converting them into a uniform set of three product streams: uranium metal, a metal waste form, and a ceramic waste form. The separation of the constituents of spent fuel into these product streams is accomplished by electrorefining the spent fuel.

A demonstration of the EM process is currently underway using sodium-bonded metallic fuel from EBR-II, the fuel type for which the process was designed.[1] At the same time, the Chemical Technology Division (CMT) of ANL is evaluating whether the EM process can also be used to treat non-metallic DOE fuel types. Because the electrorefining process requires a metallic feed, non-metallic fuels must first undergo a head-end step to convert the actinide components into metals state before electrorefining. For oxide fuels, CMT has developed a process to reduce the actinide oxides that uses lithium at 650°C in the presence of molten LiCl, yielding the metallic actinides and Li_2O. The Li_2O, which is soluble in LiCl, is then electrolytically decomposed to lower its concentration in the reduction salt before the salt is recycled to the reduction vessel. The lithium metal, recovered from the reduction salt, is also recycled to the reduction vessel for subsequent reductions.

A significant amount of work has already been accomplished to investigate the basic chemistry of the lithium reduction process and to demonstrate its applicability to the treatment of light-water reactor- (LWR-) type spent fuel.[2] The success of this work has led to conceptual plans to construct a pilot-scale oxide reduction (PSOR) facility at ANL's

Idaho site.[3] In support of the design effort, a series of laboratory and engineering-scale experiments is being conducted using simulated fuel. These experiments have focused on the engineering issues associated with scaling-up the process and proving that the reduction and electrorefining steps are compatible. Specific areas of investigation included reduction reaction kinetics, evaluation of various fuel basket designs, and issues related to electrorefining the reduced product. This paper summarizes the results of these experiments and outlines plans for future work.

II. PROCESS DESCRIPTION

Figure 1 is a simplified flowsheet that illustrates the different portions of the lithium reduction process and its interfaces with other steps in the electrometallurgical treatment technique. Fuel elements are chopped into segments, and the resultant mixture of oxide fuel and cladding is loaded into a fuel basket. The fuel basket is then transferred to the reduction vessel, where it is reduced with lithium dissolved in molten LiCl at 650°C. Molten lithium in contact with the salt maintains the lithium activity at unity. The actinide oxides are reduced, and the actinide metals and Li_2O are formed. The Li_2O, which is soluble in LiCl, is then electrolytically decomposed at 650°C in a salt-recovery step. The resulting salt, which is low in Li_2O concentration, and the lithium metal are recycled to the reduction vessel for subsequent fuel reductions. The fuel basket from the reduction vessel, which contains the reduced product including uranium, transuranics, and cladding hulls, is transferred for electrorefining. The electrorefiner is operated at 500°C and uses LiCl-KCl eutectic salt, with dissolved UCl_3 as the electrolyte. The electrorefining process then separates the constituents of spent fuel into three product streams: metallic uranium, a metal waste form, and a ceramic waste form.

III. EXPERIMENTAL

A. Laboratory-Scale Equipment

The laboratory-scale equipment at CMT was built to support testing of process chemistry and scale-up issues related to the lithium reduction process. All the laboratory-scale experiments were performed in a high-purity helium ($H_2O < 5$ ppm) atmosphere glovebox. The reduction experiments were performed in 6-in.- (15.2-cm-) diam. furnace wells. The primary crucible used in these experiments was made of 304 stainless steel, with a volume of 600 cc. A stainless steel stirrer was used in some of the experiments. The mass of fuel used in these experiments varied from 20 to 200 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 at CMT was designed to support testing of all of the process steps at fuel loadings of up to 20 kilograms per batch. The facility consists of three major components: the reduction vessel, the electrochemical vessel, and a casting station. All were enclosed in a large (7.6 m x 2.4 m x 2.6 m) argon atmosphere glovebox. The reduction vessel holds the salt, fuel, and lithium during the reduction step. The electrochemical vessel holds the molten salt during the salt recovery step and can be configured for electrorefining the reduced product. Each vessel is approximately 1.2 m tall and 1 m in diameter and contains a crucible that holds the molten salt. The inner crucibles are 0.4 m in diameter and 0.7 m tall. A casting station is provided to allow the salt to be cast into ingots for storage between process steps. The facility is qualified to handle limited quantities of plutonium and other transuranics. Figure 2 shows a cut-away view of the reduction vessel as configured for the engineering-scale experiments described here.

