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Uranium Metal Dissolution in the Presence of Fluoride and Boron

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REVIEWS AND APPROVALS

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SUMMARY

H-Area Operations is planning to process plutonium-contaminated (Pu-contaminated) uranium metal scrap in its efforts to de-inventory excess nuclear materials. The use of H-Canyon and HB-Line was evaluated for feasibility in meeting processing targets and requirements. SRTC performed flowsheet development to support the decision about how and where the scrap will be processed. Specifically, experimental work was performed to (1) gather reaction rate data at a range of processing conditions, (2) generate data for calculating hydrogen and total gas generation rates, (3) propose a process flowsheet, and (4) demonstrate that the proposed flowsheet does not pose a criticality hazard.

Uranium metal dissolution experiments have shown that acceptable dissolution rates can be achieved for the Pu-contaminated scrap program using either nitric acid (HNO_3) concentrations above 7M or low HNO_3 concentrations (1-4M) in the presence of fluoride and boron. At low acid concentrations in the absence of fluoride, the reaction rates are unacceptably slow for the Pu-contaminated scrap program. The observed behavior of dissolution rates as a function of acid concentration and temperature are in general agreement with what is expected based on the literature.

Gas generation tests have demonstrated that hydrogen generation is not an issue at the conditions being proposed for plant operations. At HNO_3 concentrations above 2M, the hydrogen component of the offgas is less that 0.1% by volume. The total amount of gas generation will be approximately 18.6 mL/hr per square centimeter of exposed metal surface area.

Mixing studies have shown that criticality is not a likely event in the dissolver insert either at room temperature or at 100^oC. In 2M HNO_3/0.025M potassium fluoride (KF) and 2 g/L boron (B) at room temperature, a steady gas stream is generated from the surface of uranium metal. The gas generation rate is sufficient to mix the contents of the dissolver insert. In 4M HNO_3/0.025M KF and 2 g/L boron, there is insufficient gas generation to disperse the dissolved uranium. Instead of mixing, the denser uranium solution drops down out of the dissolver insert and away from the metal being dissolved. Variations in acid concentration away from 2M HNO_3 should not be a problem since dissolution in both 1M or 3M HNO_3 (with KF and boron) at room temperature produces gas generation comparable to that of 2M HNO_3. When the temperature is raised to 100^oC, the gas generation at 1-4M HNO_3 in 0.025M KF and 2 g/L boron exceeds that of 2M HNO_3 at room temperature, and thus will provide excellent mixing in the dissolver insert.

Based on reactions at room temperature and boiling, and the rates of reaction at 100^oC, SRTC recommends the use of 2M HNO_3/0.025M KF and 2 g/L boron at boiling in H-Canyon to process the Pu-contaminated scrap material.

INTRODUCTION

H-Area Operations is planning to process plutonium-contaminated (Pu-contaminated) uranium metal scrap in its efforts to de-inventory excess nuclear materials. The use of H-Canyon and HB-Line was evaluated for feasibility in meeting processing targets and requirements. The Actinide Technology Section of the Savannah River Technology Center (SRTC) performed flowsheet development to support the decision about how and where the scrap will be processed.

Experimental work was performed with a piece of uranium sheet. The study had four primary objectives. First, gather reaction rate data at a range of processing conditions to compare against reaction rate data reported in earlier studies and recommend a flowsheet for H-Canyon and/or for HB-Line. Second, develop new data for calculating hydrogen and total generation rates during uranium metal dissolution. Third, the tests intend to provide data to help demonstrate that the proposed flowsheet does not pose a criticality hazard.   Last, use the data to recommend a process flowsheet.

EXPERIMENTAL

The experimental program for the Pu-contaminated scrap campaign involved three basic types of experiments. The first type was the collection of general dissolution rate data as a function of temperature and solution concentrations. The second type of test was for gas generation designed to measure offgas volume and concentration as a function of solution concentrations. The third set determined if sufficient mixing occurs during dissolution to prevent the creation of conditions that could lead to a criticality event. All tests were performed with small pieces of enriched uranium metal all cut from a larger sheet of metal. The sheet has a uniform thickness.

