

**Dissolution of Highly Enriched Uranium from the
Idaho National Engineering and Environmental Laboratory**

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Summary

Since the capability to purify uranium (U) was terminated at the Idaho National Engineering and Environmental Laboratory (INEEL) in the early 1990's, excess highly enriched uranium (HEU) from the cleanout of uranium trioxide (UO_3) production equipment will be shipped to the Savannah River Site (SRS) for disposition. The excess material will be dissolved in Phase I of HB-Line, purified by solvent extraction, and blended with normal U to an enrichment which can be used to fabricate fuel for Tennessee Valley Authority (TVA) reactors. The proposed HB-Line processing strategy is to dissolve up to 3 kg of material per 18 L dissolver batch. To demonstrate the proposed processing strategy, two samples of the HEU were shipped to the Savannah River Technology Center (SRTC). The material was used in a series of small-scale experiments in which prototypical amounts were dissolved to characterize the offgas and measure the dissolution time under varying process conditions.

Initially, an examination of the HEU by x-ray diffraction showed that the material was a mixture of UO_3 and two monohydrated forms of UO_3 . Subsequent thermogravimetric analyses showed that the samples contained 8-9 wt% volatile components which were predominately water. The dissolution of several grams of material from each sample in a closed system with the capability to measure and sample the offgas showed that essentially no gas was generated as the material dissolved. This observation was consistent with the presence of UO_3 which generates no offgas upon dissolution in nitric acid (HNO_3). The generation of hydrogen (H_2) during the dissolution of the HEU is not a concern.

Complete dissolution of the U was obtained in 15-30 min for experiments performed at 23-60°C. The HEU was dissolved in 3.5M HNO_3 using the solids to liquid ratio proposed for use in HB-Line. The experiment performed at 23°C demonstrated that rapid heat generation during the dissolution is not a concern. The temperature peaked 5 min into the dissolution at 28°C and quickly cooled back down to 23°C. During filtration of the dissolving solutions, a small amount of black solids was collected; the material was identified as graphite by subsequent x-ray diffraction analysis. A temperature of at least 60-70°C for the dissolution is recommended to minimize the amount of undissolved impurities.

Two additional dissolution experiments were performed at 80°C to characterize the U and impurity content of the HEU. Uranium and elemental analyses of the two dissolving solutions and the solutions generated by the offgas characterization experiments were used to estimate the composition of the HEU by assuming the impurities generally occurred in the material as oxides.

The estimated composition of the samples shipped from INEEL was nominally 80 wt% UO_3 , 10 wt% volatiles (primarily water), and 10 wt% oxide impurities. The principal impurity was aluminum oxide (Al_2O_3). Accounting for the UO_3 , volatile components, and analyzed impurities (as oxides) resulted in material balance closures of 81-98%. Analysis of the initial and final HNO_3 concentrations of the dissolving solutions showed that 0.005-0.010 mole of HNO_3 was consumed per gram of HEU. To achieve a final HNO_3 concentration of nominally 2M, desired for subsequent solvent extraction operations, a starting HNO_3 concentration of 3.0-3.5M is recommended.

Introduction

To support the disposition of HEU from the INEEL, excess material will be shipped to the SRS for blending the ^{235}U content down to an enrichment which can be used to fabricate fuel for TVA reactors. The HEU was accumulated during cleanout of equipment used to produce a UO_3 product. The HEU has been stored at the INEEL since the termination of reprocessing activities at the site. The HEU is scheduled for dissolution in Phase I of the HB-Line Facility. The U will then be purified by solvent extraction and blended with normal U as part of the TVA Blend-down Program.

The proposed HB-Line processing strategy is to dissolve up to 3 kg of material per dissolver batch. The working volume of the Phase I dissolvers is nominally 18 L which will result in a final U concentration in the 100-120 g/L range. A dissolution temperature of 60-70°C is desired; although, the Phase I dissolvers are capable of operating at or near the boiling point of the solution. A final HNO_3 concentration of approximately 2M is desired to facilitate subsequent purification by solvent extraction. To develop and demonstrate a dissolution flowsheet with the features described above, two samples of the HEU were shipped to the SRTC. The material was used in a series of small-scale experiments to measure the time required to dissolve the HEU using conditions proposed for HB-Line. Experiments were also performed to measure and characterize the offgas and identify exothermic behavior during dissolution. Elemental analyses of dissolving solutions, x-ray diffraction analysis of the HEU and undissolved solids, and thermogravimetric analysis of the HEU were used to characterize the INEEL material. A description of the experiments performed and a discussion of the results are provided in the following sections.

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Experimental

X-ray Diffraction Analysis

Since the HEU was removed from equipment utilized in the production of UO_3 , complete conversion to the intended product may not have occurred for all of the material. To determine the predominate forms of U in the samples from the INEEL, approximately 100 mg of each sample were analyzed by x-ray diffraction.

Thermogravimetric Analysis

Removal of the HEU from the INEEL production process also created the potential for the material to contain volatile components such as nitrogen and carbon-containing compounds and water. To detect and quantify the amount of these materials, 100 mg of each INEEL sample were analyzed using a thermogravimetric analyzer (TGA) coupled to a mass spectrometer (MS). The mass loss of each sample was measured using a Netzsch (model STA 409PC/LUXX) TGA while heating in air from 25 to 1000°C at 40°C/min. Offgas from the sample was analyzed using a Pfeiffer ThermoStar (model GSD 301TS) MS.

Offgas Characterization

Prior to the dissolution of the HEU in HB-Line, the potential to generate an offgas containing H_2 was evaluated. The concentration of H_2 in the offgas must not exceed 25% of the lower flammability limit in air (4 vol%).[1] To perform the measurements, approximately 2.5 g of material from each INEEL sample were dissolved using laboratory-scale equipment designed for offgas generation measurements and sampling. The equipment consisted of a cylindrical glass vessel with a 30-40 mL capacity for holding the dissolving solution connected to a gas sampling bulb, vacuum source, and inverted graduated cylinder immersed in water to collect and measure the volume of gas. A sketch of the system is shown on Figure 1.

The dissolutions were initiated by measuring the mass of HEU (by difference) and transferring the sample into the dissolving vessel. The system was sealed and evacuated until water nearly filled the graduated cylinder. A 17 mL aliquot of nominally 3.5M HNO_3 was added to the dissolving vessel using a syringe and the septum on the top of the vessel. The use of 17 mL of solution to dissolve 2.5 g of material results in the same solids to liquid ratio as desired in the HB-Line dissolvers. A starting HNO_3 concentration of 3.5M would result in a final concentration of 2.3M assuming the material was pure UO_3 . Once the acid addition was complete, stirring was initiated and the solution heated to 40-60°C by heating the water bath on the hot plate/stirrer. A summary of the conditions used to perform the dissolutions is provided in Table 1.

Table 1 Summary of Conditions for Offgas Characterization Experiments

Experiment ID	HEU Mass (g)	Volume 3.5M HNO ₃ (mL)	Temperature (°C)
746-1	2.73	17.0	40-60
747-1	2.60	17.0	40-60

The temperature was monitored using a thermocouple immersed in the water bath. As the material dissolved, offgases were collected by the displacement of water from the graduated cylinder. The removable gas sample bulb provided the capability to collect and analyze a sample of the offgas upon completion of the dissolution. The dissolutions were terminated by visual observation when the solutions no longer appeared to contain UO₃ powder; although, a small amount of fine black solids could still be seen.