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. The size of these fuel segments is an important design parameter: The largest particle size determines the minimum time for the reduction to be completed, while the smallest presents containment problems. Studies performed at Oak Ridge National Laboratory (ORNL) on shearing fuel bundles provided a basis for selecting the size distribution of the material used in these tests.[4] The ORNL studies estimated that shearing a fuel bundle into 1-in. (2.54-cm) segments would dislodge 50% of the UO_2 from the cladding. For testing the lithium reduction process, we conservatively assumed that the material not dislodged remained as an intact fragment. Unirradiated stainless steel-clad fuel rods, 0.95 cm O.D., were cut into 1-cm-long segments to represent the maximum expected particle size if fuel assemblies were sheared into 1-in. (2.54-cm) segments.

The ORNL work also examined the particle size distribution of material dislodged from chopping single UO_2 rods into 0.5-in. (1.27-cm) segments. The dislodged fragments were all smaller than 2000 μm. Half of the particles (by mass) were larger than 100 μm (corresponding to a 170 mesh screen). Five percent of the particles were less than 1 μm. For testing the lithium reduction process, material obtained from crushing unirradiated UO_2 pellets was used to represent fuel dislodged from the cladding during the chopping operation. The individual pieces of crushed UO_2 ranged in size from several millimeters down to 45 microns. Smaller particles were not used because the equipment to contain them in the reduction system has not yet been fully developed.

Note that the ORNL work was done using unirradiated fuel and simulated fuel bundles. Because of the nature of irradiated fuel, it will probably be more easily fragmented than unirradiated UO_2. Thus, the simulated fuel used in these experiments is considered to be a conservative representation of actual spent fuel for estimating reduction kinetics.

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 Li_2O concentration of salt samples periodically drawn from the reduction salt. This method was very useful in monitoring the rate of reduction. 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. EXPERIMENTAL RESULTS

A. Laboratory-Scale Experiments

In preparation for the engineering-scale experiments, a series of laboratory-scale experiments was performed to identify the factors affecting reaction kinetics. Specifically, the experiments focused on the relationship between the reduction rate and the stirring speed, fuel morphology, and the basket dimensions. These experiments were intended to predict the required reduction times in the engineering-scale experiments.

Experiments were run in which crushed UO_2 and clad UO_2 fuel rod sections were reduced with and without stirring. In these experiments, the fuel was held in a 1.5 cm x 1.5 cm x 5-cm-tall basket. Lithium-saturated stainless steel foam was the source of lithium. This method was chosen because the lithium recovered in the salt-recovery step is contained in a stainless steel foam cathode. The results of these experiments suggest that complete reduction of the crushed UO_2 could be accomplished in as little as 12 hours, with adequate stirring. Stirring had little effect on the reduction rate of clad UO_2 pellets: They required 36 hours to be completely reduced. The difference in the effect of stirring on the crushed UO_2 and on the clad pellets is thought to result from differences in the relationship between particle size and basket dimensions. Stirring increases the rate of crushed UO_2 reduction because it increases contact between the bulk salt (containing dissolved lithium) and the fuel particles. Without stirring, the bed of crushed UO_2 tends to act like a single pellet whose length is related to the basket thickness. The results of these experiments are plotted in Figure 3.

B. Engineering-Scale Experiments

Two engineering-scale experiments, designated ES-5 and ES-6, are discussed in this paper. They were essentially identical, except for the design of the fuel basket used to hold the UO_2. The primary purpose of ES-5 was to test whether the reduction rates obtained at laboratory-scale could be achieved at engineering-scale. Because the thickness of the fuel basket is a critical parameter in determining reduction rate, the geometry of the fuel basket used in ES-5 was specifically designed to resemble the one used in the laboratory-scale work. The primary purpose of ES-6 was to evaluate the suitability of using an existing electrorefiner basket[1] (the Mk V) for the reduction step. The Mk-V basket is considerably thicker than the fuel basket tested in ES-5 and thus required an independent test. Additional objectives in both ES-5 and ES-6 were checking whether lithium contained on prototypical cathodes can be used for reductions, evaluating bulk salt sample titration as a means of monitoring reaction progress, and characterizing the reduction product.