Dissolution Rate Measurements

Initial reaction rates were measured at six process conditions: 2M nitric acid (HNO_3), 4M HNO_3, 7M HNO_3, 10M HNO_3, 2M HNO_3/2M $NaNO_3$, and 4M HNO_3/3M sodium nitrate ($NaNO_3$). Subsequent studies evaluated reaction rates for 2M HNO_3 and 4M HNO_3 in the presence of 2 g/L boron and 0.01-0.1M potassium fluoride (KF).   Several temperatures were studied for most of the solutions.

Dissolution rates were measured as follows. A small piece of uranium metal plate was cut from a larger piece. The small piece was then pickled in 10M HNO_3 at room temperature for 3-4 minutes to remove the oxide coating; initial pickling typically removed about 5% of the weight as oxide. The physical dimensions (width, length, thickness, mass) of the sample were then measured. A balance was used to measure weight; calipers were used to measure width, length, and thickness. It is important to note that the balance in the glovebox measures only to 0.001 grams. Therefore, the uncertainty on small weight changes can be quite large.

Next, a beaker was filled with a known amount of dissolver solution and placed on a hot plate/stirrer. The beaker also contained a sample holder to allow solution access to both sides of the sample without interfering with the stirring (see Figure 1). The solution was heated to a set temperature while the contents were stirred. When at temperature, a pickled sample was placed in solution for a measured amount of time. At the end of the test, the metal sample was removed, rinsed with water, dried, and weighed. Reaction rate was determined as weight loss per unit surface area per unit time.

Gas Generation Tests

Tests were performed to measure both the generation rates and composition of gases generated during the dissolution of uranium metal at different acid concentrations. Of particular interest is the amount of hydrogen gas generated per mass of metal dissolved. Conditions tested include 10M HNO_3, 7M HNO_3 and 4M HNO_3 without boron or fluoride; in presence of 2 g/L boron and 0.025M KF, 4M HNO_3, 2M HNO_3, and 1M HNO_3 solutions were tested.

Figure 1. Reaction Rate Setup

A system was set up as shown in Figure 2. The system was a sealed glass vessel designed to prevent the introduction or loss of gas. The vessel was filled with 350 mL of liquid to fill the majority of the 400 mL of space in the system. The liquid was heated to 100°C, the dissolution temperature selected for these tests. Once at temperature, the head space and lines of the system were purged with an inert gas. For 10M HNO_3 and 7M HNO_3, nitrogen was used to purge the system; CO_2 was used for the other four test conditions to avoid interference with nitrogen analyses when dissolving at lower acid concentrations.

After the system had been purged, a pickled and weighed uranium metal sample was added to the vessel, and the vessel was sealed. The sample sits on the bottom of the vessel. As gases are generated, they were collected in a gas-sample bag fitted with a valve and sample septum. After the metal sample had dissolved and gas generation had ceased, 20 mL of gas sample was collected in a syringe and the residual gas volume was measured using displacement of water.

Figure 2. Gas Generation Setup

It should be noted that the first gas generation test (10M HNO$_3$) was performed with an inverted burette to capture the gas and measure its volume. However, it was found that the water in the burette was absorbing the nitrogen dioxide (NO$_2$) from the gas phase faster than anticipated. As a result, the gas volume could not be measured. Nonetheless, a gas sample could still be obtained from the dissolution vessel. Also, the gas generation test at 1M HNO$_3$/ 0.025M KF and 2 g/L boron was initiated at room temperature to observe the room temperature gas generation and mixing in support of the mixing studies discussed below.

Mixing Studies

Another system was set up to observe the mixing that occurs during dissolution of uranium metal in a simulated dissolver insert at room temperature. No external mixing was provided so that system mixing was solely a function of gas generation due to reaction. The tests aim to determine whether dissolved uranium concentrated in a stagnant layer around the piece that was dissolving, hence creating a criticality concern.

A picture of the system used for the mixing studies is provided in Figure 3. The outer tube (LEFT) represents the dissolver that will contain the bulk dissolver solution. The simulated dissolver dissolver insert is shown CENTER and RIGHT. The simulated dissolver insert contains a perforated plate up from the bottom of the dissolver insert, similar to the actual dissolver insert, to allow liquid to access the sample from above and

Figure 3. Mixing Test Assembly

below. The sample will sit on the perforated plate as a half circle (RIGHT). The simulated tube also contain holes above the sample to allow solution to flow between the dissolver insert and bulk solution in a manner comparable to the actual dissolver insert.

