Contract No.:

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Dissolution of Low Enriched Uranium from Experimental Breeder Reactor-II Fuel

William E. Daniel, Jr., Tracy S. Rudisill, Patrick E. O'Rourke, and Philip M. Almond[*]

Savannah River National Laboratory, Aiken, SC 29808

*For all correspondence, contact Philip M. Almond

Philip M. Almond

Savannah River National Laboratory

Building 773-A

Aiken, SC 29808

e-mail: Philip.almond@srnl.doe.gov

telephone: 803-725-0711

fax number: 803-725-2756

Key Words

Uranium

H-Canyon

Dissolver

Running Title

Dissolution of Low Enriched Uranium

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Abstract: A dissolution flowsheet for the Low Enriched Uranium (LEU) ingots generated at the Idaho National Laboratory (INL) from the electrochemical processing of the EBR-II fuel was demonstrated at the laboratory scale. Dissolution experiments were performed using samples of the LEU and a carbon steel can and an integrated experiment was performed in which an Al 1100 alloy was dissolved as a surrogate for Spent Nuclear Fuel (SNF) followed by the dissolution of samples of the LEU and carbon steel can to demonstrate the complete flowsheet. The flowsheet allows the dissolution of a SNF batch in an H-Canyon dissolver using existing flowsheets followed by the dissolution of nominally 75 kg of LEU in the 6.4D dissolver or 45 kg of LEU in the 6.1D dissolver which were recovered from the Experimental Breeder Reactor-II (EBR-II) fuel. In the demonstration experiment, the rate of dissolution of the LEU metal was significantly slower than the dissolution rate of the Al 1100 alloy (4.7 versus 27 mg/min/cm^2) which projects to a longer cycle time for the LEU metal (compared to a SNF charge). The H$_2$ generation rate from the dissolution of samples of the LEU metal and a carbon steel can were monitored by mass spectrometry and Raman spectroscopy and were shown to be inconsequential; therefore, the dissolution of the LEU ingots has no significant impact on the generation of H$_2$.

INTRODUCTION

The Idaho National Laboratory (INL) has been active in the development of pyroprocessing technology since the 1980's. The R&D activities have included two primary missions: treatment of the spent fuel from the Experimental Breeder Reactor-II (EBR-II) and the development of advanced technology to assist in the closure of the nuclear fuel cycle. The electrorefiner is the key unit operation in pyroprocessing. It is where the U in the spent fuel is electrochemically separated from the cladding hulls, sodium bond, and noble metals. The U product from the electrorefiner is in dendritic form and is coated with chloride salts. After removal from the electrorefiner, the U is loaded into the cathode processor where the U is melted and nearly all of the salt removed by distillation. The U product is then transferred from the cathode processor to a receiver crucible for solidification.[1] The U ingots, which contain less than 20 wt % U-235, are currently stored at the INL Fuel Conditioning Facility until a disposition pathway is selected.

INL and Savannah River Site (SRS) personnel have identified a potential disposition pathway for the Low Enriched Uranium (LEU) ingots generated from the treatment of irradiated EBR-II U-5Fs fuel, consisting of uranium 5 wt % fissium (2.5 wt % Mo, 2.0 wt % Ru, 0.3 wt % Rh, 0.1 wt % Pd, and 0.1 wt % Zr). The U-5Fs fuel was an early generation fuel used in the EBR-II reactor from the 1960's through the late 1980's containing 95 wt % U metal alloyed with 5 wt % noble metals or fissium.[2] The potential disposition pathway would include the shipment of LEU from the pyroprocessing of the fuel to the SRS for dissolution in H-Canyon. The LEU would be sealed in dissolvable nylon bags and placed in carbon steel cans in the same manner that was used for dissolution of Pu metal in the 6.1D dissolver to produce feed material for the HB-Line plutonium

oxide production mission.[3] The cans would be loaded into reusable charging bundles in the H-Canyon Crane Maintenance Area and charged to an H-Canyon dissolver. The LEU dissolution would be accomplished as the final charge in a dissolver batch. Approximately 75 kg U (15 kg U-235) would be dissolved following the dissolution of a batch of spent nuclear fuel (SNF) in the 6.4D dissolver and approximately 45 kg of U (9 kg of U-235) would be dissolved following the dissolution of a batch of SNF in the 6.1D dissolver. If the dissolvers are filled to their nominal working volume ranges, the U concentration following dissolution of the LEU charges would be approximately 8-12 g/L. To support the new mission, the SRNL was requested to develop a dissolution flowsheet for the LEU based on the testing of four 25 g samples of the material from INL.[4]

Large pieces of U metal dissolve in HNO_3 at a moderate rate; however, as the surface area increases so does the metal dissolution rate.[5] The dissolution chemistry is complex, with the acid reduction products varying from nitrogen dioxide (NO_2) to N_2. In general, dissolutions performed using 8 M HNO_3 or less generate nitric oxide (NO) as the principal gaseous product; those carried out at higher acidities produce NO_2 as the principal product.[6] The LEU from the EBR-II reactor will readily dissolve in an H-Canyon dissolver using HNO_3 concentrations in the 1-2 M range which are present in the solution following the dissolution of a batch of SNF. It may be necessary to add HNO_3 to the solution to ensure the final concentration is greater than 0.5 M to preclude the polymerization and precipitation of any plutonium in the dissolver. Although Hg would be present in the dissolver as a catalyst for SNF dissolution, it is not required to catalyze the LEU dissolution. As part of the flowsheet development, Savannah River National Laboratory (SRNL) measured the dissolution rate of the LEU samples from INL to allow prediction of the dissolution cycle time.

The LEU ingots from INL are relatively pure U metal. All noble metal fission product elements in the EBR-II U-5Fs fuel are generally removed by the electrorefining process with the exception of Zr. Zirconium is present in the electrorefiner at a higher concentration from the processing of other fuel. The presence of Zr in the LEU is of potential concern. Explosions, fires, vigorous to violent reactions, and other off-normal events involving the dissolution of U-Zr alloys in HNO_3 have been documented within the Department of Energy complex dating back to the 1950's.[7] It has been shown that exothermic reactions result from the rapid oxidation of finely divided solids released by the preferential dissolution of the U metal matrix. The explosive portion of such solids has been identified as an intermetallic compound with the approximate composition of UZr_2.[8] (Other researchers have cited UZr_3 as the stoichiometry and refer to the intermetallic compound as the epsilon phase in the U-Zr phase diagram.) If uniformly distributed throughout the LEU matrix, a low concentration of Zr should not be a concern during dissolution of the INL ingots. In a thorough investigation of the explosion of U-Zr alloys when treated with HNO_3, Larsen et al. concluded that depending on the composition, homogeneity, and previous thermal history, U-Zr alloys with 1-50 wt % Zr will contain some amount of the finely divided epsilon phase in a matrix of alpha-U.[9] Concentrations below 1 wt % (10,000 ppm) were not reported to exhibit exothermic behavior.