The feed material for ES-5 comprised 5.2 kg of crushed UO_2 and 77 kg of salt. After crushing, the particles were sieved and a particle size distribution was obtained consisting of four size fractions: 45-590 μm, 590-1190 μm, 1190-2830 μm, and >2830 μm.. The crushed UO_2 was loaded into the fuel basket such that the different particle sizes

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[1] One of the design criteria for the PSOR facility is that it be compatible with the Mk-V electrorefiner. This requires that the oxide fuel be reduced in the Mk-V basket assembly, which is then transferred to the electrorefiner.

occupied separate layers in the fuel basket. The fuel basket itself consisted of two separate compartments bolted to a single steel plate at the bottom. The compartments were separated by a 1-cm gap to allow free access of salt to all faces of the fuel basket. The compartments were made of a thick gauge (10 mesh) stainless steel screening with a 325 mesh stainless steel screen lining on the inside. Each basket compartment was 1.5 cm thick, 3.5 in. (8.9 cm) wide, and 15 in. (38.1 cm) long. A photograph of the basket is provided in Figure 4. Lithium was contained in a cylindrical porous metal matrix, prototypical of the cathode used to collect lithium in the salt recovery step. The progress of the reduction was measured by periodically taking salt samples and titrating them to determine the Li_2O concentration.

The results of ES-5 were very encouraging. Based on the Li_2O concentration in the salt samples, the reduction rate was similar to that obtained in laboratory-scale experiments. The reduction was essentially complete in 12-20 hours; there was no significant increase in the Li_2O concentration after 20 hours. This reduction is the fastest to date in the engineering-scale system. Figure 5 illustrates the extent of reduction as a function of time. The reduced product showed no evidence of unreduced UO_2, either by visual examination or by XRD.

The mass of entrained/occluded salt in the reduction product as a function of the fuel particle size was also determined. The dissolved Li_2O in the entrained/occluded salt reacts with the UCl_3 in the electrorefiner to form UO_2, requiring that the UCl_3 be replenished periodically. Thus, it is important to estimate the salt carryover from the reduction step to the electrorefiner. The mass of entrained/occluded salt was found to increase with decreasing particle size of the fuel. The coarsest fuel fraction contained 1.4 wt% salt, while the finest fuel fraction contained as much as 12 wt% salt. The average entrained/occluded salt in the fuel basket was estimated to be 11 wt%.

The ES-6 reduction was performed in a Mk V basket. The Mk V basket consists of a perforated sheet metal shell with a single insert made of 325 mesh stainless steel screening. The insert was about 2.7 cm thick. Figure 6 is an illustration of the outer shell and the insert in a Mk V basket. Thus, the Mk V basket is distinctly different in two aspects from the ES-5 basket: (1) it is about twice as thick and (2) its exterior is made of perforated sheet metal instead of 10 mesh screening. While the basket thickness is likely to affect the reduction kinetics, the second factor may affect the extent of salt access in the basket area. The feed material for ES-6 was 3.7 kg of crushed UO_2. The reduced loading as compared to ES-5 results from the smaller volume of the Mk V basket. The fuel was separated into the same four size fractions as in ES-5. The loading of the fuel basket was arranged so that the finest fuel fraction lay at the bottom and the coarsest fuel fraction was at the top of the fuel basket. The basket was loaded with the crushed fuel to a height of 12.5 in. (31.8 cm). A few 1-cm clad fuel rod sections were also included in the fuel basket. The same salt that was used in ES-5 was used here.

The reduction rate in ES-6 was significantly slower than that measured in ES-5; the two reduction rates are compared in Figure 5. The ES-6 reduction was stopped after about 78 hours when it was apparent that the reduction was essentially complete. A clad pellet removed from the fuel basket after 72 hours was sectioned and found to be completely reduced. Visual examination of the reduced product at the end of the reduction showed no evidence of unreduced UO_2. The XRD results are pending. The two remaining 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 those of the completely reduced clad pellets in earlier laboratory-scale experiments. It was not clear from the measured titration data when the reduction was complete because of the scatter in the data. The bulk of the reduction appears to have been completed in about 50-60 hours. The salt entrainment in the reduction product was not measured as a function of the fuel particle size in ES-6, but the average entrained/occluded salt in the fuel basket was estimated to be 13 wt%.

V. CONCLUSIONS

The experiments described in this paper confirmed that the large-scale reduction of oxide fuel is feasible using equipment compatible with the major interfacing processes: fuel element chopping, salt recovery and electrorefining. The fundamental parameters controlling the reduction rate have been identified and successfully modeled at the laboratory-scale. Based on the characteristics of the reduced uranium product (i.e., salt carryover and extent of reduction), it appears that the lithium reduction process can provide a suitable feed material for the electrorefiner.