Following completion of the dissolutions, the dissolving solutions were cooled and filtered using a coarse glass frit; however, the porosity of the frit was too large to retain the black solids. The solids were removed by centrifuging and decanting the liquid. The solids did not dissolve in hydrochloric acid which indicated they did not contain U. The volume of the dissolving solution, which included deionized water used to rinse the dissolver and filter, was determined by measuring the mass and specific gravity of the solution. Samples of the dissolving solutions were prepared for total U and trace metal analyses by transferring a 1 mL aliquot into plastic sample vials containing 9 mL of deionized water. Dilution of the dissolving solution was necessary to prevent the transfer of accountable quantities of ²³⁵U in the samples. The diluted samples were analyzed for total U by inductively coupled plasma – mass spectroscopy (ICP-MS) and trace metals by inductively coupled plasma – emission spectroscopy (ICP-ES). Samples of the HNO₃ solution prepared for the dissolutions and the diluted dissolving solutions were analyzed for free acid by titration.

Timed Dissolution Experiments

The time required to achieve complete dissolution of the HEU was measured in a series of small-scale experiments in which nominally 2.5 g of material were dissolved in 17 mL of nominally 3.5M HNO₃. The dissolutions were performed in a 50 mL beaker with the pour spout removed. A watch glass filled with water was placed on top of the beaker to reduce the evaporation rate of the dissolving solution. A thermometer was inserted through the watch glass into the dissolving solution using a feedthrough equipped with a compression fitting. A magnetic stir bar was added to the beaker during each dissolution and the beaker was heated and stirred using a hot plate/stirrer. The dissolving temperatures ranged from ambient (23°C) to 80°C.

Three experiments were performed in which the magnetic stirrer was periodically (every 0.25 or 0.50 h) switched-off and solids allowed to settle for 1 min prior to removing a 200 µL aliquot of the dissolving solution. The 200 µL aliquot was transferred to a glass sample vial containing 2000 µL of deionized water. A small sample of the dissolving solution was removed to conserve solution and prevent the transfer of accountable amounts of ²³⁵U in the analytical samples. Dissolution times for these experiments ranged from 2-4 h. Following the removal of the last

sample for U analysis, a sample of the dissolver solution was removed for a free acid analysis. The 200 μL aliquot was transferred to a glass sample vial containing 2000 μL of deionized water. The samples were analyzed for total U by ICP-MS and free acid by titration.

The calibrations of the 200 and 1000 μL pipettes used to prepare the samples were checked by measuring the mass of deionized water transferred to a beaker. The measurements were performed 10 times for each pipette. Upon review of the data, it was clear that the errors associated with the transfers were much less than the error associated with the U analysis; therefore, the nominal value of the pipettes could be considered the exact volume for these experiments.

Once the dissolution was complete, the dissolving solution was cooled to ambient temperature and filtered using paper with a 0.45 μm pore size. The volume of the filtrate was measured using a 25 mL graduated cylinder. A small amount of undissolved solids was collected on the filter paper for analysis. After air drying, the solids were examined by x-ray diffraction to identify the undissolved materials. Following the analysis of the initial samples, it became apparent that the solids required washing with water to remove uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2$) prior to analysis. The small volume of solids retained enough $\text{UO}_2(\text{NO}_3)_2$ that its presence dominated the x-ray diffraction spectra. To remove the water-soluble $\text{UO}_2(\text{NO}_3)_2$, five, 15 mL aliquots of deionized water were poured through the filter assembly.

In two subsequent experiments, nominally 2.5 g of the HEU were dissolved in 17 mL of 3.5M HNO_3 at 80°C. The dissolution time for each experiment was 1.5 h. These experiments were performed to quantify the amounts of U and trace metal impurities in the two samples from the INEEL. The dissolutions were performed in the same manner as the previous three, except the dissolving solution was not periodically sampled. After dissolving for 1.5 h, the solution was allowed to cool to ambient temperature and filtered. The volume of the dissolving solution was then measured using a 25 mL graduated cylinder. Samples of the solutions were prepared for total U, trace metal, and free acid analyses by transferring a 1 mL aliquot into plastic sample vials containing 9 mL of deionized water. Triplicate samples of the solution were analyzed for total U by ICP-MS. Samples of the solution were analyzed for trace metals by ICP-ES and free acid by titration.

A summary of the process conditions used to perform the dissolutions and the sampling frequency are given in Table 2.

Table 2 Summary of Conditions for Timed Dissolution Experiments

Experiment ID	HEU Mass (g)	Volume 3.5M HNO_3 (mL)	Temperature (°C)	Dissolution Time (h)	Sampling Frequency (h)
746-2	2.531	17.0	60	2.00	0.25
747-2	2.595	17.0	60	2.00	0.25
747-3	2.573	17.0	23	4.00	0.50
746-3	2.441	17.0	80	1.50	1.50
747-4	2.501	17.0	80	1.50	1.50

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Results and Discussion

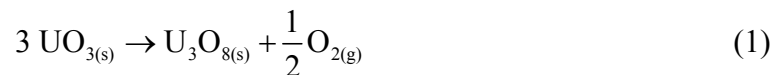
X-ray Diffraction Analysis

The x-ray diffraction spectra for the two INEEL HEU samples (746 and 747) are shown on Figures 2 and 3, respectively. The spectra are almost identical showing only UO_3 and two hydrated forms of UO_3 associated with one molecule of water ($\text{UO}_3 \cdot \text{H}_2\text{O}$). The intensity of the peaks assigned to one of the hydrated forms is very strong suggesting that the HEU may contain a significant amount of water. The amount of water and other volatiles in the samples was quantified by thermogravimetric analyses discussed in the following section.

Thermogravimetric Analysis

Based on the indication provided by the x-ray diffraction analysis that the samples of HEU from the INEEL contained a significant amount of water, a thermogravimetric analysis was performed for each sample. The TGA curves are shown on Figures 4 and 5. The mass loss from sample 746 (Figure 4) and 747 (Figure 5) were 8.1 and 8.6%, respectively. The offgas from the thermogravimetric analysis of sample 746 was analyzed by the attached MS. The MS was not operational when the analysis of sample 747 was performed. The offgas from sample 746 was predominately water. Trace amounts of nitrogen oxides and carbon dioxide were seen indicating the presence of very minor amounts of nitrate and carbon. Since the shape of the TGA curves for both samples are nearly the same, it would be a reasonable assumption that the composition of the offgas generated during the heating of sample 747 was primarily water.

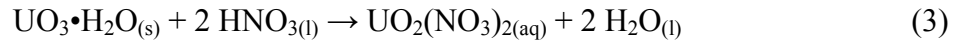
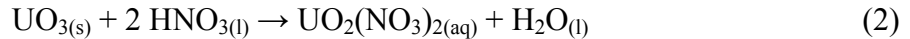
It should be noted that a portion of the mass loss at temperatures above 600°C could be attributed to the conversion of UO_3 to U_3O_8 (triuranium octaoxide) (equation 1); however, heating the HEU in air during the thermogravimetric analyses prevented the detection of any oxygen (O_2) liberated from the sample.



Many U compounds (including UO_3) decompose to U_3O_8 above 650°C . [2] In fact, U_3O_8 is conveniently prepared by heating UO_3 to nominally 650°C . The theoretical decrease in mass during the UO_3 to U_3O_8 conversion is 1.88%. Icenhour [3] measured the mass loss from UO_3 during thermogravimetric analysis using material prepared by thermal decomposition of uranyl nitrate hexahydrate. A 1.78% mass loss beginning at 570°C was attributed to the liberation of O_2 during the conversion to U_3O_8 . However, the sample heating rate for these analyses was much slower (1 or $2^\circ\text{C}/\text{min}$ versus $40^\circ\text{C}/\text{min}$) compared to the heating rate used to analyze the INEEL samples. For this reason, a complete conversion to U_3O_8 is doubtful. The MS used to analyze the offgas from sample 746 also detected water in the offgas at 600°C . This may have been due to the relatively fast heating rate.