The U product from the INL electrorefiner is in dendritic form and is coated with active metal chloride salts (typically 20 wt % of the product) before being transferred to cathode processing. In the cathode processor, the U and chloride salts are melted and the salts are removed by distillation. Over numerous runs during the treatment of EBR-II driver fuel, the distillation efficiency for the active metal salts ranged from about 98.6 to 99.96%.[1] The presence of chloride salts with the LEU ingot could potentially increase corrosion in the H-Canyon dissolver and downstream processing

operations (e.g., high activity waste evaporation and acid recovery); although, the Hg present in the dissolving solution may precipitate chloride salts associated with the LEU ingots. When the scrub alloy from the Rocky Flats Plant was dissolved in F-Canyon to recover Pu from the reductive stripping of sodium/potassium chloride salts from the molten salt extraction process, mercuric nitrate was added to the dissolving solution prior to Head End centrifugation to precipitate the chloride.[10-11] The mercurous chloride precipitate would be removed during centrifugation and discarded as waste.

The generation of H_2 in the offgas during the dissolution of the LEU ingots must be shown to be below 60% of the lower flammability limit (LFL) for H_2.[12] A significant concentration of H_2 in the offgas from the LEU dissolution is not expected.[6] The dissolution of Al-clad, U-Al alloy fuels are known to generate H_2 during dissolution; however, the H_2 generation during dissolution of Materials Test Reactor (MTR) or High Flux Isotope Reactor (HFIR) fuels is addressed by the existing H-Canyon flowsheets.[13,14]

Following dissolution of the MTR or HFIR fuels and LEU ingots, the U-containing solution would be processed through Head End and centrifuged to remove particulate matter. After Head End treatment, the U would be recovered and purified by solvent extraction (1st and 2nd U Cycles), and the waste processed for transfer to the H-Area Tank Farm. The enriched U from the MTR or HFIR fuels and LEU from the ingots would be blended down for subsequent use as reactor fuel.

EXPERIMENTAL

Surrogate Materials

In previous flowsheets developed for the dissolution of HFIR[14] and MTR fuels[13], Daniel et al. demonstrated that Al 1100 provided a bounding estimate for the generation of H_2 and was subsequently used as a surrogate for these fuels. Although, the development of a new flowsheet is not required for the dissolution of SNF prior to the dissolution of LEU ingots in H-Canyon, an experimental Al 1100 dissolution was performed as part of the flowsheet demonstration. The Al 1100 dissolution was performed to simulate the dissolved fuel prior to dissolution of samples of the LEU and carbon steel from a food pack can. The food pack can was provided by H-Canyon personnel and simulates the cans which would be used to ship the LEU ingots to SRS.

Dissolution Experiments for Offgas Characterization

The generation of H_2 in an H-Canyon dissolver must be demonstrated to be less than 60% of the LFL during dissolution of the LEU ingots.[12] To ensure this requirement is met, dissolution experiments were performed using an Al 1100 alloy coupon and samples of the LEU and a carbon steel can. The dissolution of the nylon bags used as primary containment for contamination control would not contribute any significant offgas to the dissolution process.[15] The flammable gas generation from a small piece of a carbon steel food pack can was previously evaluated for a Pu metal dissolution flowsheet.[16] Two additional experiments (Experiments 80 and 109) were performed to characterize the offgas from the dissolution of the LEU samples received from INL. Characterization data from the analysis of the two LEU ingots used to produce the experimental samples are shown in Table 1. In Experiment 80, a sample of the LEU received from INL was dissolved. In Experiment 109 a complete demonstration of the flowsheet was performed in which an Al 1100 alloy coupon was initially dissolved followed by samples of the LEU and a carbon

steel can. The dissolution of the Al 1100 alloy coupon was performed using the same general flowsheet used in H-Canyon for the dissolution of MTR and HFIR fuel.[13,14] A summary of the objective and dissolution conditions for each experiment are provided in Table 2. All experiments were performed at the boiling point of the solution except for Experiment 86 which was performed at room temperature. The experimental numbering sequence corresponds to data recording practices.

Preparation of Coupons

The Al 1100 alloy used in the dissolution experiment was prepared by cutting coupons to the desired dimensions. The coupon was then lightly sanded, washed with soap and water to remove any residue, and then weighed and measured. The coupon was sanded to maximize reactivity as well as to generate consistent results.

The LEU used in the dissolution experiments was cut from samples provided by INL. The samples were rods with an approximate 3.0 mm diameter that were cut to lengths of approximately 25 mm. The cut samples were wiped clean and then weighed and measured prior to the dissolution. The carbon steel coupon was cut from a carbon steel can supplied by H-Canyon. The masses, dimensions, and surface areas of the coupons used in the experiments are provided in Table 3.

Dissolving System

The vessel and offgas condenser used to perform the LEU flowsheet demonstration was fabricated from borosilicate glass. The dissolving vessel was made from a 300-mL round-bottom flask. Penetrations were added for a condenser, Hg addition (using a syringe pump), thermocouple, and

gas purge. The bottom of the flask was flattened slightly to facilitate heating and agitation using a hot plate/stirrer with a magnetic stir bar. During the dissolutions, coupons were charged to the dissolver in a glass basket suspended by a glass rod which was held in place by a compression fitting. The compression fitting allowed adjustment of the basket height during dissolution. The dissolver solution temperature was controlled using a hot plate with an external thermocouple inserted into the solution. Offgas exiting the dissolving vessel was sampled for analysis by mass spectrometry using a sample line connected to a port just above the condenser (which was used in Experiments 80 and 86). A manometer, also connected to the offgas sample port, acts as a pressure relief device and provides a measurement of the pressure in the system. The offgas leaving the condenser subsequently passes through a cell containing a Raman probe and terminates in a bubbler (i.e., beaker containing 700 mL or 3.5 in of deionized water). The bubbler prevents air in-leakage from the vent side of the system. The Raman spectrometer was used to measure non-condensable gases such as H_2, N_2, O_2, Ar, NO, N_2O and NO_2 in real time during the experiment. A photograph of the equipment is shown in Figure 1.