Laboratory-scale work identified the effect of basket design, stirring, and fuel morphology on the reduction kinetics. Use of lithium-filled cathodes as the lithium source in the reduction step has been demonstrated as a viable option. This ensures compatibility between the reduction and the salt recovery step and will enable lithium-filled cathodes from the salt recovery step to be used directly as a lithium source in the reduction step.

Chemical titration of salt samples was found to be a very useful analytical technique to monitor the rate and extent of reduction. However, a significant degree of scatter was observed in the measured data, especially in the engineering-scale reduction ES-6. These results suggest that the sampling procedures and/or the titration methods have to be improved. An excellent reduction rate was achieved with the fuel basket geometry used in ES-5. Although reduction was apparently complete with the Mk V basket, its thickness significantly increased the reduction time required. Thus, it is important to determine if the measured reduction time with the Mk V basket is acceptable. This depends, in part, on the rate of the other major interfacing processes: salt recovery and electrorefining.

Future work will focus on the development of a suitable containment for fine particles (<45 μm) and the reduction of the consolidated fines. Reduction of actual spent fuel and laboratory- and engineering-scale tests of electrorefining the reduced product are also planned.

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While the engineering- and laboratory-scale experiments were the result of efforts of many individuals, we want to acknowledge the contributions of the following people as having special significance: R. E. Everhart, D. W. Warren, and E. J. Wesolowski for their part in building and operating the equipment and D. L. Bowers and C. S. Sabau of the ANL Analytical Chemistry Laboratory for the analytical work associated with the project.

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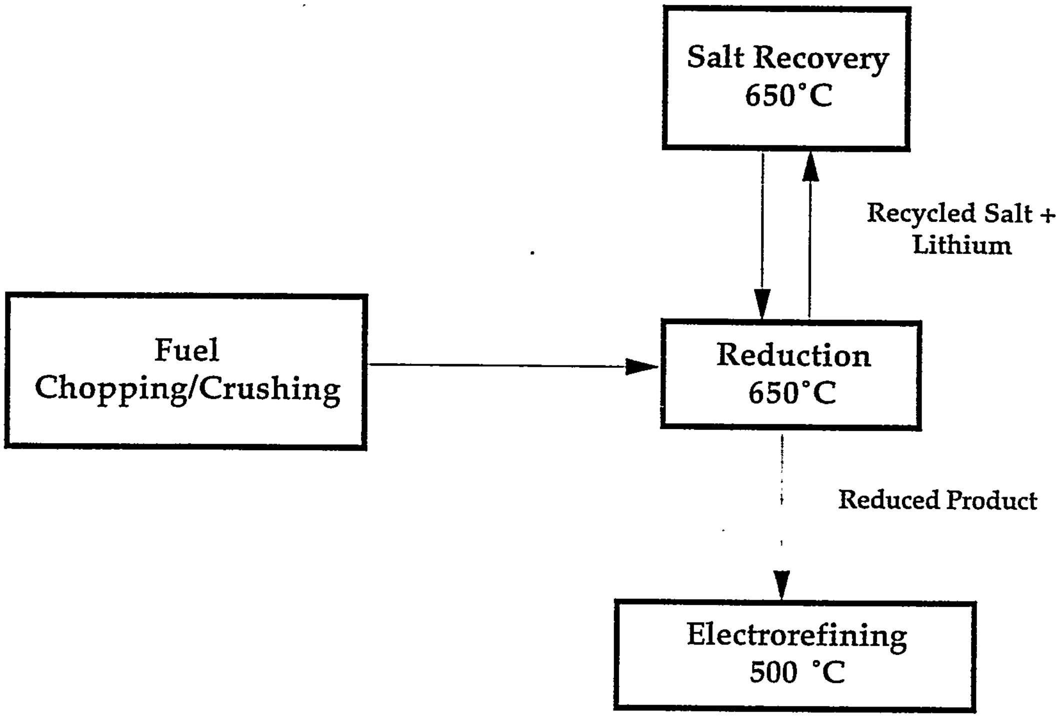

Fig. 1. Simplified flowsheet of the lithium reduction process and its interfaces with the other steps in the electrometallurgical treatment technique

