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This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

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# **Dissolution of Zircaloy-2 Clad UO<sub>2</sub> Commercial Reactor Fuel**

(Nuclear Technology manuscript MS#09-019)

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20 pages text

6 Tables

## Abstract

The primary goal of this investigation was to evaluate the effectiveness of the chop-leach process, with nitric acid solvent, to produce a nominally 300 g/L [U] and 1 M [H<sup>+</sup>] product solution. The results of this study show that this processing technique is appropriate for applications in which a low free acid and moderately high U content are desired. The 7.75 L of product solution, which was over 450 g/L in U, was successfully diluted to produce about 13 L of solvent extraction feed that was 302 g/L in U with a [H<sup>+</sup>] in the range 0.8 – 1.2 M.

A secondary goal was to test the effectiveness of this treatment for the removal of actinides from Zircaloy cladding to produce a low-level radioactive waste (LLW) cladding product. Analysis of the cladding shows that actinides are present in the cladding at a concentration of about 5000 ηCi/g, which is about 50 times greater than the acceptable transuranium element limit in low level radioactive waste.

It appears that the concentration of nitric acid used for this dissolution study (initial concentration 4 M, with 10 M added as the dissolution proceeded) was inadequate to completely digest the UO<sub>2</sub> present in the spent fuel. The mass of insoluble material collected from the initial treatments with nitric acid, 340 g, was much higher than expected, and analysis of this insoluble residue showed that it contained at least 200 g U.

## Introduction

Head-end processing of spent nuclear reactor fuel (SNF) to prepare it for separation of fissile material from fission products and inert materials has been practiced for six decades and the experimental techniques have been discussed by numerous investigators over the past five decades (a few general references are provided).<sup>1,2,3,4</sup> A variety of chemical processes have been developed for head-end processing of Zircaloy-clad  $\text{UO}_2$  fuels. The Zircex process involves high-temperature chlorination of fuel cladding with  $\text{HCl}(\text{g})$  to form  $\text{ZrCl}_4(\text{g})$ , leaving the  $\text{UO}_2$  to be processed by other techniques.<sup>5,6</sup> The Zirflex process involves decladding (dissolution of Zircaloy cladding) in heated, aqueous  $\text{NH}_4\text{F}-\text{NH}_4\text{NO}_3$ , followed by dissolution of the  $\text{UO}_2$ .<sup>7,8,9</sup> An alternative to chemical decladding is mechanical decladding. For example, mechanical removal of cladding by processes such as extrusion, rolling and milling have been proposed for decladding of Al-clad metallic and alloy fuels. A third approach is mechanical preprocessing that exposes the  $\text{UO}_2$  to chemical attack by a dissolvent that reacts vigorously with the  $\text{UO}_2$ , but slowly with the cladding. This alternative is known as the chop-leach process. In the present work, Zircaloy 2-clad  $\text{UO}_2$  fuel was treated by the chop-leach process to leach the  $\text{UO}_2$  from the cladding.

The purpose of this work is two-fold. The primary goal of this work was to use the chop-leach process, with nitric acid dissolvent, to produce a feed solution for the Uranium Extraction (UREX) solvent extraction process. This separation process is designed to partition the pertechnetate and uranyl species into the same phase (aqueous) so that both Tc and U can be recovered as “pure” streams later in the process, while the other soluble fission products and the higher actinides are extracted into the organic

phase. The UREX separation process requires a feed that is moderately high concentration of U (~300 g/L) and relatively low acid (~1 M H<sup>+</sup>), which is different than the characteristics of the feed for the various PUREX separation processes. The low acid (0.95 M HNO<sub>3</sub>) and high acid (2 M HNO<sub>3</sub>) Purex extraction sequences require much higher [U] feed concentrations (~430g/L), while the Darex version requires 1 M HNO<sub>3</sub> and low [U] (~117 g/L), and the Zirflex/Sulfex version requires higher acid (3 M HNO<sub>3</sub>) and low [U]~100 g/L.<sup>10</sup>

A secondary goal was to test the efficacy of this treatment for Zircaloy cladding decontamination. In a production process, removal of sufficient actinides from the cladding residues could result in a cladding stream that could qualify as low-level radioactive waste (LLW). Alternatively, inadequate decontamination of the cladding would result in a cladding stream classified as transuranic (TRU) or Greater-Than-Class-C (GTCC) waste. The LLW versus TRU/GTCC waste classification issue is significant because of cost and availability of TRU/GTCC waste disposal.