Monitor Mass Spectrometer

The mass spectrometer (MS) used during the dissolution experiments was a Monitor Instruments LAB 3000 Cycloidal MS. The Monitor MS samples a portion of the non-condensable offgas stream using vacuum and provides the volume percent of the gases in the sample based on calibration gas standards. The Monitor MS was calibrated using the gases listed in Table 4. The MS is controlled by a computer using Monitor v6.00 software.

To calculate offgas generation rates, an Ar tracer gas was metered into the system through a flow controller at a set rate (10 cm^3/min @ 21 °C, 1 atm). The total offgas rate was then calculated by dividing the set input rate by the measured Ar concentration in the offgas.

Raman Spectrometer

The Raman spectrometer non-intrusively analyzes the offgas through a quartz window using the excitation of a laser passing through a fixed portion of the offgas stream. The Raman scattering technique identifies and measures the concentration of gases in the offgas stream through the use of gas calibration standards shown in Table 4. Concentrations of the offgas species were measured approximately every 12-13 seconds. The Raman spectrometer was controlled by and data was logged using a computer running EZRamanReader v8.3.9 software and a Microsoft Excel® spreadsheet.
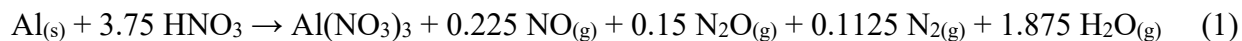
To calculate offgas generation rates, a CO_2 tracer gas was metered into the system through a flow controller at a set rate (20 cm^3/min @ 21 °C, 1 atm). The total offgas rate was then calculated by dividing the set input rate by the measured CO_2 concentration in the offgas.

Dissolution Experiments

Prior to performing a dissolution experiment, the dissolving system was checked for leaks by connecting a Tedlar® bag inside a glass kettle filled with water (Figure 1) to the dissolver and adding sufficient Ar, N_2, or CO_2 to the bag to generate a column of water 18-28 cm tall. The Tedlar® bag system was then closed and monitored for any observable decrease in the water column height over 2-3 min. After the system integrity was confirmed, the experiment was started.

To perform the dissolutions, a metal coupon was initially placed in the perforated glass basket or tied to a glass rod. For Experiment 80, the basket containing a sample of an LEU ingot was lowered completely into the solution at boiling. For Experiment 86 a carbon steel coupon was tied to a glass rod and lowered into the solution at room temperature. For Experiment 109 Phase 1, the basket containing an Al 1100 coupon was lowered to a depth of 10 mm at room temperature and the solution was then heated to boiling. Chilled water (at 3 °C) was circulated through the condenser during the dissolutions to remove water vapor from the offgas stream before the gas flowed through the Raman cell. For the Al 1100 coupon dissolution, once the solution reached boiling, there was a hold time of 45 minutes before starting the Hg addition. The initial volume of HNO_3 and the volume of the Hg solution added (Table 5) were based on the mass of the Al 1100 coupon and the target Al and Hg concentrations.

In Experiment 109, an estimate of the amount of HNO_3 consumed during the dissolution of Al, U, and Fe metals was required to allow the adjustment of the acid concentration prior to the dissolution of samples of a carbon steel can and a LEU ingot in Phase 2 of the experiment. The stoichiometry of Hg-catalyzed Al dissolution in HNO_3 has been discussed in many references such as Almond et al.[17] where the general overall reaction of Al with HNO_3 is given by equation 1. Based on equation 1, 3.75 moles of HNO_3 are needed to dissolve 1 mole of Al.

$$Al_{(s)} + 3.75\ HNO_3 \rightarrow Al(NO_3)_3 + 0.225\ NO_{(g)} + 0.15\ N_2O_{(g)} + 0.1125\ N_{2(g)} + 1.875\ H_2O_{(g)} \quad (1)$$

To estimate the amount of HNO_3 required to dissolve the carbon steel coupon, offgas composition data from the dissolution of a carbon steel can coupon were examined and the reactions given by equations 2-4 were assumed.

$$Fe_{(s)} + 6\ HNO_3 \rightarrow Fe(NO_3)_3 + 3\ NO_{2(g)} + 3\ H_2O \qquad (2)$$

$$2\ Fe_{(s)} + 8\ HNO_3 \rightarrow 2\ Fe(NO_3)_3 + 2\ NO_{(g)} + 4\ H_2O \qquad (3)$$

$$2\ Fe_{(s)} + 8\ HNO_3 \rightarrow 2\ Fe(NO_3)_3 + N_{2(g)} + O_{2(g)} + 4\ H_2O \qquad (4)$$
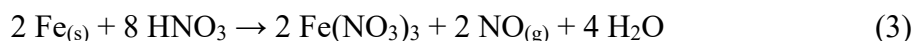
Based on the steady state offgas composition from the carbon steel coupon dissolved in Experiment 86, a weighted average of the three reactions above (equations 2-4) was used to estimate the overall consumption of HNO_3 per mole of Fe as shown in Table 6. Based on these reactions, 4.12 moles of HNO_3 are required to dissolve 1 mole of Fe.

The amount of HNO_3 consumed during the dissolution of U metal was based on the theoretical requirement for compete oxidation of the U and absorption of the nitrogen oxides in the dissolving solution and subsequent oxidation back to HNO_3 (equation 5).

$$U_{(s)} + 2\ HNO_3 + 3/2\ O_2 \rightarrow UO_2(NO_3)_2 + H_2O_{(g)} \qquad (5)$$

Based on the estimated amount of HNO_3 needed to dissolve the Al, Fe, and U, projections of the concentrations of the various metals and HNO_3 were made for Experiment 109 (Table 7). In Phase

1 of the experiment, the Al 1100 coupon was dissolved using 0.002 M Hg in 135.6 mL of 7 M HNO$_3$. The final volume in Phase 1 was 128 mL due to evaporation losses from solution boiling. After Phase 1 was complete, aliquots of trim solutions containing 308 g ^{238}U/L in 0.45 M HNO$_3$, and 15.8 M HNO$_3$ were added to the solution to bring the HNO$_3$ concentration up to about 1.4 M and the U concentration up to 4.5 g/L. The HNO$_3$ was adjusted based on the estimated amount of HNO$_3$ necessary to dissolve the Fe and LEU samples during Phase 2 of the experiment (Table 7). The final volume after Phase 2 was complete was 132 mL due to evaporation losses which gives projected final concentrations of approximately 26.8 g U/L, 1.66 M Al, 1.1 g Fe/L, and 1.17 M HNO$_3$.