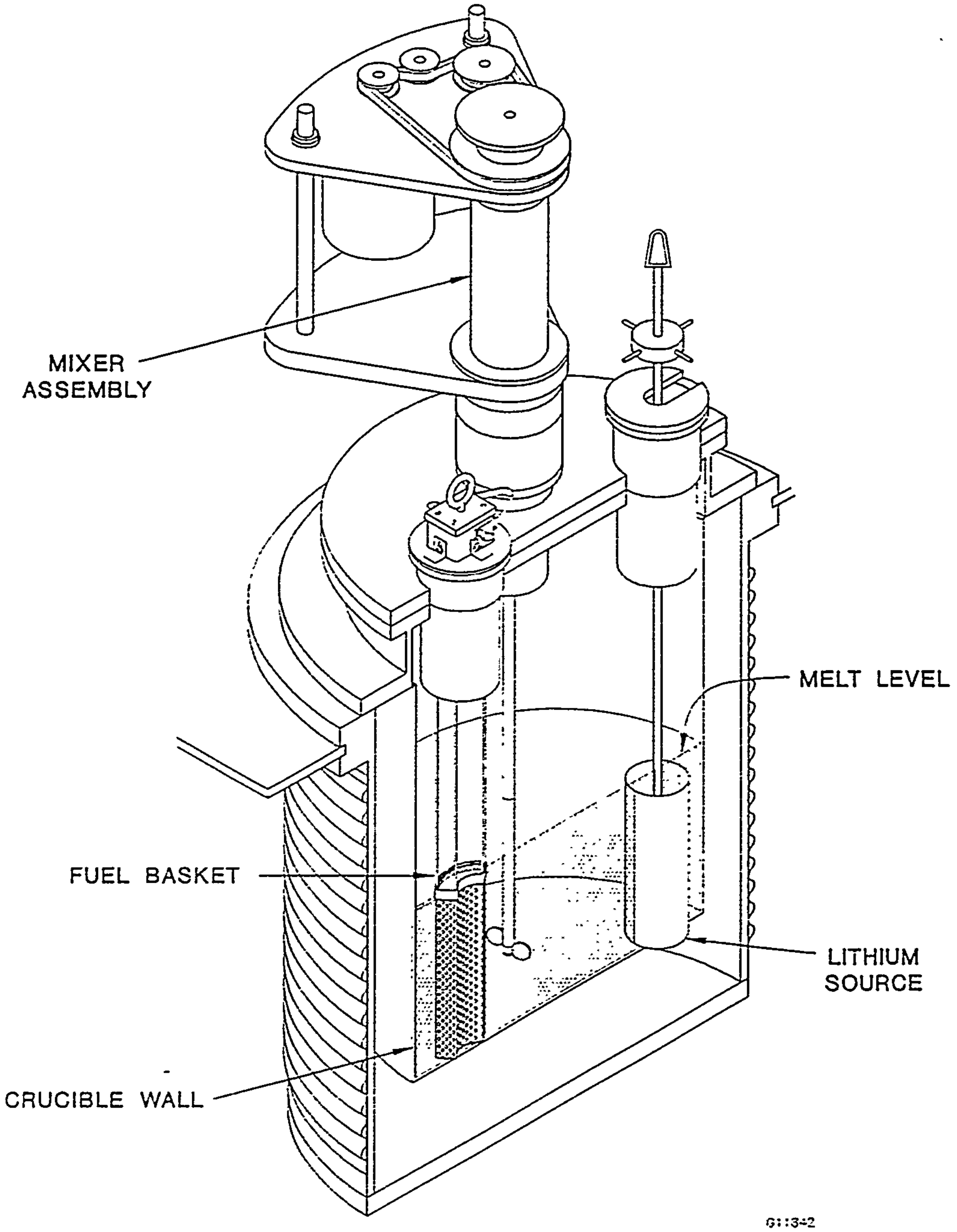

Fig. 2. Cut-away view of the reduction vessel as configured for the latest engineering-scale experiments