Offgas Characterization

Essentially no offgases accumulated in the inverted graduated cylinder as the HEU in the two INEEL samples dissolved in the test apparatus. This observation is consistent with the results from the x-ray diffraction analysis which showed that the only significant forms of U were UO_3 and $\text{UO}_3 \cdot \text{H}_2\text{O}$. These compounds dissolve in HNO_3 by equations (2) and (3).



Neither equation (2) or (3) predicts the generation of an offgas which is consistent with the observations during the experiments. The generation of H_2 during the dissolution of the HEU is not a concern. Additional data generated during these experiments are discussed and compared with the results from the time dissolution experiment in the following section.

Timed Dissolution Experiments

The U analyses for the samples generated during the dissolution experiments in which 200 μL aliquots were periodically removed from the dissolving solution are presented in Appendix A. Before the concentrations can be correlated with the dissolution time, they must be corrected for the change in volume which occurred as a result of sample removal and evaporation losses. A small correction must also be made for the dissolved U removed in samples prior to completing the experiment. The procedure used to correct the concentrations and the calculated values is presented in Appendix B.

The corrected U concentrations for the dissolution experiments are plotted as a function of sample time on Figure 6. Examination of the data shows that complete dissolution of the U was obtained in 15-30 min even for the dissolution performed at ambient temperature (23°C). This result is not surprising, as UO_3 is readily soluble in HNO_3 . [4] The average U concentration measured at each sample time for each dissolution experiment is also shown on the figure to illustrate the rapid dissolution. There is extensive scatter about the average concentration which was attributed to variations in the small (200 μL) sample size of the concentrated U solution.

Experiment 747-3 was performed at ambient temperature (23°) to evaluate the potential for rapid heat generation during the dissolution of the HEU. The temperature of the dissolving solution was closely monitored during the initial stages of the dissolution. The dissolving solution temperature peaked at 28°C about 5 min into the dissolution. The temperature of the solution then cooled back down to 23°C . Based on these results, the rapid generation of heat during the dissolution of the HEU is not a processing concern.

During the filtration of the dissolving solutions for each experiment, a small amount (estimated to be <100 mg) of black solids was collected on the filter paper. The solids were identified by x-ray diffraction analysis. The spectrum, shown on Figure 7, shows that the solids are graphite. The talc identified in the sample was likely due to handling the solids during sample preparation with plastic gloves which are frequently coated with this material. The source of the graphite in

the HEU is unknown. One could speculate that the HEU contained a small amount of organic solvent which was converted to graphite during the UO_3 production process.

The final U concentrations and volumes for the dissolving solutions generated during the offgas characterization and timed dissolution experiments are given in Table 3. The concentrations were corrected for all dilutions.

Table 3 Measured U Concentrations Following HEU Dissolutions

Experiment ID	Final U Concentration (g/L)	Final Solution Volume (mL)
746-1	56.68	26.16
747-1	36.84	41.34
746-2	113	11.7
747-2	121	11.8
747-3	129	14.2
746-3	110.0	16.0
	100.4	
	96.0	
Mean	102.1	
Std. Dev.	7.2	
746-4	76.6	16.8
	101.0	
	81.1	
Mean	86.2	
Std. Dev.	13.0	

The mass of U recovered during each dissolution experiment was calculated from the product of the concentrations and volumes given in Table 3. The mass of U recovered in Experiments 746-2, 747-2, and 747-3 was corrected for the mass of U removed during periodic sampling. The initial mass of UO_3 dissolved in each experiment was calculated from the difference in the mass of the HEU and volatile components (e.g. water) measured during the thermogravimetric analysis of each sample. The U recovery was then calculated based on the assumption that the oxide was pure $^{235}\text{UO}_3$. The calculations are summarized in Table 4.

The data in Table 4 generally show that the measured U mass cannot account for the total U added to the dissolving vessel if one accounts for volatile components and assumes that the INEEL material is pure $^{235}\text{UO}_3$. However, trace metal impurities are present in the HEU and will account for a portion of the missing mass. Elemental analyses were performed on the dissolving solutions from Experiments 746-1, 746-2, 746-3, and 747-4. These results are presented in Appendix C. To estimate the mass of impurities in the HEU, the mass of each element was initially calculated from the product of the concentration and the volume of dissolving solution.

Table 4 U Recovery During HEU Dissolution Experiments

Exp't ID	Initial HEU (g)	Initial UO ₃ (g)	Initial U (g)	Measured U (g)	U Recovery (%)
746-1	2.73	2.51	2.08	1.48	71.2
747-1	2.60	2.38	1.97	1.52	77.2
746-2	2.531	2.33	1.93	1.45	75.1
747-2	2.595	2.37	1.97	1.58	80.2
747-3	2.573	2.35	1.95	2.01	103.1
746-3	2.441	2.24	1.86	1.63	87.6
747-4	2.501	2.29	1.90	1.45	76.3

The elemental masses were then converted to an oxide basis assuming the impurities were present as oxides. A small amount of sulfur was detected during the analysis of the dissolving solutions from Experiments 746-3 and 746-4. The sulfur was assumed to be present in the HEU as sulfate and was accounted for as aluminum sulfate (Al₂(SO₄)₃). A summary of the calculations are presented in Appendix C. The total recovered mass was then calculated as the sum of the U and trace metal impurities (as oxides) and volatile component masses measured during the thermogravimetric analysis. The calculated masses and material balance closure for each experiment are summarized in Table 5. Material balance closures were based on the starting mass of HEU given in Table 4.

Table 5 Material Balances for HEU Dissolution Experiments

Experiment ID	UO ₃ (mg)	Impurities (mg)	Volatile Components (mg)	Material Balance Closure (%)
746-1	1780	215	222	81.2
747-1	1830	190	223	86.3
746-3	1960	237	198	98.1
747-4	1750	237	215	88.0

Accounting for impurities and volatile components in the HEU improved the material balance closure considerably; although, significant mass is still unaccounted for in the experiments. The missing mass can likely be attributed to the loss of dissolving solution and mass associated with elements which were not analyzed or detected due to the 1 to 10 sample dilution. Since the volume of the dissolving solutions used for the experiments were relatively small, any loss of solution during filtrations and other solution transfers would have a significant effect on the recovery of U given the concentration in most of the experiments was 60-100 g/L.

The composition of the HEU dissolved in Experiments 746-1, 747-1, 746-3, and 747-4 can be estimated using the recovered mass of UO₃ (Table 5) and oxide impurities (Appendix C) and the amount of water (and other volatile components) detected during the TGA-MS analysis. The estimated compositions are presented in Table 6.