During the experiments, samples of the final dissolving solutions were collected for analysis. Samples were analyzed for total acid and free acid, and metals concentrations in reagents and in the final solutions after the dissolutions were performed. The free acid and metals concentrations were determined by titration, inductively-coupled plasma emission spectroscopy (ICPES) or inductively-coupled plasma mass spectroscopy (ICPMS), respectively. The analyses were used as checks on the concentrations since the initial and final volumes of the dissolver solutions were measured as well as the mass of Al added to each solution.

Dissolution Experiments to Evaluate LEU Reactivity

To assess the uniformity of the Zr concentration in the LEU, multiple pieces of the samples received from INL were dissolved and analyzed for Zr. To ensure that the concentrations of Zr in the LEU ingots are well below levels at which the material would exhibit any violent exothermic behavior, dissolution experiments were performed by heating 2-4 g samples in an open glass

beaker containing 7 M HNO_3. The beaker was heated to approximately 70 °C using a hot plate/stirrer. The contents of the beaker were mixed at 200 RPM using a magnetic stir bar. A watch glass containing water was placed on top of the beaker to limit the evaporation of the dissolving solution. The dissolutions took about 4 h to complete. The sample was observed throughout the experiment for violent exothermic behavior and to determine when the LEU dissolution was complete.

RESULTS AND DISCUSSION

Dissolution Flowsheet for LEU Ingots

Samples of LEU ingots from the pyroprocessing of the EBR-II U-5Fs fuel at the INL were dissolved in experiments simulating two potential H-Canyon processing scenarios. In Experiment 80, an LEU sample was dissolved using 7 M HNO_3 to simulate the dissolution of the LEU ingots in an H-Canyon dissolver prior to dissolving any SNF. Although, the preferred processing scenario is the dissolution of LEU ingots following the batch of SNF, data for this experiment are reported to illustrate other aspects of the dissolution flowsheet. For Experiment 109, an Al 1100 alloy was dissolved as a surrogate for SNF (phase 1) followed by a carbon steel and LEU sample dissolution in a 1.4 M HNO_3 solution containing 1.6 M Al and 4.3 g U/L (Phase 2). The Phase 2 initial concentrations are representative of the solution composition following the dissolution of a batch of SNF with the HNO_3 concentration adjusted (upward) to allow the dissolution of 75 kg of LEU. Experiments 86 and 109 Phase 2 were performed to evaluate the H_2 generation for a sample of a carbon steel can, representative of the ones proposed for shipment of the LEU from INL to SRS that would be dissolved with the LEU.

Rate of Dissolution

The total offgas generation rate curves (which illustrate the extent of dissolution) for these experiments are plotted as a function of time in Figure 2. Time zero for the dissolution of the LEU and carbon steel can samples (Experiment 80 and 86, respectively) represents the time when the offgas generation started. For Experiment 109 Phase 1, time zero represents the start of the Hg addition. The LEU material takes much longer to dissolve than the Al 1100 alloy. The LEU material in Experiment 109 Phase 2 dissolved in about 16,500 s (275 min) and in Experiment 109-Phase 1, the Al 1100 alloy dissolved in 2,611 s (43.5 min). In Experiment 80, the average LEU dissolution rate was 5.6 mg/min/cm^2 or 13 mg/min when the dissolving solution initially contained 7 M HNO_3. In Experiment 109 Phase 2, the average LEU dissolution rate was 4.7 mg/min/cm^2 or 11 mg/min when a 1.4 M HNO_3 solution containing 1.6 M Al and 4.3 g U/L was used to dissolve the LEU metal. For comparison, in Experiment 109 Phase 1, the average dissolution rate of the Al 1100 alloy was approximately 27 mg/min/cm^2 or 135 mg/min starting with a 7 M HNO_3 solution (containing 0.002 M Hg catalyst). The dissolution rate of the carbon steel can observed in Experiment 86 was approximately 68 mg/min/cm^2 or 828 mg/min.

The dissolution rate of a sample of an LEU ingot was also measured by periodically removing the sample from the dissolving solution and measuring the mass and physical dimensions. Table 8 shows the masses and dimensions of a subsample from an LEU sample at various time intervals. The measured dissolution rate was obtained as the slope of the regression line from a plot of the mass-to-surface area ratio versus time (Figure 3). Based on this experiment, the dissolution rate for the LEU metal sample was 12 mg/min/cm^2.

Offgas Characterization

The dissolution of SNF prior to dissolving LEU ingots from INL must be performed using either the MTR or HFIR flowsheet developed specifically for these fuels.[13,14] The conditions specified by the flowsheet and the constraints on the number of L-Bundles or cores which can be charged to an H-Canyon dissolver as a function of the Al concentration ensure that the predicted H_2 concentration in the offgas from dissolution is less than 60% of the H_2 LFL at 200 °C.[12] The H_2 generation rate from either the dissolution of the LEU metal or the carbon steel can is inconsequential. Figures 4 and 5 show the H_2 generation rates during the dissolution of samples from an Al 1100 alloy (Experiment 109 Phase 1), a LEU ingot (Experiment 80), a carbon steel can (Experiment 86), and a LEU ingot plus a carbon steel can (Experiment 109 Phase 2). In Experiments 80 and 86, the samples from a LEU ingot and a carbon steel can, respectively, were dissolved in pure 7 M HNO_3. Samples of the two materials were dissolved at the same time in Experiment 109 Phase 2 using a 1.4 M HNO_3 solution containing 1.6 M Al, which models the dissolution of the LEU ingots in an H-Canyon dissolver after a batch of MTR or HFIR fuel. Figure 5 shows that the H_2 generation rate from the dissolution of a sample of an LEU ingot is very low and the generation rate from the dissolution of a sample of a carbon steel can is essentially zero; therefore, the dissolution of neither material generates an offgas which is a flammability concern. Dissolution and offgas measurement experiments have been performed to evaluate the behavior of nylon bags (proposed for the primary containment of the LEU ingots) in other flowsheets developed for H-Canyon. Nylon bags dissolve in HNO_3 and do not contribute any significant offgas to the dissolution process.[15]

Solution Analyses from the Flowsheet Demonstration

The predicted Al molarity following the dissolution of the Al 1100 alloy coupon in Experiment 109 Phase 1 was 1.66 M and the measured Al molarity was 1.68 M. The predicted U concentration following completion of Phase 2 of the experiment was 26.8 g/L while the measured value was 25.1 g/L. The predicted free acid at the end of the LEU dissolution was 1.16 M and the predicted total acid was 6.37 M while the measured free acid was 1.1 M and the measured total acid was 6.45 M.