Three tests were performed in the mixing test assembly – 2M HNO_3, 3M HNO_3, and 4M HNO_3, all in the presence of 2 g/L boron and 0.025M KF. The system was charged with a pickled, weighed sample of uranium metal. The piece was bent to form a 180° arc similar to Figure 3. Next, 500 mL of liquid was added to the system so that the liquid level was above the level of the holes. Observations were then made of gas generation and uranium partitioning in the system as a function of time. Pictures and videos of the tests were taken for additional studies of the test results.

The first test was performed with 4M HNO_3 and ran for 22 hours. The second test was run in 2M HNO_3 and operated for 5.5 hours. After 3.5 hours in the 2M HNO_3 test, a second metal sample was introduced to develop a better understanding of the reaction and mixing characteristics. The test with 3M HNO_3 was an abbreviated test (3.25 hours) that was aimed at only observing the gas generation characteristics for comparison with the first two tests. The 3M HNO_3 solution was prepared from 50:50 mixture of used 2M and 4M HNO_3 solutions used in the first two tests. In addition to the results obtained from the above mixing studies, other observations of mixing during other studies were obtained, as appropriate.

RESULTS

Dissolution Rate Measurements

The first set of tests focused on using only HNO_3 at 100-105°C. The data are contained in Table 1.   A general increase of dissolution rate with increasing acid concentration is observed. Also, the two data sets at 4M total nitrate and the two sets at 7M total nitrate show good agreement even though the acidity varies within the data sets.

Table 1. Measured Dissolution Rates in Nitric Acid

Rate (mg/min-cm^2) at Temperature (^{o}C)				
Solution	**20-25°C**	**50°C**	**60°C**	**80°C**	**100°C**
2M HNO_3	---	---	nd*	0.007	0.051
nd = not detected					
Rate (mg/min-cm^2) at Temperature (^{o}C)				
Solution	**20-25°C**	**50°C**	**65°C**	**85°C**	**105°C**
2M HNO_3/2M $NaNO_3$	---	---	---	---	0.254
4M HNO_3	---	---	0.003	0.041	0.309
4M HNO_3/3M $NaNO_3$	---	---	---	---	1.258
7M HNO_3	0.005	---	0.074	0.841	1.285
10M HNO_3	---	---	1.637	3.496	4.057

During the tests with 2M and 4M HNO_3, it was observed that the gas generation would start and stop throughout the test. Closer inspection of the samples indicated that the samples had a dull surface to them. Because it was speculated that there was an oxide

coating on the samples even in the acid, additional experiments were performed with varying amounts of KF and boron (2 g/L boron added as boric acid). Although there is an initial oxide coating on the sample from exposure to air, empirical data suggests that a coating persists (or reforms) in solution at low KF concentration.

The data are listed in Table 2 to show the effect of varying KF concentrations. Except where stated, all solutions in Table 2 included boron. After boron was added, an increased shine on the surface of the samples was observed with increasing KF concentration. This shine was observed when the samples were being weighed after dissolution. A sample dissolved in 2M HNO_3/0.1M KF is shown in Figure 4.

Figure 4. Stripped Uranium Metal

Table 2. Measured Dissolution Rates in Nitric Acid with Fluoride and Boron

	Rate (mg/min-cm^2) at Temperature (^{o}C)				
Solution	**20-25°C**	**50°C**	**60°C**	**80°C**	**100°C**
2M HNO_3 (no boron)	---	---	nd*	0.007	0.051
2M HNO_3/0.01M KF	0.099	0.308	---	---	1.066
2M HNO_3/0.025M KF	0.137	0.54	---	---	2.348
2M HNO_3/0.05M KF	---	---	---	---	6.480
2M HNO_3/0.1M KF	---	---	---	---	12.574
2M HNO_3/0.1M KF (no boron)	0.213	---	---	---	18.491
	nd = not detected				
	Rate (mg/min-cm^2) at Temperature (^{o}C)				
Solution	**20-25°C**	**50°C**	**65°C**	**85°C**	**105°C**
4M HNO_3 (no boron)	---	---	0.003	0.041	0.309
4M HNO_3/0.01M KF	0.097	0.293	---	---	1.307
4M HNO_3/0.025M KF	0.097	0.37	---	---	3.163
4M HNO_3/0.05M KF	---	---	---	---	6.485
4M HNO_3/0.1M KF	0.541	---	---	---	20.464