## **Dresden Reactor Fuel**

The fuel dissolved during this investigation originated at the Dresden boiling-water reactor (BWR) located near Morris, Illinois, and was discharged from the reactor on September 1, 1975, after a burn up of 23,480 MWdays/metric ton of heavy metal. The fuel was sent to Oak Ridge National Laboratory in the late 1970's, where the fuel rods were sheared to expose the UO<sub>2</sub>; the sheared fuel was subsequently transferred to Savannah River National Laboratory in the early 1980's. Shearing produced cylindrically shaped pieces of fuel rod about 7-8 cm (3") long, with the ends of the sections smashed to produce ellipsoidal cross-sections. This processing resulted in some

sections with some or all of the  $\text{UO}_2$  intact, other sections of cladding that contained essentially no  $\text{UO}_2$ , and  $\text{UO}_2$  rubble. The rubble included pieces that ranged from finely-divided, powdery-appearing material that coated the surface of the sectioned fuel rods to chunks of material with dimensions up to about 1 cm. Prior to the dissolution experiment, it was estimated that the fuel contained ~3.98 kg of U and ~28.54 g of Pu.

## **Equipment**

Fuel dissolution was performed remotely in a dissolver fabricated from glass. The dissolver was equipped with a glass lid that was sealed to the vessel with an o-ring and clamp and a mesh stainless steel bucket that facilitated charging of the dissolver and removal of the leached fuel cladding. The dissolver lid was fabricated with five penetrations. The temperature of the solution was measured using an ungrounded, 304 stainless steel sheathed, type “K” thermocouple connected to channel #1 on an OMEGA model 199 multi-channel thermocouple readout. Solutions were transferred to and from the dissolver by a peristaltic pump through dip tubes entering the dissolver through two other penetrations. One of the remaining penetrations was equipped with a condenser. The last penetration was plugged with a stopper during dissolution, but could be fitted with a funnel for addition of finely-divided solids that might otherwise pass through the mesh of the stainless steel basket. The dissolver was heated with a heating mantle powered by a 120 V variable voltage source.

## **Experimental Methods**

The general approach to fuel dissolution, which is based on previously published work,<sup>11,12,13,14</sup> is described below. The general approach is accompanied by specific

descriptions of the experimental activities associated with the actual dissolution experiments.

## **General Considerations**

The total mass of fuel (cladding + fuel meat) available for dissolution was 4.596 kg. The fuel mass dissolved during each dissolution was determined either by weighing the sample removed from the can containing the fuel “by difference” or by weighing the fuel on a piece of smooth paper prior to transfer of the material to the dissolver basket. The dissolver was initially charged with about 1 L of 4 M HNO<sub>3</sub> to which the basket containing the fuel was introduced. Reaction of fuel and acid was immediate, and the generation of NO<sub>2</sub> gas (hereafter referred to as “NO<sub>x</sub>”) was easily observable through the cell window. The temperature increase due to addition of the solution was generally quite modest. Ambient temperatures in the cell were approximately 30 °C and the maximum temperatures after fuel addition (but before heating) were near 40 °C. Once the initial temperature increase ceased, the dissolver was heated and 10 M HNO<sub>3</sub> was added to the mixture. Using the combination of the heat produced during the exothermic dissolution reaction and the heating mantle, the dissolver temperature was increased to about 90 °C. The amount of 10 M acid added was determined by estimating the amount of acid required to completely dissolve the UO<sub>2</sub> and produce a product about 1.5 M in H<sup>+</sup>(aq) and over 400 g U/L, based on the chemical reaction:



The addition rate for acid was based on the temperature of the reaction vessel (the desire was to keep the temperature near 90°C) and the opacity of the brown vapor in the dissolver. When leaching of the UO<sub>2</sub> from the cladding appeared complete, the dissolver solution was pumped into a 20 L polyethylene carboy. In general, each batch required about 14 hours of dissolution time spread over two to three days. Before the cladding was removed from the dissolver, about 1L of 4 M HNO<sub>3</sub> (that was to be used as the dissolver heel for the next dissolution) was added to the dissolver, and the solution was heated to about 90 °C for 2-6 hours. The leached cladding was then removed from the dissolver and the next batch of fuel was charged to the partially spent acid heel.