Potential Explosive Behavior of U-Zr Alloys during H-Canyon Dissolution

A potential concern during the HNO_3 dissolution of U metal containing Zr is the explosive behavior that has been reported for alloys of this material.[7,8,9] No violent exothermic behavior was observed during the dissolution of any pieces of the LEU samples from the INL ingots. To benchmark the concentration of Zr in the 4 LEU samples received from INL, the concentration of Zr was measured in a number of the dissolving solutions. In the first series of experiments (Experiments 79-81), samples of the solution following dissolution of the metal in a pure HNO_3 solution were analyzed by ICPMS. Although the LEU sample appeared to dissolve (i.e., no visible solids were observed), the analyzed concentrations of Zr were 43-56% lower than reported by INL (Table 9). To address this issue, additional samples of the LEU were dissolved (Experiments 102-104) using a 7 M HNO_3 solution containing 0.2 M KF and analyzed by ICPMS assuming that insoluble Zr was present in the previous solutions, that could not be seen. The Zr analyses from the second series of dissolution experiments were consistent (within analytical uncertainty) with the values provided by INL (Table 9). These low concentrations of Zr in the LEU ingots are not a concern for the dissolution of the material in an H-Canyon dissolver based on the literature (Larsen

et al.[9]) and the laboratory experiments. Complete dissolution of the Zr in an LEU ingot is not required during dissolution in an H-Canyon dissolver; therefore, no fluoride is required in the dissolving solution to fully solubilize Zr. Undissolved solids should be easily removed by the Head End centrifuge using the standard gelatin strike process.

Potential for Chloride Corrosion

The solutions from the dissolution of samples of the LEU ingots in Experiments 80 and 104 were analyzed for chloride by ion chromatography. Table 10 shows that the concentration of chloride in both dissolving solutions was less than the detection limit (100 µg/mL). The upper limit on the concentrations of chloride associated with the LEU samples are also provided in Table 10. However, the chloride salts associated with the samples of the LEU may not be a good measure of the chloride salts associated with the ingots due to the sample casting operation. Therefore, monitoring the chloride concentration in the H-Canyon dissolver used to process the LEU ingots received from INL is recommended.

Downstream Processing of Dissolved SNF and LEU Ingots

Following dissolution of a MTR or HFIR fuel batch and LEU ingots from INL, the solution would be processed through Head End and the 1st and 2nd Cycles of solvent extraction to recover the enriched U for subsequent down-blending for use as commercial reactor fuel. No issues associated with the processing of the enriched U solutions through Head End and solvent extraction are anticipated. The combined solution from the dissolution of the SNF and LEU ingots will contain undissolved solids such as transition metal fission products (e.g., Zr, Mo, Ru, Tc, Pd, and Ag), Si (as SiO_2) which is present in the Al alloys and produced from the transmutation of Al during fuel

irradiation, and likely a small amount of undissolved or precipitated Zr from the LEU ingot. These solids should be easily removed by the Head End centrifuge using the standard gelatin strike process.[18] Once the solution is clarified, purification by solvent extraction should proceed in the same manner as in previous campaigns. High and low activity waste generated from the processing will be neutralized and prepared for disposal using existing SRS facilities.

CONCLUSIONS

A dissolution flowsheet for LEU ingots generated at the INL from the pyroprocessing of EBR-II U-5Fs fuel was demonstrated on the laboratory scale. The flowsheet allows the dissolution of a SNF batch in an H-Canyon dissolver using the existing MTR or HFIR fuel dissolution flowsheet,[13,14] followed by the dissolution of nominally 75 kg of LEU recovered from the EBR-II fuel in the 6.4D dissolver and 45 kg of the LEU in the 6.1D dissolver. It may be necessary to add additional HNO_3 to the dissolver prior to dissolving the LEU to ensure the final acidity is greater than 0.5 M. In the demonstration experiment, the HNO_3 concentration was increased to nominally 1.4 M prior to dissolving samples of the LEU and a carbon steel can. In the demonstration experiment, the rate of dissolution of the LEU metal was significantly slower than the dissolution rate of an Al 1100 alloy used to model the dissolution of SNF (4.7 mg/min/cm^2 versus 27 mg/min/cm^2). The H_2 generation rate from the dissolution of samples of the LEU metal and a carbon steel can were inconsequential; therefore, the dissolution of the LEU ingots has no significant impact on the generation of H_2.

The LEU samples received from the INL contained up to approximately 1000 µg Zr/g U. A potential concern during the HNO_3 dissolution of U metal containing Zr is the explosive behavior

that has been reported for alloys of these materials; however, concentrations below 10,000 µg Zr/g U have not resulted in violent dissolution behavior. No violent exothermic behavior was observed during the dissolution of any pieces of the LEU samples from the INL ingots. The presence of chloride salts from the INL electrorefiner which are associated with the LEU ingots are a potential H-Canyon corrosion concern. The concentration of chloride in solutions from the dissolution of samples of the LEU were less than the detection limit (100 µg/mL); however, the chloride salts associated with the LEU samples may not be a good measure of the chloride salts associated with the ingots due to the sample casting operation.