For one test in 2M HNO_3/0.025M KF and 2 g/L boron, the sample was dissolved at room temperature without being pickled prior to coming in contact with the acid. No stirring was provided. The dissolution rate at room temperature was 0.323 mg/min-sq.cm over 20 minutes. When compared to the pickled rate of about 0.137 mg/min-sq.cm, the data indicates that the oxide coating dissolves faster than the base metal. Also, after the 20 minutes of dissolution, the sample no longer had a visible oxide coating; it had a dull silver color instead of charcoal gray.

Gas Generation Tests

The rate of dissolution for each of the gas generation tests reflected what was observed in the dissolution rate measurement experiments. The gas volume measurements are made with the gas at ambient temperature and pressure. In each case, a significant amount of

orange fumes was observed in the gas sample bag, indicating the presence of NO_2. The raw data are listed in Table 3. Based on the presence of oxygen, it appears as though some air has leaked into the 7M HNO_3 sample and may have affected the $NO:NO_2$ ratio. All data listed as "<0.1%" in Tables 3 and 4 are below the detection limit.

When the data are normalized to omit the presence of the purge gas and list the "Undefined" as NO_2, the data in Table 4 are obtained. As will be discussed later, there is reason to expect that some of the "Undefined" gas of 1M HNO_3/0.025M KF also contains a significant fraction of N_2O. The total gas generated (in mL/g U) is not affected by the presence of the purge gas because the total displacement of gas into the sample bag is solely a function of the amount of gas generated by the reaction.

Table 3. Gas Generation Data

Solution	Gas (mL/g U)	H_2 (%)	N_2 (%)	O_2 (%)	CO_2 (%)	NO (%)	Undef (%)*
1M HNO_3/0.025M KF and 2 g/L boron	131	4.4	<0.1	<0.1	18	3.2	74
2M HNO_3/0.025M KF and 2 g/L boron	64	0.07	<0.1	<0.1	13	77	10
4M HNO_3/0.025M KF and 2 g/L boron	132	<0.1	<0.1	<0.1	2.1	83	15
4M HNO_3	103	<0.1	<0.1	<0.1	30	32	38
7M HNO_3	111	<0.1	80	4.1	<0.1	0.7	15
10M HNO_3	n/a	<0.1	71	<0.1	<0.1	8.1	21

 * Undefined component is likely NO_2 and/or N_2O

Table 4. Normalized Gas Generation Data

Solution	Gas (mL/g U)	H2 (%)	O2 (%)	NO (%)	NO2 (%)
1M HNO3/0.025M KF	131	5.4	<0.1	3.9	90.7*
2M HNO3/0.025M KF	64	0.08	<0.1	88.5	11.5
4M HNO3/0.025M KF	132	<0.1	<0.1	84.8	15.2
4M HNO3	103	<0.1	<0.1	45.7	54.3
7M HNO3	111	<0.1	<0.1	4.4	95.6
10M HNO3	n/a	<0.1	<0.1	27.9	72.1

* May contain high fraction of N_2O

Mixing Studies

The two primary mixing studies at room temperature (2M and 4M HNO_3 with KF and boron) yielded very different results, particularly in comparison with their behavior at $100^{o}C$ (in gas generation and dissolution rate tests). At $100^{o}C$, both conditions create an abundance of gas that creates mixing within the vessel. A picture of metal dissolution in 4M HNO_3/0.025M KF and 2 g/L boron is shown as Figure 5.

When the mixing study was performed with 2M HNO_3/0.025M KF and 2 g/L boron at $25^{o}C$, the behavior was consistent with what is observed at $100^{o}C$ except that the gas

generation rate is slower. After the sample comes in contact with the acid, it is only a few minutes before very tiny gas bubbles begin to effervesce from the metal surface. Because of the presence of fluoride, the uranium first forms a relatively stable blue U(IV) complex.[1] Over time in HNO_3, or in the presence of heat, the U(IV) is converted to the distinctive yellow U(VI) form as seen in Figure 5.