### **Dissolution #1**

The first dissolution involved 1926 g of fuel. The dissolver was charged with a heel of 1 L of 4 M HNO<sub>3</sub>, to which the basket containing the fuel was introduced. This dissolution occurred over a period of three days (during which time the solution was twice heated to about 80 °C for about 2 hours), followed by a longer (about 6 hour) heating to about 90°C on the third day. After charging the fuel to the acid, and placing the lid on the dissolver, the temperature was observed to be 35 °C and brown vapor was present in the dissolver. When the temperature stabilized, about 1 L of 10 M HNO<sub>3</sub> was added to the mixture; this addition resulted in more NO<sub>x</sub> generation. After about 10 minutes the temperature was 41 °C, and an additional half liter of 10 M HNO<sub>3</sub> was added during this initial heating. An additional half liter of 10 M HNO<sub>3</sub> was also added during the second heating. During the third heating, the mixture was held at about 90 °C for about 6 hours.



After the dissolver had cooled overnight, the contents of the dissolver were inspected, revealing hollow pieces of cladding (in the basket), a dark-colored liquid, and dark-colored solids. The solids appeared to be floating on the surface of the liquid, stuck to the inside wall of the dissolver and stuck to the cladding. The dark colored liquid was pumped to the product collection vessel. After the liquid was removed from the dissolver, about 700 mL of 4 M HNO<sub>3</sub> were added to the dissolver and the basket and cladding were returned to the dissolver. The dissolver was heated to about 90 °C and the cladding was allowed to soak in the fresh acid for 3-4 hours at this temperature before it was removed from the dissolver. No brown vapor was observed in the dissolver during this heating.

The cladding was rinsed, separated from free liquid, and placed in a container. The mass of recovered cladding was 425 g. Using this mass, it was concluded that 1400 g of UO<sub>2</sub> were dissolved. If it was assumed that the 1400 g were entirely UO<sub>2</sub>, this mass and the volumes of acid added may be used to compute approximate values for [U] and [H<sup>+</sup>], 411 g/L and 3.26 M, respectively.

## **Dissolution #2**

The second dissolution involved 1350 g of fuel. The fuel basket was charged to the dissolver heel (the 700 mL of acid added to leach the cladding from Dissolution #1) while the heel was still warm (about 60 °C). The temperature of the dissolver increased to as high as 78 °C over a period of 7 minutes due to the heat produced by the dissolution reaction. After 13 minutes the temperature was fairly steady at 77 °C. The mixture was allowed to slowly come to room temperature overnight.

During the second heating about 500 mL of 10 M HNO<sub>3</sub> were added to the dissolver. After about 2 hours, the dissolver product from Dissolution #1 was pumped into the dissolver. The addition of the dissolver product resulted in the generation of brown vapor in the dissolver. The reason for reintroduction of the dissolver product to the dissolver was two-fold. First, it was believed that additional acid was required to complete the dissolution. Second, the dissolver product was >3 M in acid, which was about 2 times greater than desired. After the solution had been heated to about 90 °C for another 4 hours, the dissolver was opened and the contents of the basket inspected. Inspection of the cladding showed that UO<sub>2</sub> was still present in some sections of cladding, so the dissolver was heated again (to about 90 °C) for an additional 9 hours. At the end of this heating, no UO<sub>2</sub> was visually detected in the cladding, and the dissolver product was pumped to the product vessel.

Approximately 1.3 L of 4 M HNO<sub>3</sub> was pumped into the dissolver, the basket containing the cladding was placed in the dissolver, and the dissolver was heated about 2 hours at temperatures near 90 °C. The mass of cladding recovered from this dissolution was 73 grams.

Calculations were performed to estimate the acidity and U content of the product solution. Based on the masses of fuel dissolved and the amount of acid added, it was estimated that the product solution was about 450 g/L U with no excess H<sup>+</sup>(aq), and that the residue that contained 300-400 g of U. It is likely that any undissolved UO<sub>2</sub> was partitioned between the dissolver vessel and the product vessel.