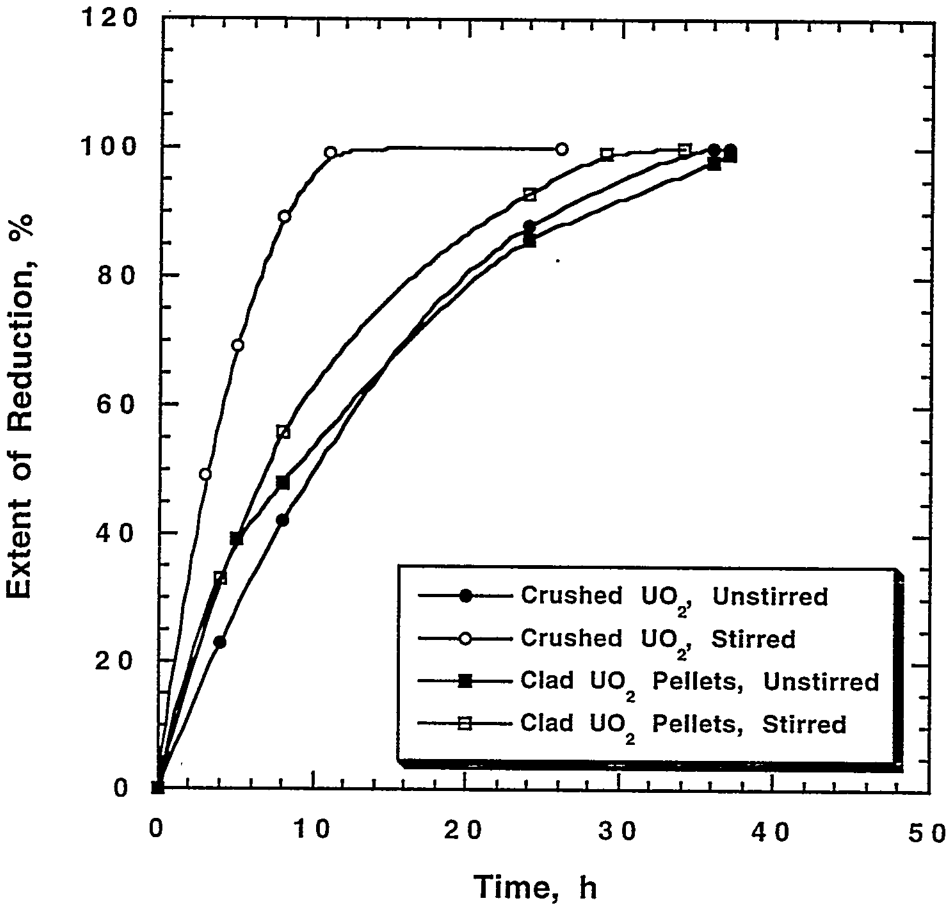

Fig. 3. Effect of stirring on the reduction rate of crushed and clad UO_2 pellets in laboratory-scale experiments