The generation of gas disperses the dissolving uranium throughout the insert and outer vessel. After about 90 minutes, the gas generation begins to stop and start. On a few occasions, the vessel was bumped and almost immediately the gas generation was renewed. Late into the test, a second piece of uranium was added. It was observed that the two samples tended to react and stop reacting at essentially the same time. An estimated dissolution rate for the initial sample was calculated at 0.108 mg/min-cm^2 across the 5.5-hour test. Considering the differences between the mixing test and the rate measurement tests, the rate shows good agreement with the value of Table 2.
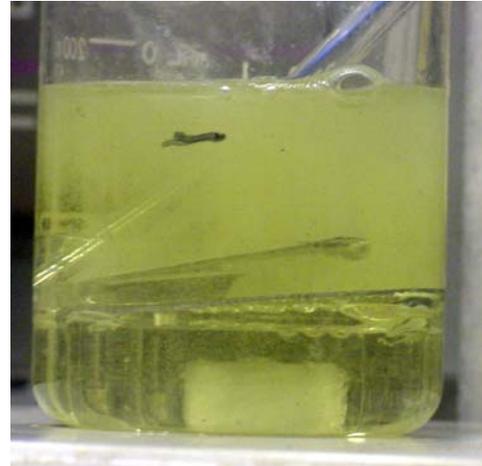
Figure 5. Dissolution in 4M HNO_3
0.025M KF/ 2 g/L B at 100°C

Pictures of the test are included as Attachment 1. The pictures at 5, 170, and 240 minutes clearly depict the abundance of fine gas bubbles being generated from the metal surface and filling both the dissolver insert and outer vessel. The pictures at 75 and 170 minutes show that a layer of dissolved uranium does not form as a stagnant layer near the metal surface. At most, the presence of blue U(IV) is slightly more concentrated at the bottom of the vessel than it is at the top.

When the mixing study was performed with 4M HNO_3/0.025M KF and 2 g/L boron at room temperature, the behavior exhibits no resemblance to what is observed in the tests at 100°C. After the sample comes in contact with the acid, only a few tiny bubbles are ever observed at one time. The size of the bubbles is comparable to the 2M HNO_3/ 0.025M KF test, but the quantity is drastically reduced such that they are barely visible to the naked eye. As the test progresses, the gas generation remains barely visible.

As with the previous test, the presence of fluoride causes the uranium to form an initial blue U(IV) complex. Because of the scarcity of bubbles, the system is unmixed and the denser uranium solution sinks. The uranium solution leaves the dissolver

Figure 6. Dissolution in 3M HNO_3
0.025M KF/ 2 g/L B at 25°C

insert and is distributed fairly-evenly in the bottom section of the outer vessel. In spite of the absence of gas generation, an estimated dissolution rate for the sample was calculated at 0.135 mg/min-cm^2 across the 22-hour test. Considering the differences between the mixing test and the rate measurement tests, the value shows reasonable agreement with the value of Table 2.

Pictures of the test are included as Attachment 2. All six pictures show the absence of mixing caused by gas generation. The last five pictures show the gradual increase in uranium concentration in the bottom of the test unit with the uranium level always remaining below the level of the uranium metal sample. At the same time, the pictures clearly indicate that no layer of dissolved uranium forms around the metal sample. The picture at 1165 minutes depicts the gradual conversion of blue U(IV) to a mixture of U(IV) and yellow uranyl (U(VI)) nitrate. The solution eventually changes completely to yellow U(VI).

The brief test using 3M HNO$_3$/0.025M KF and 2 g/L boron shows much resemblance to the behavior of the 2M HNO$_3$ test. Gas generation occurs as an effervescent stream of tiny bubbles that mix the contents of the vessel. The gas generation rate is muted because the solution was a mixture of solution used from the previous two mixing tests and probably has a reduced level of uncomplexed fluoride. A picture of the gas generation is shown as Figure 6. It should also be noted that the gas generation test at 1M HNO$_3$/0.025M KF and 2 g/L boron was initiated at room temperature in order to observe the room temperature gas generation. Its gas generation characteristics at room temperature are consistent with both the 2M and 3M tests.