ACKNOWLEDGEMENTS

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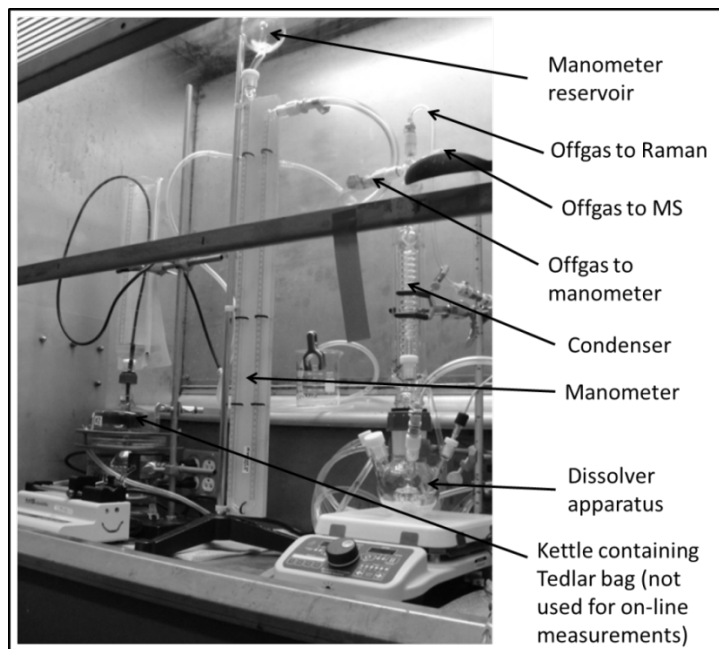
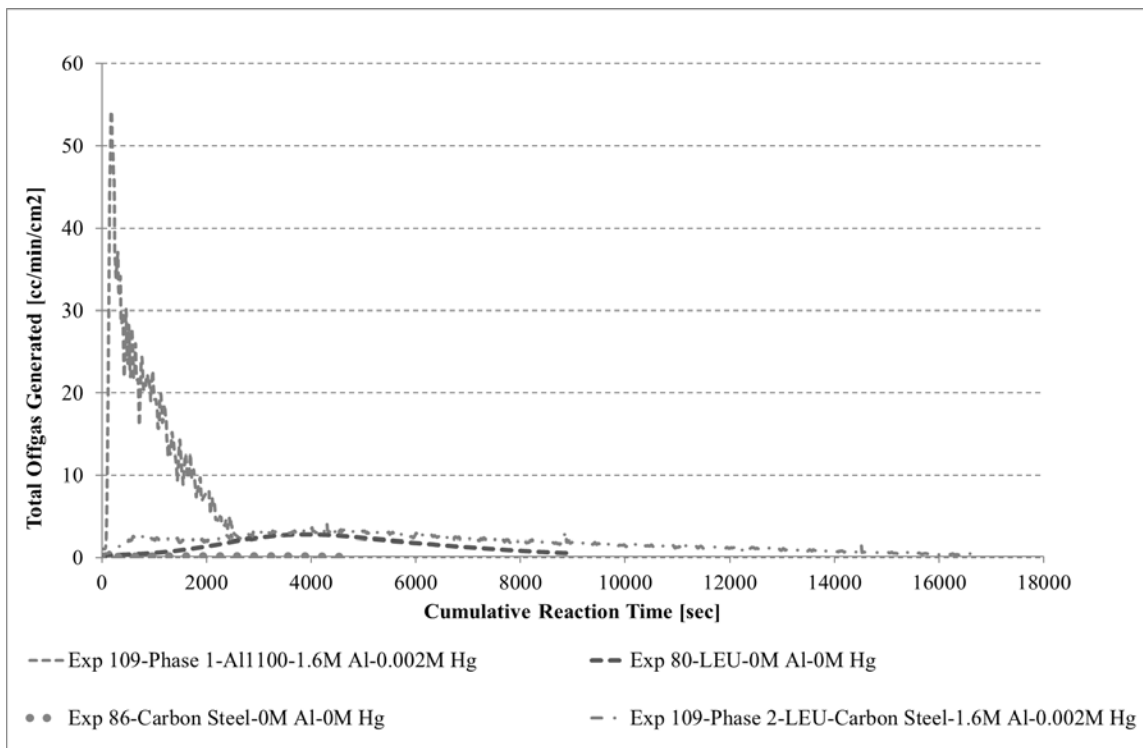FIG. 1. Dissolver Setup with Online MS and Raman Offgas Analyzers

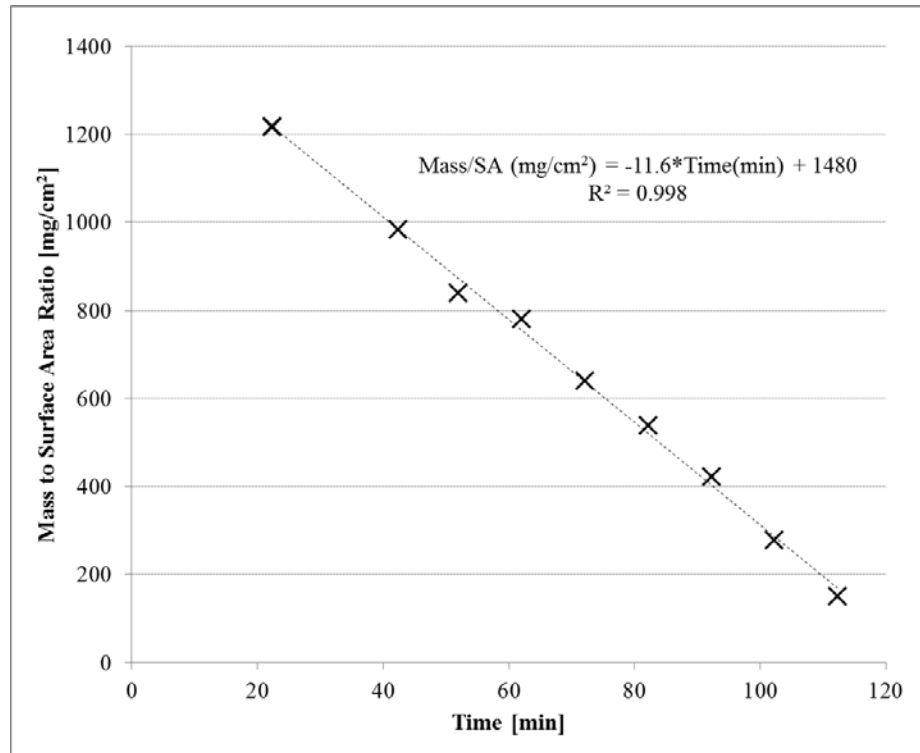FIG. 2. Offgas Generation Rates for LEU, Carbon Steel, and Al 1100 Alloy Samples