### **Dissolution #3**

The remainder of the fuel, contained in fraction M000552-2 (1320 g), was charged to the dissolver. The temperature increased from 28 to 41 °C upon fuel addition. When the temperature was no longer increasing, the dissolver was heated to about 90 °C and about 450 mL of 10 M HNO<sub>3</sub> were added. After heating at about 90°C for a period of about 5 hours and adding about 400 mL of 0.5 M HNO<sub>3</sub> to rinse the fuel storage containers and as well as another 400 mL of 4 M HNO<sub>3</sub>, the contents of the dissolver were inspected. The sections of fuel inspected appeared to be intact, so an additional 250 mL of 10 M acid was added to the dissolver and the dissolver was heated for another 2 hours (until brown vapor was no longer visible in the dissolver). Inspection of random fuel pieces revealed partially digested material, so 850 mL additional 10 M acid was added over a period of 9 hours while the dissolver was heated again to about 90 °C. At the end of this heating regimen, there was still brown vapor visible in the dissolver vessel but it appeared to be dissipating. Inspection of the cladding showed pieces devoid of fuel meat.

At the end of the first two dissolutions, the dissolver product was pumped out of the dissolver and fresh acid was added to leach the cladding. Since a final [H<sup>+</sup>] of about 1.5 M was desired, and the [H<sup>+</sup>] of the dissolver product solutions were unknown, no additional acid was added to the dissolver product. Instead, the cladding was allowed to soak for 7 hours in the dissolver product, at about 90 °C, in an attempt to leach actinides from the cladding.

After cooling overnight, the dissolver was opened and the contents inspected. Along with the cladding, the basket was nearly filled with what appeared to be

precipitated solids. The material appeared crystalline, with both needle-shaped and plate-like shapes that had shiny, faceted surfaces. It was theorized that this material was  $\text{UO}_2(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  that had precipitated from the solution due to evaporation of water, but it was not possible to discern the color of the solids due to the poor lighting in the cell and the tint of the cell window.

Initially, the dissolver product from the first two dissolutions was recirculated through the dissolver vessel in an attempt to dissolve the precipitated material. While this treatment resulted in partial dissolution of the precipitate, there was still a large volume of crystalline material present. Next, about 2.4 L of de-ionized water was added to the vessel and heated. This treatment appeared to solubilize the remaining crystalline material (large needles and platelets); however, there was still finely divided material present in the dissolver. It was supposed that this material was primarily the noble-metal fission products that were insoluble in nitric acid. Approximately 215 g of cladding were recovered from the dissolver.

### **Filtering Dissolver Product Solution**

After the completion of the third dissolution, the products from the three dissolutions were homogenized and filtered with Nalgene MF75 Series Disposable Sterilization Filter Units with type CN general-purpose membrane (0.45  $\mu\text{m}$  pore diameter). The recovered solids were dried at temperatures below 100 °C. The mass of collected material was 341 grams.

## **Results and Discussion**

The products of the initial three dissolutions, cladding, dissolver product and insoluble residues were sampled. Analyses performed on both the solutions and the solids (which were digested prior to analysis) included gamma scan ( $\gamma$  scan), alpha pulse height analysis ( $\alpha$ PHA), inductively coupled plasma-emission spectroscopy (ICP-ES), and inductively coupled plasma-mass spectrometry (ICP-MS).

### **Mass of Dissolved Material**

As stated in the **Experimental** section above, 4.596 kg of fuel and cladding were charged to the dissolver during the three dissolutions. The solids recovered from the dissolver subsequent to those dissolutions included 341 g of insoluble, finely-divided solids and 713 g of cladding, for a total of 1.054 kg of insoluble material. The mass of the soluble material was computed to be 3.542 kg. During the subsequent leaching of the 341 g of insoluble material recovered from the dissolver after the three dissolutions, all but about 17.9 g were dissolved, resulting in a total of 3.865 kg of soluble material.

### **Insoluble Residues**

Replicate samples were dissolved by each of two procedures, aqua regia dissolution and KOH fusion (followed by acid dissolution of the fused solid). Aliquots of the aqua regia product and the solution produced from the KOH fusion were analyzed by ICP-MS, ICP-ES, as well as alpha and gamma counting. The results in Table I are the mean values for five ICP-MS analyses of the insoluble residue. Based on these results, it was estimated that more than 100 g U and 5.1 g Pu remained in the 341 g of insoluble material. (For this discussion it is assumed that all the  $m/z = 238$  signal is U and all the

m/z = 241 signal is Am).