DISCUSSION

Much of the background for this discussion is drawn from an earlier document discussing the feasibility of dissolving this material in either H-Canyon or HB-Line.[2]

Chemistry Fundamentals: Several different acid-dependent chemical reactions can be written for the dissolution of uranium metal in HNO$_3$. Plant experience indicates that the dissolution reaction is best represented by:[3]

$$U + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2NO + 2H_2O \qquad (1)$$

It has been proposed that the dissolution of aluminum in HNO$_3$ might provide insight into the dissolution chemistry of uranium.[4]

$$Al + 6HNO_3 \rightarrow Al(NO_3)_3 + 3NO_2 + 3H_2O \qquad (2)$$

[HNO$_3$]
Increase

$$Al + 4HNO_3 \rightarrow Al(NO_3)_3 + NO + 2H_2O \qquad (3)$$
$$8Al + 30HNO_3 \rightarrow 8Al(NO_3)_3 + 3N_2O + 15H_2O \qquad (4)$$
$$10Al + 36HNO_3 \rightarrow 10Al(NO_3)_3 + 3N_2 + 18H_2O \qquad (5)$$
$$2Al + 6HNO_3 \rightarrow 2Al(NO_3)_3 + 3H_2 \qquad (6)$$
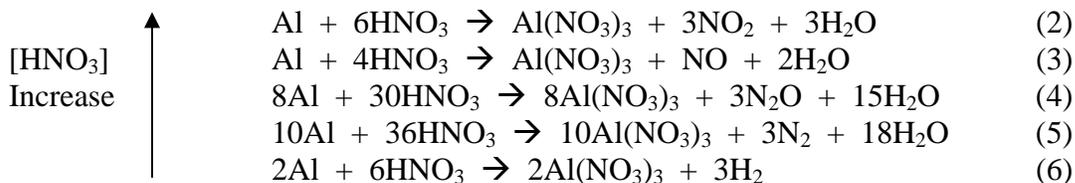
All of the reactions occur simultaneously during aluminum metal dissolution. However, at higher HNO_3 concentrations, the dissolution shifts towards Eq. (2). At lower acid concentrations, the dissolution shifts towards Eq. (6). Experience suggests that Eq. (3) is the dominant reaction in 6-8M nitric acid, which is analogous to Eq. (1).

Offgas Composition and Hydrogen Generation: It is known that the reaction of uranium metal with HNO_3 has the potential to form hydrogen gas. It is also known that the presence of high concentrations of HNO_3 during the reaction sets up competing reactions that inhibit the formation of hydrogen gas. Lower hydrogen generation rates as a function of higher HNO_3 concentrations has been observed for uranium metal dissolution and other analogous systems, which is in agreement with the dissolution of aluminum as a function of HNO_3 concentration.

The literature shows that in 55% HNO_3 (11.6M) the percent hydrogen generated in the offgas is 0.01% by volume.[5] Similar behavior was observed in the cathode compartment of equipment employing electrochemical dissolution techniques. In 2M HNO_3, nominal hydrogen generation was 2-3% by volume. In 4M HNO_3, the hydrogen rate drops to nominally 0.4%. In 6M HNO_3 and higher, the hydrogen generation rate drops to less than 0.1% by volume.[6] As a result, literature data show that hydrogen evolution is very low at concentrations above 1M or 2M HNO_3.[4] Conversely, below 2M HNO_3, hydrogen generation rates may exceed the lower flammability limit (LFL) of 4%.[6] The best explanation of this behavior is given with respect to the chemical reaction for aluminum dissolution in HNO_3 listed above. At lower acid concentrations, the dissolution shifts towards Eq.(6) where hydrogen generation occurs.

The data in Table 4 show reasonable agreement with the parallel chemistry of aluminum and earlier data with uranium. As acid concentration decreases, dissolution of uranium shifts towards Eq. (6), and H_2 and nitrogen oxide (NO) concentrations increase. Hydrogen and NO are products of a more reductive environment when compared to NO_2 (Eq. 2). The only exception to the trend is at 7M HNO_3. Because of the presence of oxygen in the sample, it is likely that air in the sample reacted with NO since NO reacts with air to form NO_2.[5]

Conversely, as acid concentration increases, dissolution shifts towards Eq. (2), and NO_2 concentration increases since NO_2 is the product of a more oxidative system. The only exception is at 1M HNO_3. The difference is probably due to the definition of unknowns in Table 3 as purely NO_2. As Eq. (4) shows, a decrease in acid might also produce an increase in N_2O. However, N_2O is unidentifiable by the gas chromatography method used and would be grouped with NO_2. One flaw in the gas data of Table 4 relative to Eqs. (2)-(6) is the absence of nitrogen in any of the lower acidity samples. Yet this statement is predicated on the assumption that uranium dissolution chemistry will perfectly mirror that of aluminum. That may be a faulty assumption. Other possibilities are that the acid concentration range for Eq. (5) is very narrow and does not apply to the conditions tested, or not enough N_2 generation occurs to measure N_2 reliably.