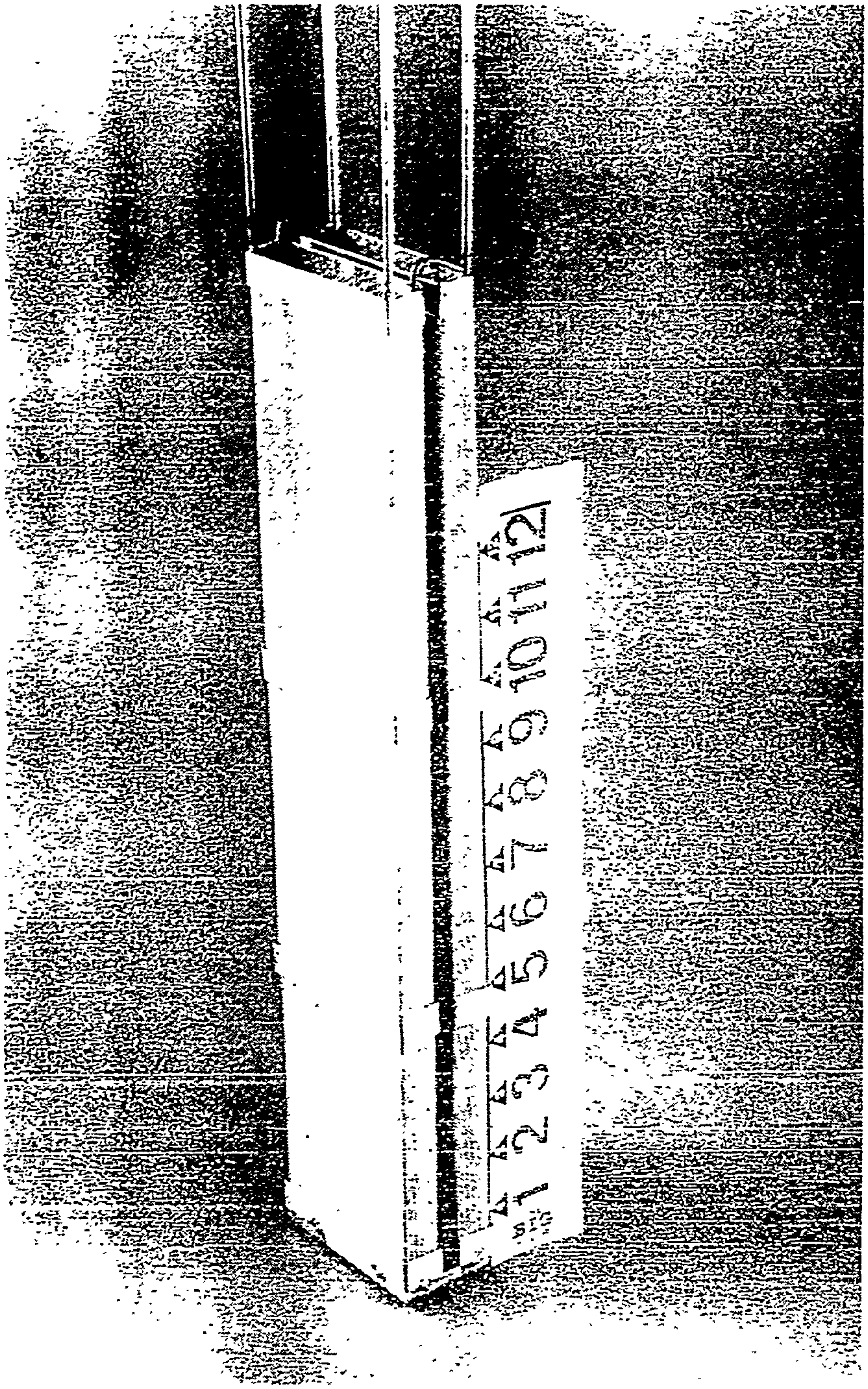

Fig. 4. Illustration of the ES-5 fuel basket

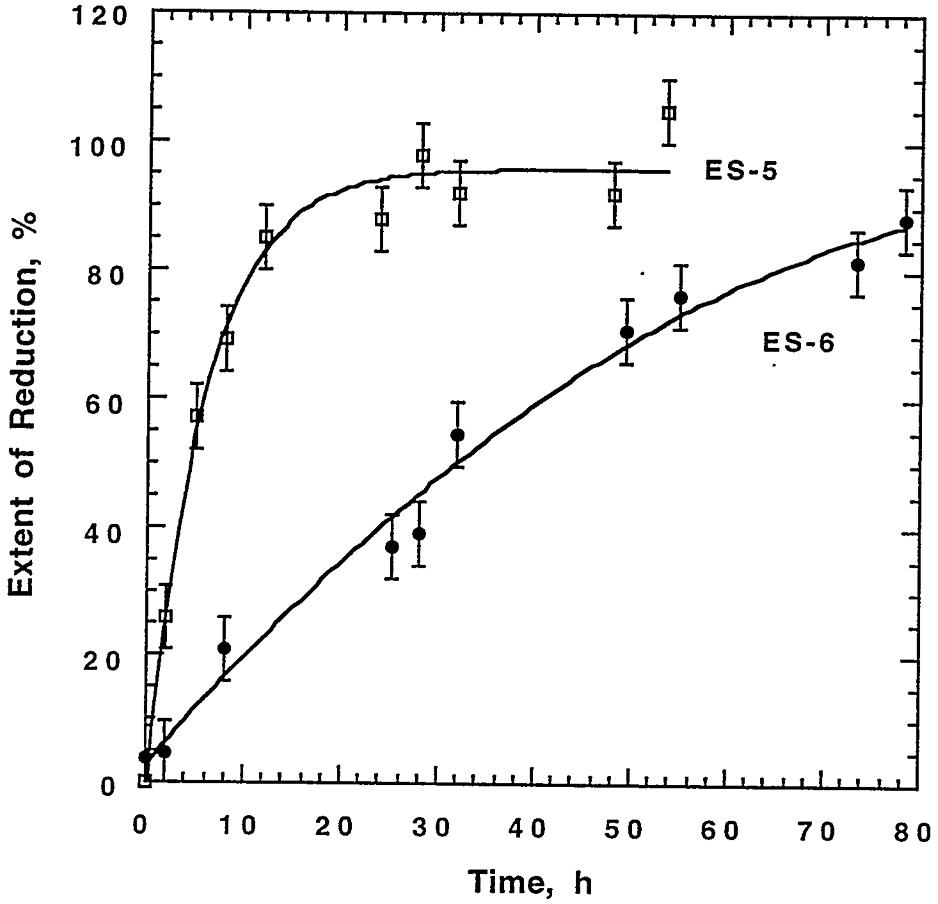

Fig. 5. Extent of reduction as