Table 6 Estimated Composition of HEU from the INEEL

HEU Component	746-1 (wt%)	747-1 (wt%)	746-3 (wt%)	747-4 (wt%)
UO ₃	80.3	81.6	81.9	79.5
Volatiles	10.0	9.9	8.3	9.8
Impurities	9.6	8.4	9.9	10.8
Ag ₂ O	0.1	0.1	0.2	0.2
Al ₂ O ₃	7.0	6.6	5.0	5.7
BaO	ND	ND	0.0	0.0
BeO	0.0	0.0	NM	NM
CaO	0.2	ND	0.1	0.1
Ce ₂ O ₃	0.1	ND	0.3	0.4
Cr ₂ O ₃	0.1	0.1	0.0	0.0
CuO	0.4	0.2	0.1	0.1
Fe ₂ O ₃	0.8	0.8	0.7	0.7
Gd ₂ O ₃	ND	ND	0.2	0.2
La ₂ O ₃	ND	ND	0.1	0.1
Li ₂ O	ND	ND	0.0	0.0
MgO	0.0	0.0	0.0	ND
MnO	0.0	0.0	0.0	0.0
MoO ₃	ND	ND	0.1	0.1
Na ₂ O	0.5	0.4	0.4	0.5
NiO	0.1	ND	0.0	0.0
P ₂ O ₅	ND	ND	0.1	0.1
PbO	ND	ND	0.1	0.1
Al ₂ (SO ₄) ₃	ND	ND	1.6	1.6
Sb ₂ O ₃	ND	ND	0.1	0.1
SiO ₂	0.2	0.2	0.2	0.2
SnO ₂	ND	ND	0.1	0.1
SrO	0.1	0.0	0.1	0.1
TiO ₂	0.0	ND	0.1	0.1
V ₂ O ₅	ND	ND	0.0	0.0
ZnO	0.2	0.0	0.0	0.0
ZrO ₂	NM	NM	0.3	0.3

ND – Not Detected

NM – Not Measured

The estimated composition of the HEU from samples 746 and 747 are quite similar. Both samples contained nominally 80 wt% UO₃, 10 wt% volatiles, and 10 wt% impurities (as oxides) based on the analyses performed. The volatile components of the material were predominately water based on the TGA-MS results discussed above. The primary impurity in the HEU was Al₂O₃ based on the assumption that all impurities were present in the material as oxides.

The consumption of HNO₃ during the HEU dissolutions was measured by analyzing the initial and final concentrations for each experiment. Data for the experiments are summarized in Table 7.

Table 7 Consumption of HNO₃ during HEU Dissolution Experiments

Experiment ID	Initial HNO ₃ Concentration (M)	Measured Final HNO ₃ Concentration (M)	Corrected Final HNO ₃ Concentration (M)	Consumed HNO ₃ (moles/g HEU)
746-1	3.26	1.27	1.95	0.008
747-1	3.26	0.84	2.04	0.008
746-2	3.31	3.32	2.29	0.007
747-2	3.31	3.32	2.31	0.007
747-3	3.31	2.97	2.48	0.005
746-3	3.31	2.04	1.92	0.010
747-4	3.31	1.95	1.93	0.009

The initial HNO₃ concentrations were prepared as nominally 3.5M. The measured concentrations were slightly less which was attributed to the starting acid concentration being less than the 15.7M assumed. The measured final HNO₃ concentrations in Table 7 were corrected for the dilutions made prior to sample analysis. The corrected final HNO₃ concentrations take into account the change in volume during the dissolutions. In Experiments 746-1 and 747-1, deionized water was used to rinse the dissolver and filter; therefore, the diluted concentrations were referenced back to 17.0 mL. In the other experiments, a portion of the dissolver solution was lost due to evaporation. Assuming no HNO₃ was volatilized during the dissolutions, these concentrations were also referenced back to 17.0 mL. The amount of HNO₃ consumed during the dissolutions was then calculated from the initial and final HNO₃ concentrations and the amount of HEU dissolved (see Table 4). Theoretically, based on equation (2), 1 g of UO₃ would consume 0.007 mole of HNO₃ during dissolution. The remainder of the HNO₃ consumed in the experiments was utilized to dissolve impurities and a small amount was probably volatilized with water during the (open system) experiments.

Conclusions

A series of small-scale experiments was performed to assess the dissolution behavior of samples of HEU from the INEEL. The material was transferred to SRTC as representative samples of excess HEU to be shipped to SRS for disposition. Initially, examination by x-ray diffraction showed that the material was a mixture of UO_3 and two monohydrated forms of UO_3 . Subsequent thermogravimetric analyses showed that the samples contained 8-9 wt% volatile components which were predominately water. Closed system dissolution experiments performed with several grams of material from each sample showed that essentially no offgas was generated as the material dissolved. This observation was consistent with the presence of UO_3 which generates no offgas upon dissolution in HNO_3 . The generation of H_2 during the dissolution of the HEU is not a concern.

Complete dissolution of the U in the INEEL material was obtained in 15-30 min for experiments performed at 23-60°C. The dissolutions were carried out in nominally 3.5M HNO_3 using a solids to liquid ratio of 167 g/L. The experiment performed at 23°C demonstrated that rapid heat generation during the dissolution is not a concern. The temperature peaked 5 min into the dissolution at 28°C and quickly cooled back down to 23°C. During filtration of the dissolving solutions, a small amount of black solids was collected on the filter paper. The solids were identified as graphite using x-ray diffraction analysis.

Two additional dissolution experiments were performed at 80°C to characterize the U and impurity content of the HEU. Using the U and elemental analyses of the dissolving solutions and the solutions generated by the offgas characterization experiments, the composition of the HEU was estimated by assuming the impurities generally occurred in the material as oxides. The estimated composition of the two samples was nominally 80 wt% UO_3 , 10 wt% volatiles, and 10 wt% impurities (as oxides). The principal component of the impurities was Al_2O_3 . Accounting for the UO_3 , volatile components (e.g. water) and analyzed impurities, material balance closures of 81-98% were obtained. Analysis of the initial and final HNO_3 concentrations of the dissolving solutions showed that 0.005-0.010 mole of HNO_3 was consumed per gram of HEU resulting in a final concentration of nominally 2M in the series of experiments.

Recommendations

The proposed HB-Line processing strategy for the HEU is to dissolve up to 3 kg of material per 18 L dissolver batch resulting in a final U concentration in the 100-120 g/L range. A wide range of processing conditions can be used to meet this goal. A starting HNO_3 concentration of 3.0-3.5M is recommended based on the desire to achieve a final concentration of nominally 2M. The temperature of the dissolving solution had little effect on the time required to achieve complete dissolution of the HEU; although, a temperature of at least 60-70°C is recommended to minimize the amount of undissolved impurities.