FIG. 3. Mass-to-Surface Area Ratio versus Time for Dissolution of LEU Sample
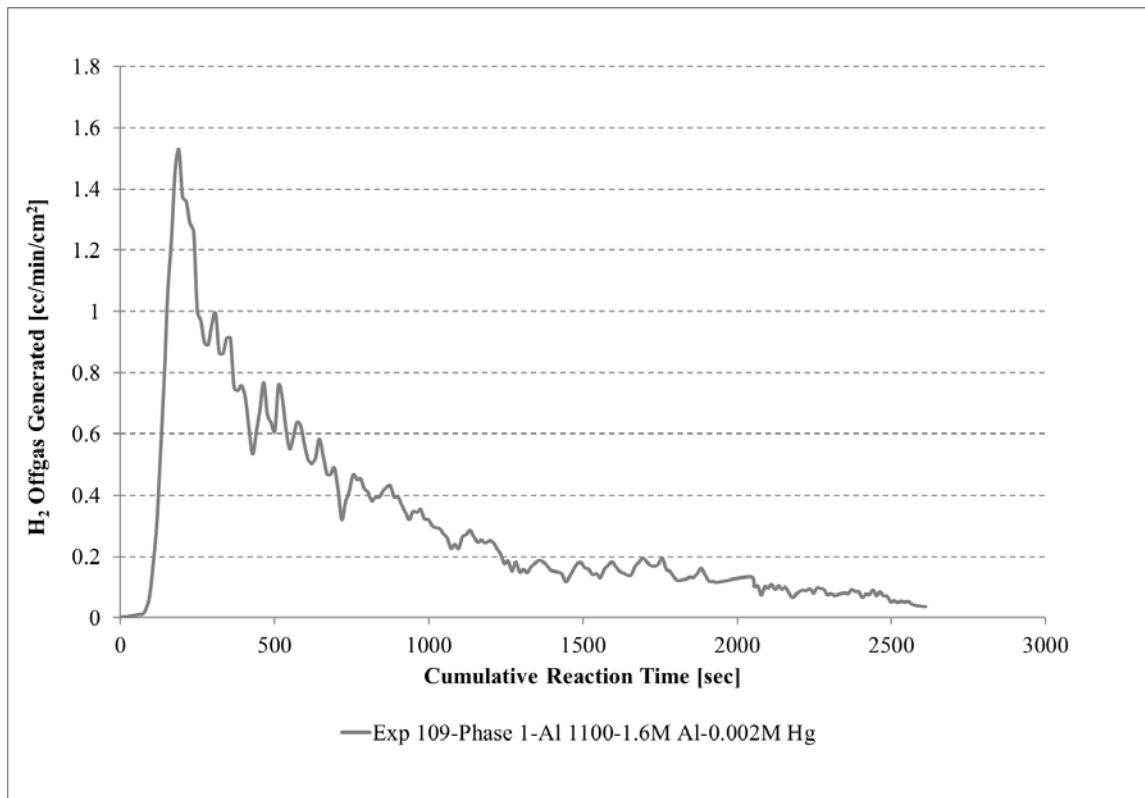

FIG. 4. H_2 Generation Rates for Al 1100 Alloy Samples
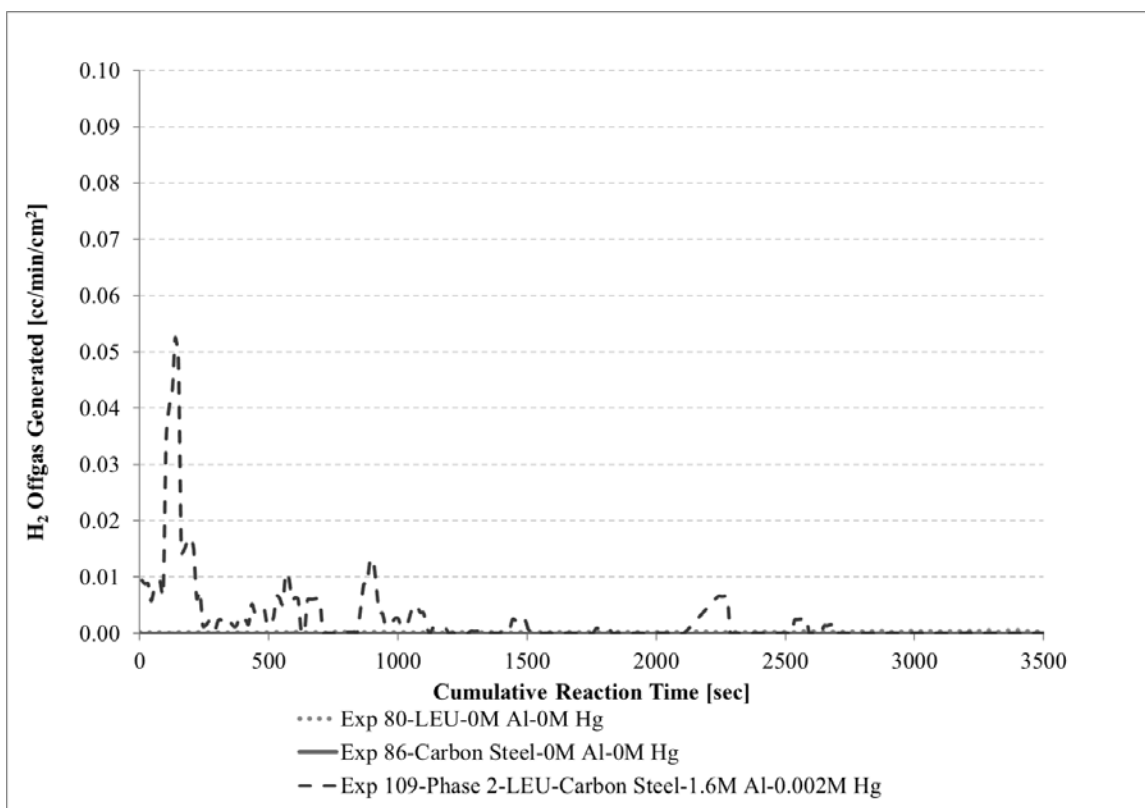
FIG. 5. H₂ Generation Rates for LEU and Carbon Steel Samples

TABLE 1

Characterization Data for U-5Fs Ingots

Element	Units	Mean Value[1]
Al	ppm	<180
Cd	ppm	<15
C	ppm	~220
Cr	ppm	<50
Fe	ppm	123
Li	ppm	<10
Mn	ppm	14
Mo	ppm	<90
Ni	ppm	<20
N	ppm	<5
O	ppm	~130
Si	ppm	~125
Zr	ppm	681
Total U	wt %	99.9
U-235	wt %	19.7