a function of time in ES-5 and ES-6 experiments

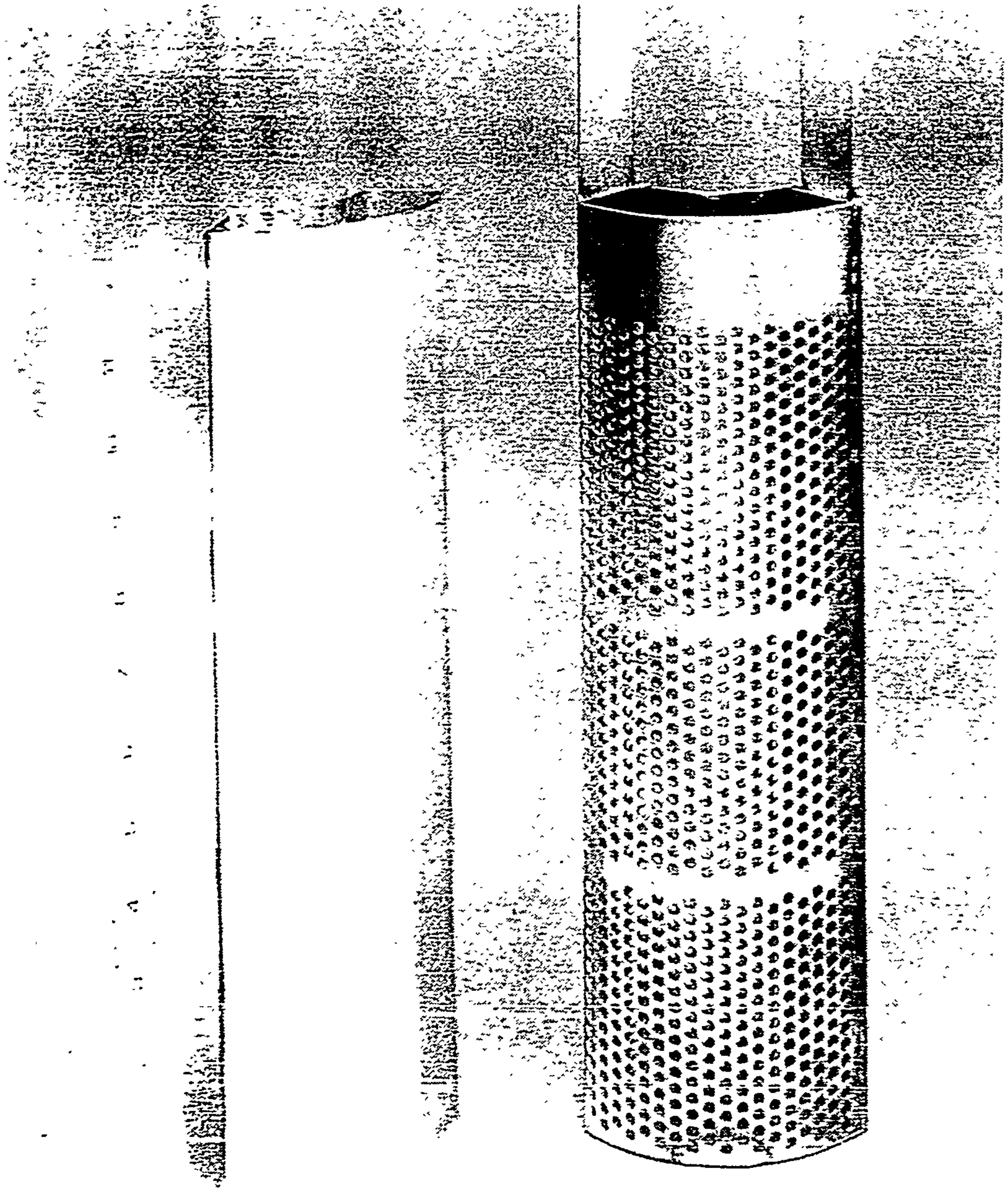

Fig. 6. Illustration of the Mk V outer basket and insert used in ES-6