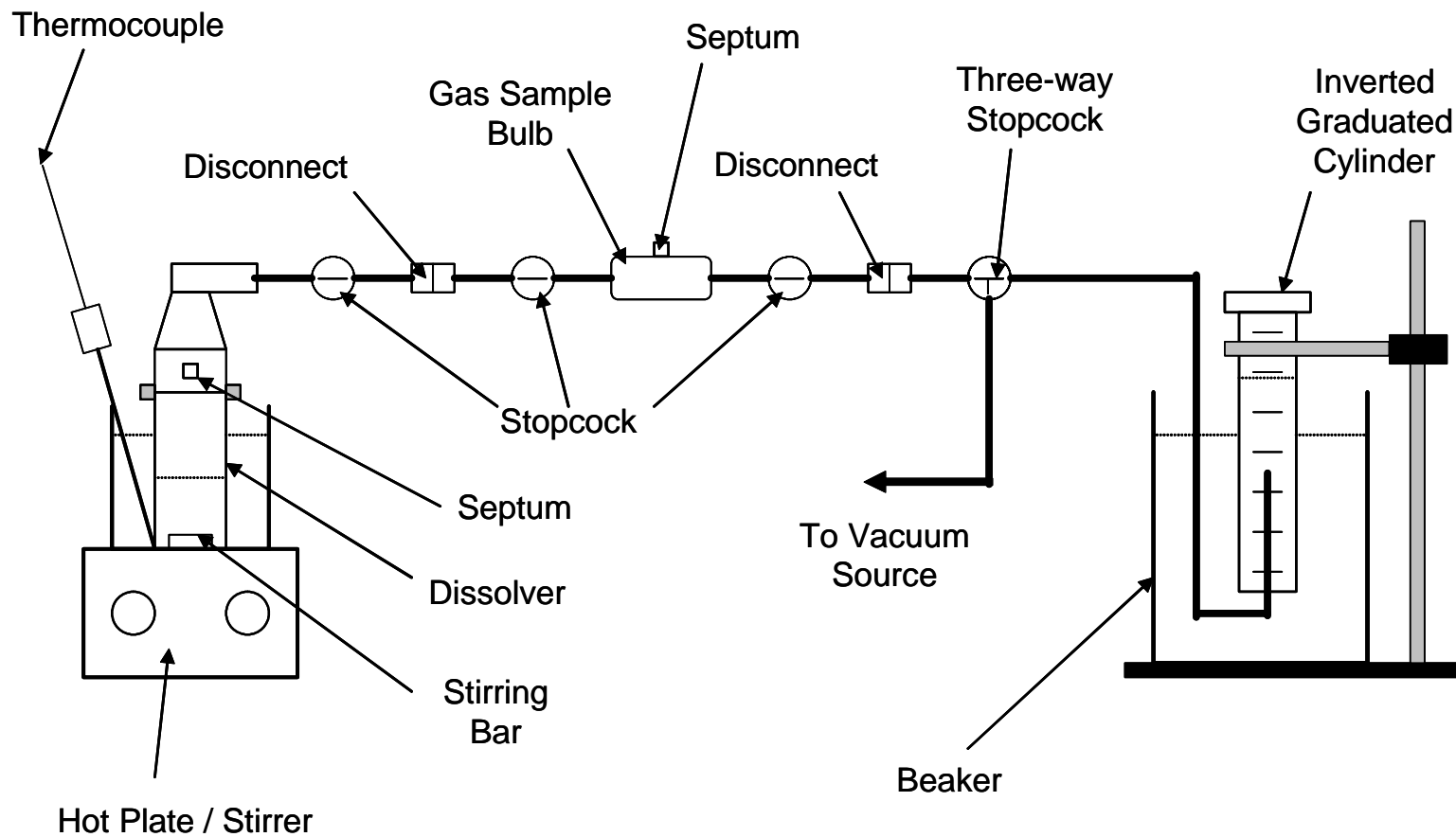
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Figure 1 Offgas Sampling and Measuring Equipment



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Figure 2 X-ray Diffraction Spectrum from Sample 746

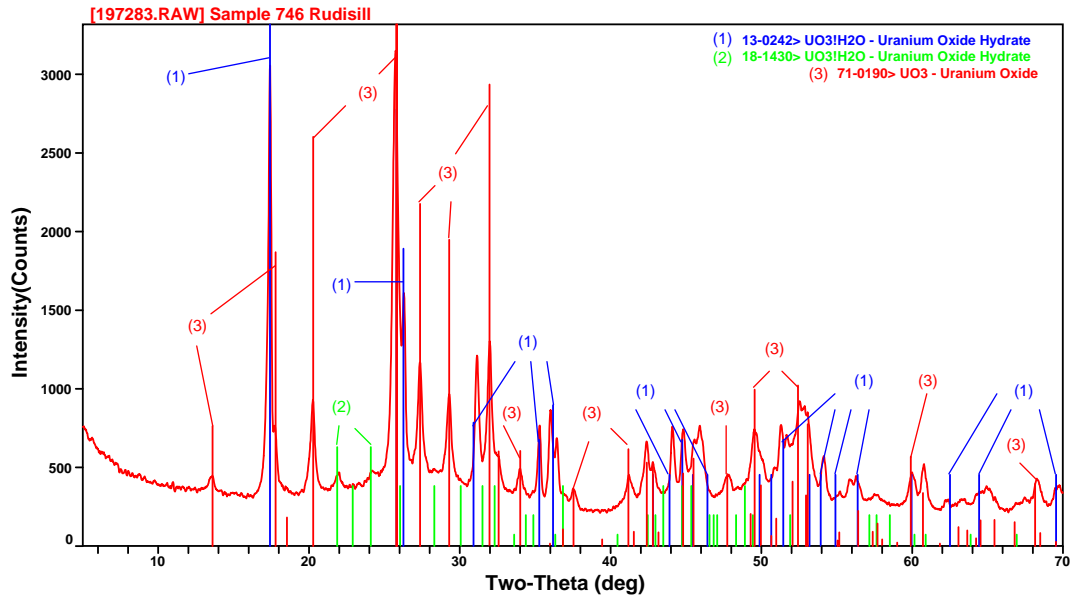
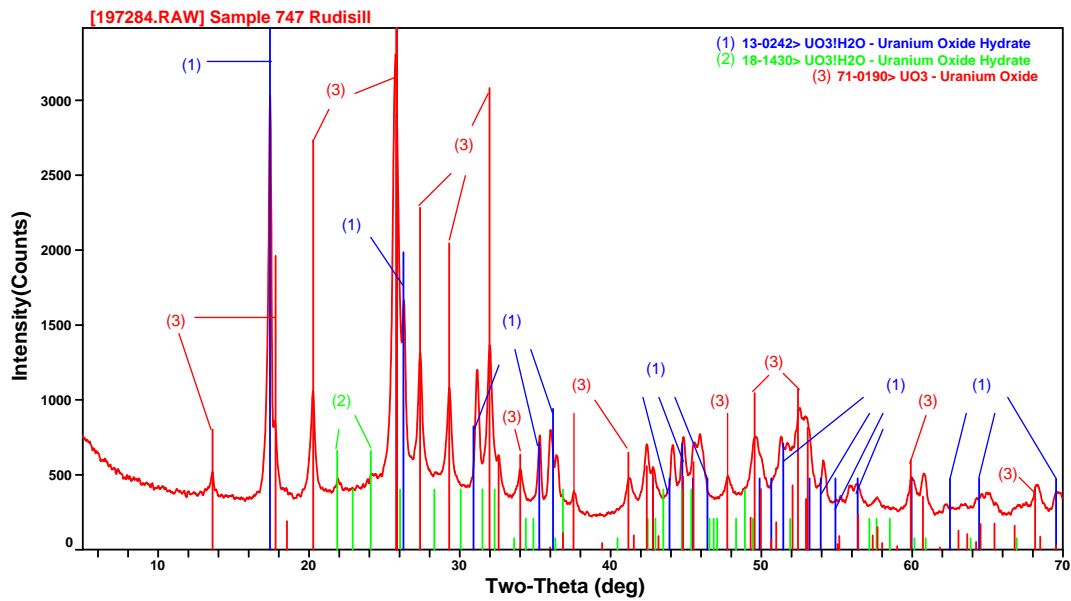
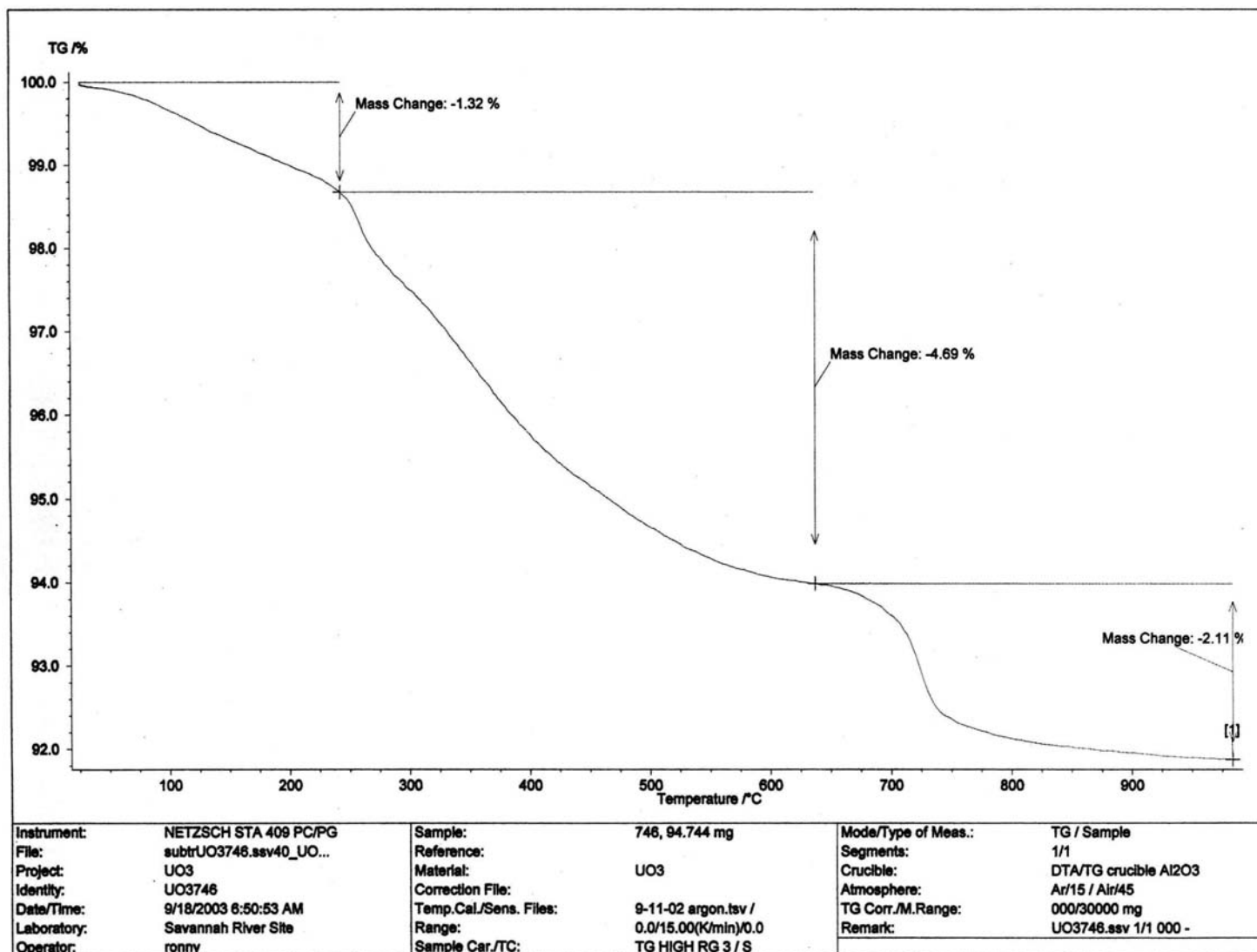