Since the insoluble residues contained so much U and Pu, these solids were placed in a stainless steel beaker with 140 mL of 10 M HNO<sub>3</sub> and heated to 90-95 °C for several hours while stirring. There was no visible sign of reaction during heating, and extensive solids were still present, so KF and 0.5 M HNO<sub>3</sub> were added to form about 500 mL of solution 0.01 M in F<sup>-</sup> (0.302 g KF), and the mixture was heated and stirred. Filtering resulted in recovery of about 500 mL of solution. The filtered and dried solids that remained weighed 17.94 g. Analysis of the leachate by a spectrophotometric technique<sup>16</sup> showed that it was 424 ± 44 g/L in U. This solution was ultimately added to the dissolver product solution.

## **Cladding**

One sample of cladding (about 0.25 g) was digested and analyzed to estimate the residual fission product and actinide content of the cladding. The results of those analyses are shown in Table II.

The cladding sample was digested in HF(aq). Dissolution appeared to be complete as it was not possible to recover any insoluble residue. Separate aliquots of the resulting solution were used for the three analyses. Based on the mass of cladding recovered, about 710 g, and these analyses, the effectiveness of the dissolution process for leaching Pu and U from the cladding can be evaluated. Presence of TRUs in the cladding, at levels greater than 100 ηCi/g of cladding, would result in the cladding being too contaminated with actinides to qualify as a LLW. The upper limit of Pu uptake by the entire 711 g of cladding was 3.10 mg (the actual level is somewhat lower, but it is not possible to differentiate the α PHA signals resulting from Pu-238 and Am-241 so it is

assumed that all the signal was a result of Pu-238). The total U dissolved in the cladding was 442 mg. The ratio, U:Pu in the cladding, 143:1, is in good agreement with the initial U:Pu in the spent fuel before dissolution, 139:1. This indicates that the efficiency of U leaching from the cladding was roughly equivalent to that for Pu. Lastly, these results show that the cladding produced from these dissolutions would not be expected to qualify as a LLW, as the TRU isotope content is about 5000  $\eta$ Ci/g, unless the TRU content could be further reduced by leaching.

### **Dissolver Product**

Due to the high fission product content, it was necessary to dilute the dissolver product solution by a factor of nearly 10,000 to remove it from the shielded facility. This high dilution resulted in a solution for which many minor components were below detection limits, so the results are not complete. After the dissolver product was mixed with the leachate and diluted to form the solvent extraction feed, a less dilute sample was also analyzed. Both sets of results are discussed below.

### **Density Determination**

Because sample dilutions and sample titrations are performed by mass in the remote environment, it is necessary to know the density of all solutions involved in these activities. The mass of a known volume of the dissolver product solution was determined remotely by weighing a 100 mL volumetric flask, filling the flask with filtered dissolver product, weighing the filled flask, and computing the difference (full flask – empty flask). This value, along with the volume of the volumetric flask, was used compute the density

of the solution. Table III shows the data from a single density measurement; the density of the solution was taken to be 1.7356 g/mL.

### **Free Acid Determination**

The free acid concentration of the dissolver product was determined by titrating, by mass, aliquots of the dissolver solution with standardized NaOH solution (Fisher lot no. 024521-24,  $0.1000 \pm 0.0005$  N NaOH), the density of which was measured remotely ( $\rho = 1.00808$  g/mL: see Table IV for data). The titration was a double end point titration. The first endpoint, which occurred at a pH in the range 5.0 to 5.5, was for the weak acids in the solution (which includes soluble metals, especially U). This endpoint was identified visually by the turbidity of the solution resulting from the formation of  $\text{UO}_2(\text{OH})_2$ . The second endpoint, which was a result of  $\text{H}^+$  neutralization, occurred at pH about 6.5. A portable pH meter (Corning model pH-20) was used to measure pH. The pH meter was either calibrated at a single pH (7) or at two values (4 and 7) before use. A magnetic stirrer was used to stir the solutions during titrations. The measurement was replicated 5 times and the results averaged to obtain a free acid concentration of 1.45 M.

### **Uranium Determination**

A sample of solution diluted to about 7g/L U in about 1 M  $\text{HNO}_3$  was analyzed by a spectrophotometric technique designed specifically for  $\text{U}^{16}$  gave a result of  $494 \pm 20$  g/L U (corrected for dilutions).