(1) Mean value for two ingots

TABLE 2

Dissolution Experiments

Exp. No.[1]	Objective	Material	Hg Conc. (M)	Target Al Conc. (M)
80	Evaluate offgas generation at 7 M HNO_3	LEU	0	0
86	Evaluate offgas generation at 10 M HNO_3, 1.5 g B/L, 0.1M KF	carbon steel	0	0
109-Phase 1	Evaluate offgas generation rate at 7M HNO_3	Al 1100	0.002	1.6
109-Phase 2	Evaluate offgas generation rate at 1.4 M HNO_3 and 4.3 g U/L	LEU, carbon steel	0.002	1.6

(1)Experimental numbering sequence corresponds to data recording practices

TABLE 3

Alloy Coupon Characteristics

Exp. No.[1]	Metal	Mass (g)	Length (cm)	Width (cm)	Thickness/ Diameter (cm)	Surface Area[2] (cm^2)
80	LEU	2.8434	2.447	—	0.282	2.293
86	carbon steel	1.0493	2.664	2.215	0.032	12.114[3]
109-Phase 1	Al 1100	5.9015	4.172	1.920	0.276	4.922
109-Phase 2	LEU	2.9502	2.497	—	0.276	2.285
109-Phase 2	carbon steel	0.1400	1.054	0.777	0.032	1.755

(1) The experimental numbering sequence corresponds to data recording practices
(2) The Al 1100 coupon surface area was calculated for a 10 mm immersion depth; the surface area for all others coupons was calculated for full immersion
(3) Carbon steel coupon had 1/16 inch hole near the top so the surface area was adjusted for this effect

TABLE 4

Calibration Gases for MS and Raman Analyzers

Supplier	Gas	Ar (%)	N$_2$ (%)	N$_2$O (%)	NO$_2$ (%)	NO (%)	O$_2$ (%)	H$_2$ (%)
Air Liquide	20% N$_2$O-80% Ar	80.00	—	20.00	—	—	—	—
Liquid Technology	5% NO$_2$-20% O$_2$-75% Ar	74.89	—	—	4.98	—	20.13	—
Air Liquide	20% NO-80% Ar	80.00	—	—	—	20.00	—	—
Air Liquide	5% N$_2$-10% H$_2$-85% Ar	85.00	5.00	—	—	—	—	10.00
SRNL	Ar[1]	99.9	—	—	—	—	—	—
SRNL	N$_2$[1]	—	99.90	—	—	—	—	—
SRNL	Air[1]	0.94	78.03	—	—	—	20.99	—

(1) Purity not measured; supplied from SRNL facility gases

TABLE 5

Dissolving Solution Volume and Composition

Exp. No.	Initial Volume (mL)	Hg Solution Volume (mL)	Target Hg Concentration (M)	Target Al Concenration (M)
—				
80	150	0	0	0
86	150	0	0	0
109-Phase 1	134	1.61	0.002	1.6
109-Phase 2	137	0	0.002	1.6

TABLE 6

Overall HNO$_3$ Consumption per mole Fe

Gas	Gas Produced on Ar Basis (vol %)	Gas Produced on Ar Free Basis (vol %)	Potential Reaction	mole HNO$_3$ used/mole Fe	weighted mole HNO$_3$/mole Fe
NO$_2$	0.4	6	Eqn 2	6	0.36
NO	5.6	85	Eqn 3	4	3.39
N$_2$	0.6	9	Eqn 4	4	0.36
Totals	6.6	100			4.12

TABLE 7

HNO$_3$ Concentration Estimates for Metal Consumption and Component Addition

Exp 109	Component	Initial Mass (g)	Initial Amount (mole)	mole HNO$_3$ used/mole Metal	mole HNO$_3$ used	Initial HNO$_3$ (mole)	Final HNO$_3$[1] (mole)	Initial Volume (mL)	Final Volume (mL)	Final HNO$_3$ (M)
Phase 1	Al	5.9015	0.219	3.75	0.820	0.897	0.077	135.6	128.0	0.60
	Hg	0.0546	2.72E-4	0	0					
Trim	U	0.5846	2.46E-3	—	—	0.077	0.189	128.0	136.9	1.38
	HNO$_3$	—	0.111	—	—					
Phase 2	Fe	0.1400	2.51E-3	4.12	0.01	0.189	0.154	136.9	132.0	1.17
	LEU	2.9502	1.24E-2	2.00	0.025					

(1) Values are cumulative based on the addition or consumption of HNO$_3$

TABLE 8

Dissolution of EBR-II LEU Metal in Boiling HNO$_3$

Time (min)	Mass (g)	Diameter (mm)	Length (mm)	Surface Area (SA) (cm^2)	Mass/SA mg/cm^2)
0.0	3.1505	2.86	26.34	2.495	1263
22.3	2.9547	2.81	26.05	2.424	1219
42.3	1.9656	2.35	25.9	1.999	983
52.0	1.5049	2.13	25.71	1.792	840
62.0	1.1110	1.76	24.82	1.421	782
72.1	0.7943	1.54	24.87	1.240	640

82.1	0.5409	1.27	24.56	1.005	538
92.2	0.3355	1.01	24.5	0.793	423
102.3	0.1717	0.80	24.15	0.617	278
112.4	0.0540	0.47	24.13	0.360	150

TABLE 9

Zr Concentration in LEU Samples

Exp No.	INL Sample Designation	Sample Mass (g)	Solution Volume (mL)	Zr Conc.[1] (μg/L)	Zr Conc (μg/g U)	Zr Conc. INL (μg/g U)
79	SADZA17	3.1505	108	2,420[2]	83[2]	146
80	SADZA18	2.8434	147	1,430[2]	74[2]	146
81	SADZA17	3.2187	135	1,520[2]	64[2]	146
102	SADZA17	2.7821	94	4,690	158	146
103	SADZA28	3.6235	110	31,000	941	1008
104	SADZA29	4.4391	146	28,900	951	1008

(1) Analysis uncertainty = ±10%
(2) Dissolutions were initially performed without fluoride, resulting in reduced Zr concentrations

TABLE 10

Chloride Analyses by Ion Chromatography

Exp No.	INL Sample Designation	Sample Mass (g)	Solution Volume (mL)	Chloride Conc. (μg/mL)	Chloride Conc. (μg/g U)
80	SADZA18	2.8434	147	< 100	< 5200
104	SADZA29	4.4391	146	< 100	< 3300