Figure 3 X-ray Diffraction Spectrum from Sample 747



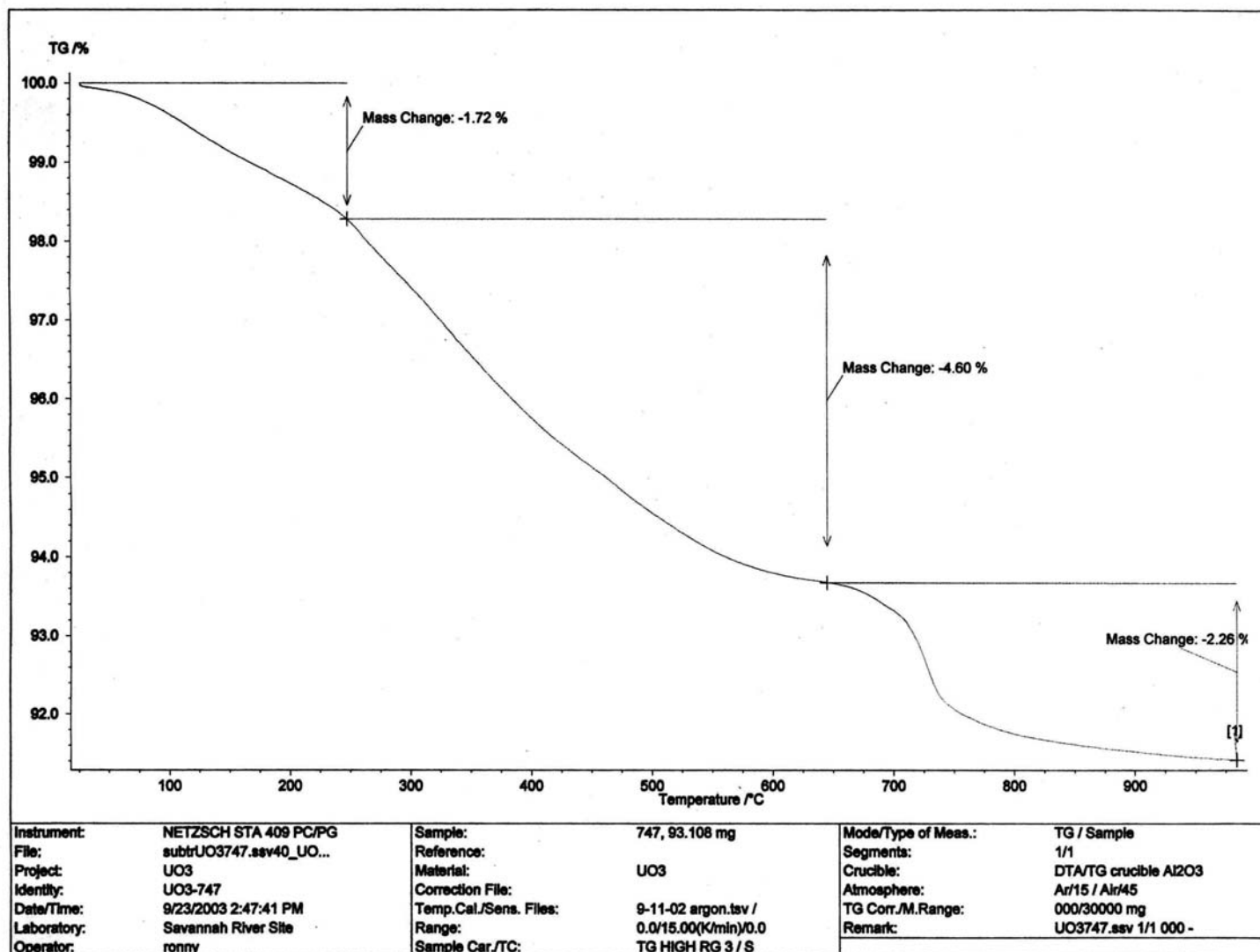
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Figure 4 TGA Curve for Sample 746