## **Solution Combination and Dilution**

After the analyses of the dissolver product and leachate from the HNO<sub>3</sub>/KF treatment of the insoluble solids, they were combined to form a single product solution with a volume of about 7.75 L. This solution was then diluted with 5 L of 0.1 M HNO<sub>3</sub> and 0.25 L of 3 M HNO<sub>3</sub> to form about 13 L of solution. A diluted aliquot of this solution was analyzed to determine the elemental composition of solutes; these results are shown in Table V. Another aliquot diluted to about 7g/L U in about 1 M HNO<sub>3</sub> was analyzed spectrophotometrically to determine U (302 ± 16 g/L);<sup>16</sup> the results of these analyses are also shown in Table V. In addition, the density of the product solution was measured twice; the average of the two determinations was 1.436 g/mL.

Three aliquots of the product were titrated with standard NaOH (in the same manner as was described earlier). The result of at least one of these titrations was considerably lower (giving a [H<sup>+</sup>] less than half that from the other two determinations). During this titration a smaller mass of product solution (0.550 g) was titrated, which increases the uncertainty of the determination as compared to the other two titrations, during which 2.455 g and 0.883 g were titrated. The average of the two higher mass determinations gave a mean [H<sup>+</sup>] value of 0.84 M (the value reported in Table V).

## **Mass Balance of Dissolution Process**

A mass balance calculation was performed for the dissolution process. (see Table VI) Subsequent to fuel dissolution and cladding leaching, 713 g of cladding was recovered. After dissolution and leaching of the undissolved solids, 17.9 g of insoluble residue was

collected. The final volume of the dissolver solution was ~13 L, with  $[U] = 302 \text{ g/L}$ , and the sum of the other dissolved cations was  $8.24 \text{ g/L}$ . It would be expected that the sum of the masses of the insoluble solids, cladding, other dissolved cations, and  $\text{UO}_2^{2+}$  should be comparable to,  $4596 \text{ g}$ , the initial mass of material. We found that the value computed from the product masses ( $5292 \text{ g}$ ) was  $696 \text{ g}$  greater than the mass of the starting material ( $4596 \text{ g}$ ).

The most significant contribution to this uncertainty is measurement of the dissolver product volume. The carboy used to store the dissolver product had manufacturer-supplied markings on the side of the carboy that indicated volume in liters. Because of the poor lighting and distance from the observer, an indelible marker was used to embellish the manufacturer's marking with a broad black tic mark that could be easily seen. The volume level of the product solution was easily viewed through the wall of the polypropylene carboy because of the dark color of the solution; however, due to the "fish-eye" magnification of the cell window, it was not possible to determine if the carboy was level. Based on these considerations, it is likely that the uncertainty in the volume measurement could be  $\pm 10\%$  or more. The other measured values all have lower uncertainties ( $5\%$  for the  $[U]$  and no more than  $1\%$  for mass measurements); however, when the uncertainties of all measured values are considered, the  $15\%$  deviation of the mass balance is not unexpected.

## Conclusions

The primary goal of this work was to evaluate the effectiveness of the chop-leach process, with nitric acid dissolvent, to produce a ~300 g/L U and 0.8 to 1.2 M  $H^+$  feed solution for solvent extraction. The results of this study show that this processing technique is appropriate for applications that require low free acid and moderately high U content. The 7.75 L of product solution, which was nearly 500 g/L in U, was successfully diluted to produce about 13 L of solvent extraction feed that was 302 g/L in U with a  $[H^+]$  in the range 0.8 to 1.2 M.

While the primary goal of the study was realized, some issues were identified that require more attention. A secondary goal was to test the efficacy of this treatment for the removal of actinides from Zircaloy cladding. This goal does not appear to have been met. It is possible that the cladding was not uniformly leached as some pieces were treated for longer periods of time in more concentrated solutions), nevertheless, the cladding that was analyzed was about 50 times too high in actinide content to qualify as a LLW. It is possible that the failure to adequately leach actinides from the Zircaloy 2 cladding is due to the use of fairly dilute (less than or equal to 4 M)  $HNO_3$  as the dissolution media. It could be, however, that Pu and U are incorporated into the cladding as intermetallic phases, such as Zr-U, Zr-Pu, and/or Zr-U-Pu phases, that are insoluble in  $HNO_3$ .<sup>17</sup>

Lastly, it is possible that the failure of nitric acid to adequately leach actinides from the spent fuel cladding is related to another apparent deficiency of this process, the inability of the nitric acid to completely digest the actinides in the  $UO_2$ . The three dissolutions produced a solution that was high in U content,  $494 \pm 20$ g/L, and low in

acid, about 1.45 M. However, the mass of insoluble material, 341 g, was much higher than expected; analysis of the insoluble residue showed that it was high in U and Pu, and subsequent leaching of the residues produced a leachate that contained about 200 g U.