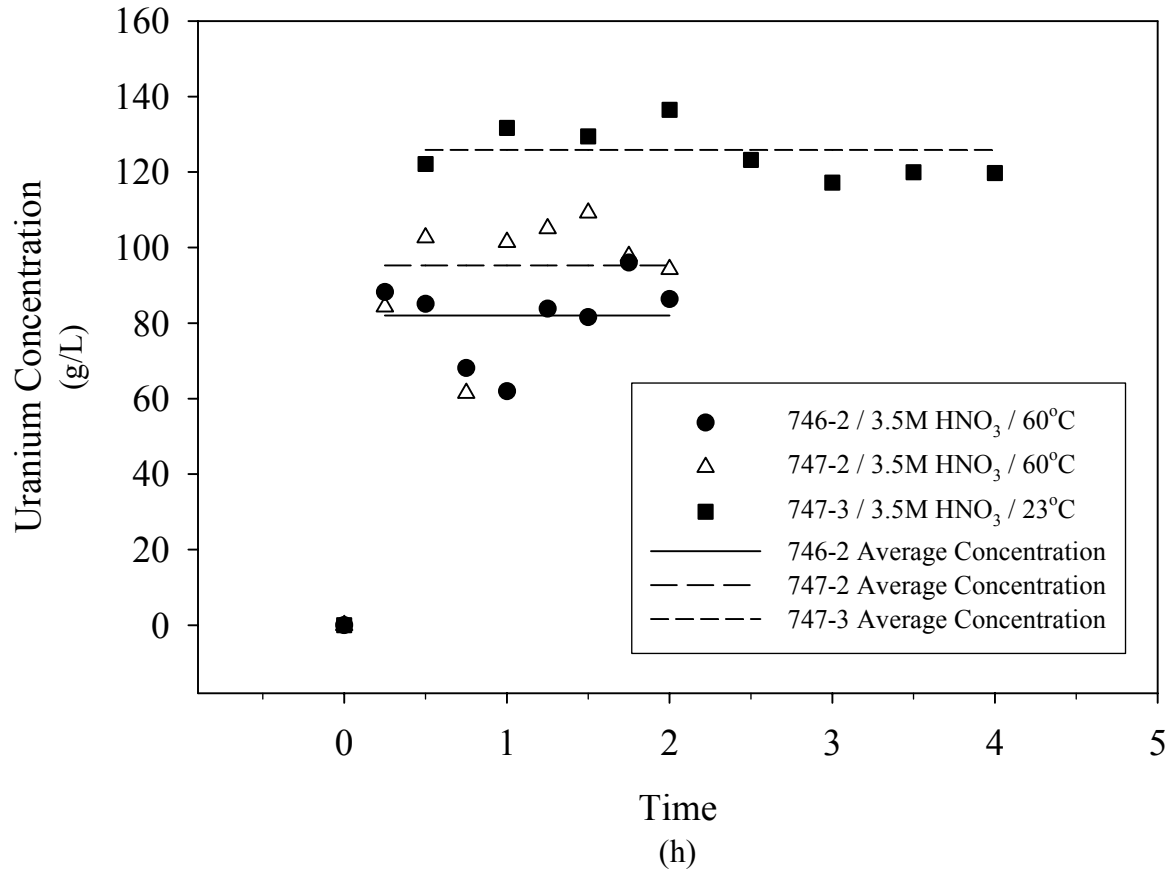
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Figure 5 TGA Curve for Sample 747



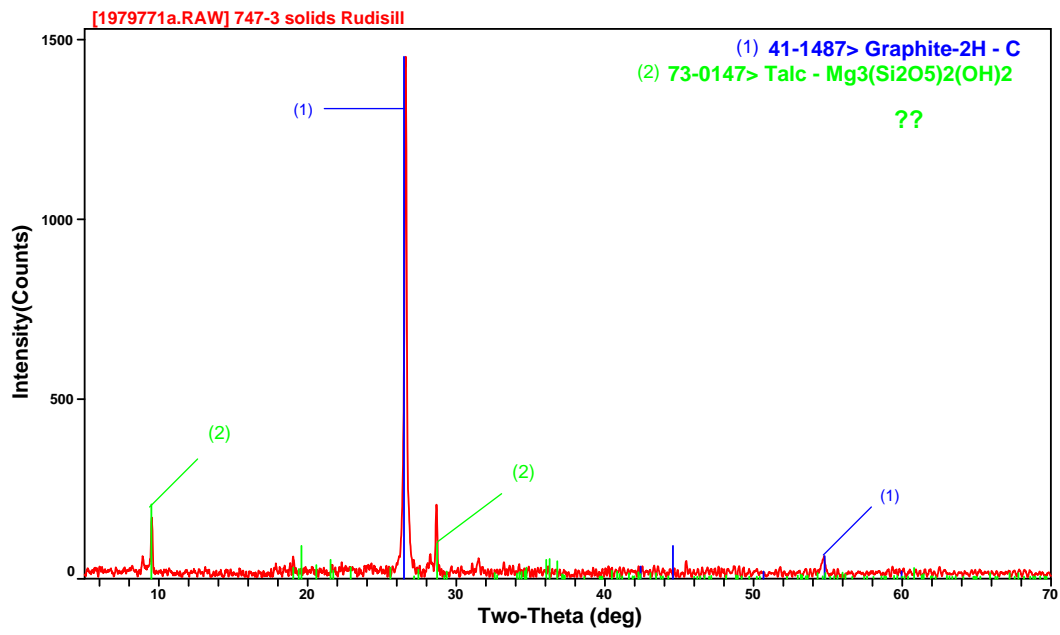
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Figure 6 Dissolution of HEU from the INEEL



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Figure 7 X-ray Diffraction Spectrum of Undissolved Solids



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Appendix A Uranium Analyses from Timed Dissolution Experiments

The U analyses for the samples generated during the dissolution experiments in which 200 μL aliquots were periodically removed from the dissolving solution are presented in Table A.1. The concentrations were corrected for the 0.2 mL to 2.2 mL dilution.

Table A.1 U Analysis for Dissolver Samples

Dissolution Time (hr)	Expt. 746-2 U Conc. (g/L)	Expt. 747-2 U Conc. (g/L)	Dissolution Time (hr)	Expt. 747-3 U Conc. (g/L)
0	0	0	0	0
0.25	90.70	86.63	0.5	123
0.50	89.94	108.67	1.0	134
0.75	73.70	65.93	1.5	133
1.00	68.85	114.52	2.0	142
1.25	97.89	122.61	2.5	129
1.50	98.47	132.12	3.0	123
1.75	121.66	121.37	3.5	128
2.00	112.57	120.99	4.0	129

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Appendix B Correction of U Concentrations for Changes in Volume

The U concentration for each of the samples must be corrected for small changes in volume which occurred due to sample removal and evaporation losses from the beaker. A small correction must also be made for the dissolved U removed in samples prior to completing the experiment. The sample volume was held constant at 200 μ L during each experiment. The evaporation rate was estimated from the initial and final dissolving solution volumes and the number of samples removed. The calculations are summarized in Table B.1.

Table B.1 Evaporation Rate During U Dissolution Experiments

Expt. No.	Initial Soln. Volume (mL)	Final Soln. Volume (mL)	Total Sample Volume (mL)	Evaporated Volume (mL)	Evaporation Rate (mL/hr)
746-2	17.0	11.9	1.6	3.7	1.9
747-2	17.0	12.0	1.6	3.6	1.8
747-3	17.0	14.4	1.6	1.2	0.3

The calculations in Table B.1 assume the evaporation rate was constant during each dissolving experiment and that no other losses of solution occurred. The estimated volumes of solution in the dissolver prior to the removal of each sample are given in Table B.2.

Table B.2 Estimated Dissolver Volume Prior to Sample Removal

Sample Time (h)	Expt. 746-2 Dissolver Volume (mL)	Expt. 747-2 Dissolver Volume (mL)	Sample Time (h)	Expt. 747-3 Dissolver Volume (mL)
0	17.0	17.0	0	17.0
0.25	16.5	16.6	0.5	16.9
0.50	15.9	15.9	1.0	16.5
0.75	15.2	15.3	1.5	16.2
1.00	14.6	14.6	2.0	15.8
1.25	13.9	14.0	2.5	15.5
1.50	13.2	13.3	3.0	15.1
1.75	12.6	12.7	3.5	14.8
2.00	11.9	12.0	4.0	14.4

The corrected U concentrations can now be calculated by adjusting for the change in volume and accounting for the small amount of material removed from the dissolving solution in each sample. The generalized expression used to calculate the corrected concentration at sample time t ($C_{\text{corrected}}$) is given as Equation (B.1),

$$C_{t\text{corrected}} = \frac{C_t V_t + V_s \sum_{i=1}^{t-1} C_i}{V_0} \quad (\text{B.1})$$

where C_t and C_i are the measured concentrations at specific samples times (see Table A.1) and V_t , V_0 , and V_s are the estimated volume at time t (see Table B.2), the initial volume (17.0 mL), and the sample volume (0.2 mL), respectively. The corrected concentrations for each experiment are given in Table B.3.

Table B.3 Corrected U Concentrations for Dissolving Experiments

Dissolution Time	Expt. 746-2 Corrected U Conc.	Expt. 747-2 Corrected U Conc.	Dissolution Time	Expt. 747-3 Corrected U Conc.
(h)	(g/L)	(g/L)	(h)	(g/L)
0	0	0	0	0
0.25	88.2	84.3	0.5	122
0.50	85.1	103	1.0	132
0.75	68.1	61.4	1.5	129
1.00	61.9	101	2.0	136
1.25	83.8	105	2.5	123
1.50	81.6	109	3.0	117
1.75	96.0	97.7	3.5	120
2.00	86.3	94.2	4.0	120

Appendix C Elemental Analyses for HEU Dissolution Experiments

The elemental analyses for solutions generated during offgas characterization (746-1 and 747-1) and the timed dissolution experiments (746-3 and 747-4) are presented in Table C.1. The concentrations were corrected for the 1 mL to 10 mL dilution. The concentrations measured (by ICP-ES) for U are presented for information only. The values measured by ICP-MS in Table 3 are considered more reliable. Past experience has shown that U concentrations measured by ICP-ES can be biased as much as 10-20% low compared to other methods of analysis.

Table C.1 Elemental Analysis for HEU Dissolving Solutions

Element	746-1 Conc. (mg/L)	747-1 Conc. (mg/L)	746-3 Conc. (mg/L)	747-4 Conc. (mg/L)
Ag	7.23	4.28	28.1	27.7
Al	312	189	438	429
B	<5.60	<5.60	<16.2	<16.2
Ba	<3.80	<3.80	2.30	2.16
Be	0.318	0.179	NM	NM
Ca	9.58	<4.60	6.12	6.07
Cd	<0.840	<0.840	<0.200	<0.200
Ce	7.56	<5.40	43.5	42.6
Cr	3.35	1.98	2.96	2.46
Cu	27.1	9.47	6.60	6.13
Fe	45.6	28.5	68.2	65.0
Gd	<4.68	<4.68	20.9	20.7
K	<188	<188	<95.2	<95.2
La	<1.44	<1.44	7.82	7.58
Li	<8.60	<8.60	2.77	2.61
Mg	2.35	1.10	0.638	<0.620
Mn	1.93	1.11	2.57	2.41
Mo	<10.6	<10.6	9.09	8.63
Na	29.2	17.1	46.3	45.7
Ni	3.86	<2.70	5.31	4.92
P	<13.8	<13.8	7.59	6.36
Pb	<6.38	<6.38	13.6	11.7
S	<27.4	<27.4	68.9	59.5
Sb	<75.6	<75.6	10.9	10.9
Si	8.02	4.51	13.4	11.4
Sn	<9.00	<9.00	11.9	11.3
Sr	4.01	1.88	7.20	6.96
Ti	1.81	<1.54	5.2	5.03
U	3930	2420	6330	6160
V	<1.20	<1.20	2.84	2.77
Zn	16.4	2.10	0.867	0.948
Zr	NM	NM	28.4	27.3

NM – Not Measured

The mass of each element detected during the analysis was calculated from the product of the concentration and the volume of the dissolving solution (see Table 3). The calculated masses are given in Table C.2.

Table C.2 Mass of Elements in HEU Dissolving Solutions

Element	746-1	747-1	746-3	747-4
	Mass	Mass	Mass	Mass
	(mg)	(mg)	(mg)	(mg)
Ag	2.0	1.9	4.8	5.0
Al	154.2	147.6	120.7	124.5
B	ND	ND	ND	ND
Ba	ND	ND	0.4	0.4
Be	0.2	0.2	NM	NM
Ca	3.5	ND	1.4	1.4
Cd	ND	ND	ND	ND
Ce	2.3	ND	8.2	8.4
Cr	1.3	1.2	0.7	0.6
Cu	8.9	4.9	1.3	1.3
Fe	17.1	16.8	15.6	15.6
Gd	ND	ND	3.9	4.0
K	ND	ND	ND	ND
La	ND	ND	1.5	1.5
Li	ND	ND	1.0	0.9
Mg	1.0	0.8	0.2	ND
Mn	0.7	0.6	0.5	0.5
Mo	ND	ND	2.2	2.2
Na	10.3	9.5	10.0	10.3
Ni	1.3	ND	1.1	1.1
P	ND	ND	2.8	2.4
Pb	ND	ND	2.3	2.1
S	ND	ND	39.2	35.6
Sb	ND	ND	2.1	2.2
Si	4.5	4.0	4.6	4.1
Sn	ND	ND	2.4	2.4
Sr	1.2	0.9	1.4	1.4
Ti	0.8	ND	1.4	1.4
V	ND	ND	0.8	0.8
Zn	5.3	1.1	0.2	0.2
Zr	NM	NM	4.5	4.6

ND – Not Detected

NM – Not Measured

The elemental masses presented in Table C.2 were converted to an oxide basis assuming the impurities were present in the HEU as oxides. A small amount of sulfur was detected during the analysis of the dissolving solutions from Experiments 746-3 and 746-4. The sulfur was assumed

to be present in the HEU as sulfate and was accounted for as $\text{Al}_2(\text{SO}_4)_3$. The resulting oxide and sulfate masses are given in Table C.3.

Table C.3 Mass of Oxide Impurities in HEU from the INEEL

Oxide	746-1 Mass (mg)	747-1 Mass (mg)	746-3 Mass (mg)	747-4 Mass (mg)
Ag_2O	2.0	1.9	4.8	5.0
Al_2O_3	154.2	147.6	120.7	124.5
B_2O_3	ND	ND	ND	ND
BaO	ND	ND	0.4	0.4
BeO	0.2	0.2	NM	NM
CaO	3.5	ND	1.4	1.4
CdO	ND	ND	ND	ND
Ce_2O_3	2.3	ND	8.2	8.4
Cr_2O_3	1.3	1.2	0.7	0.6
CuO	8.9	4.9	1.3	1.3
Fe_2O_3	17.1	16.8	15.6	15.6
Gd_2O_3	ND	ND	3.9	4.0
K_2O	ND	ND	ND	ND
La_2O_3	ND	ND	1.5	1.5
Li_2O	ND	ND	1.0	0.9
MgO	1.0	0.8	0.2	ND
MnO	0.7	0.6	0.5	0.5
MoO_3	ND	ND	2.2	2.2
Na_2O	10.3	9.5	10.0	10.3
NiO	1.3	ND	1.1	1.1
P_2O_5	ND	ND	2.8	2.4
PbO	ND	ND	2.3	2.1
$\text{Al}_2(\text{SO}_4)_3$	ND	ND	39.2	35.6
Sb_2O_3	ND	ND	2.1	2.2
SiO_2	4.5	4.0	4.6	4.1
SnO_2	ND	ND	2.4	2.4
SrO	1.2	0.9	1.4	1.4
TiO_2	0.8	ND	1.4	1.4
V_2O_5	ND	ND	0.8	0.8
ZnO	5.3	1.1	0.2	0.2
ZrO_2	NM	NM	6.1	6.2
Total	214.6	189.5	236.8	236.5

ND – Not Detected

NM – Not Measured