## **Future Studies**

The most glaring uncertainties associated with the present work are related to the ability of the nitric acid dissolvent to completely digest U and Pu in the UO<sub>2</sub> and Zircaloy cladding. While it was possible to digest the UO<sub>2</sub> residue using an HF/HNO<sub>3</sub> media, the addition of F<sup>-</sup> would result in greater waste volumes in a full-scale process, so it would be preferable to digest the fuel without addition of F<sup>-</sup>.

A starting point for future work would be to investigate the use of more highly concentrated nitric acid for the initial dissolution. It is possible that starting the dissolution with 8 or 10 M HNO<sub>3</sub> instead of 4 M acid would increase the acid concentration during the dissolution process adequately to digest more of the difficult U-bearing residues. In addition, leaching the empty cladding with the more concentrated acid might improve the efficiency of actinide removal from the cladding.

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**Table I. ICP-MS Results for Digested Insoluble Solids**

<b>Mass/z</b>	<b>Element</b>	<b>µg element/g sample</b>
235	U	1268
236	U	741
238	U(major), Pu(minor)	229167
239	Pu	8971
240	Pu	5010
241	Am(major), Pu(minor)	704
242	Pu	1043

**Table II. Analysis of cladding (not including Zr)**

<b>Element</b>	<b>µg/g sample</b>
Ag	5340
Al	786
B	5050
Ba	35.4
Ca	<20.2
Cd	<3.70
Cm-244	0.00305
Ce	4380
Co -60	0.00248
Cr	815
Cs-137	1.87
Cu	72.5
Eu-154	0.00426
Fe	1500
Gd	174
K	<826
La	76.3
Li	<37.9
Mg	57.8
Mn	21.0
Mo	461
Na	3410
Ni	<11.9
P	<60.7
Pb	<28.1
Pu-239/240	4.08
Pu-238/Am-241	0.292
Sb	<333
Sb-125	0.00130
Si	44000
Sn	13000
Sr	423
Ti	28.4
U	623
Zn	25.6



**Table III. Density data for dissolver product**

Mass of filled 100.00 mL flask	196.948 g
Mass of empty 100.00 mL flask	23.391 g
Mass of solution	173.558 g
Volume of solution	100.00 mL
$\rho$	1.7356 g/mL

**Table IV. Density data for standardized NaOH**

Mass of filled 100.00 mL flask	124.257 g
Mass of empty 100.00 mL flask	23.449 g
Mass of solution	100.808 g
Volume of solution	100.00 mL
$\rho$	1.0081 g/mL

**Table V. Chemical analysis of diluted product solution**

<b>Component</b>	<b>Analytical Results</b>
Free Acid, M	0.84
U, g/L	302
Pu, g/L	2.16
Np, g/L	6.8 E-05
Am, g/L	0.23
Cm, g/L	0.005
<sup>99</sup> Tc, g/L	1.68 E-04
Ag, g/L	0.78
Ba, g/L	0.50
Ce, g/L	1.47
Cu, g/L	0.37
Fe, g/L	0.07
Gd, g/L	0.64
La, g/L	0.49
Mn, g/L	0.02
Na, g/L	0.33
Ni, g/L	0.60
Sn, g/L	0.41
Ti, g/L	0.11
Zn, g/L	0.05

**Table VI. Mass balance of dissolution process**

<b>Material</b>	<b>Before Dissolution</b>	<b>After Dissolution</b>	<b>After dissolution – before dissolution</b>
<b>Initial Fuel Mass</b>	4596 g		
<b>UDS</b>		17.9 g	
<b>Dissolved UO<sub>2</sub></b>		4454 g	
<b>Dissolved cations</b>		107 g	
<b>Cladding</b>		713 g	
<b>Total</b>	4596 g	5292 g	696 g