It is interesting to note the significant difference between the gas composition in 4M HNO_3 compared to 4M HNO_3/0.025M KF and 2 g/L boron. Based on the presence of U(IV) in the mixing tests (blue color observed in Attachments 1 and 2) instead of the typical yellow U(IV) (see Figure 5), there seems to be a shift from more oxidative conditions (4M HNO_3) to more reductive ones (4M HNO_3/0.025 KF and 2 g/L boron). It is possible that the shift is caused by participation of KF in the reaction. The more reductive environment translates into reduced NO_2 formation.

What is most important from an operations perspective is the fact that hydrogen generation in 2M HNO_3 and higher HNO_3 concentrations is well below the LFL of 4% for hydrogen. Consequently, as long as acid concentrations are maintained above 1.5M HNO_3, the LFL for H_2 will not be exceeded even in the absence of a purge gas stream. Even in 1.0M HNO_3/0.025M KF and 2 g/L boron, the hydrogen concentration is only marginally above the LFL such that the operation of the vessel sparge systems will sufficiently dilute the reaction gases to below 4 volume percent.

Calculations indicate that if 25 kg of scrap is dissolved in a 7500-liter batch in H-Canyon, reactions will reduce the acid concentration by about 0.05M HNO_3. If carbon steel (to be used in the dissolver insert) dissolves in manner analogous to Eq. (3), calculations show that 47 kg of carbon steel could be dissolved before the HNO_3 concentration in the dissolver is reduced to 1.5M.

Gas Generation Rates: The reaction of uranium metal in nitric acid was expected to be similar to that of the Pu-Al scrub alloy that was dissolved in 4M HNO_3/0.15M calcium fluoride. The Pu-Al scrub alloy "solids dissolve readily with light, effervescent gas generation at the material surface."[7] This presumption turned out to be a reasonable assessment of reaction as can be readily seen from the pictures in Attachment 1.

The amount of gas generation was initially estimated using Equation 1 that assumes two moles of NO will be generated per mole of uranium. On a gram-of-uranium basis, assuming no absorption into the solution, the estimated gas generation ratio is 188 mL/g uranium. Table 4 shows an approximate gas generation rate of 107 mL/g uranium for dissolution in 4-7M HNO_3 and 132 mL/g uranium in 1M and 4M HNO_3/0.025M KF and 2 g/L boron. It is likely that the data for 2M HNO_3/0.025M KF and 2 g/L boron of 64 mL/g uranium represents a problem in the gas collection setup for that experiment.

Based on the observed gas generation quantities, it appears that some of the gases are being absorbed before they can be released from the test vessel. In only HNO_3, the percent NO_2 is above 50%, and below 15% for those tests with HNO_3/0.025M KF and 2 g/L boron. It is known that NO_2 can dissolve into water and other aqueous systems.[4,5] The occurrence of higher NO_2 absorption in HNO_3 in the absence of KF (hence, overall gas generation being lower) can be seen in Table 4.

When a gas generation rate of 130 mL/g uranium is multiplied by the expected dissolution rate for 2M HNO_3/0.025M KF and 2 g/L boron of 2.35 mg uranium/min-cm^2, this yields an expected gas generation rate of 0.31 mL/min-cm^2. This value is a small

amount of gas even under the worst-case conditions being considered for the processing of the uranium scrap.

Reaction Rates in Nitric Acid: Earlier researchers measured the uranium dissolution rate at different concentrations of HNO_3. At HNO_3 concentrations above 2M, the instantaneous reaction rate at boiling was stated as:

$$R = (0.0115 \text{ mg/min-cm}^2\text{-M}^3)* [NO_3^-]^3 \hspace{2cm} (7)$$

R is in mg/min-cm^2 and [NO_3^-] is the total nitrate concentration in moles per liter.[3] Above 2M HNO_3 at boiling, the literature shows the instantaneous dissolution rate to be independent of either the acid or the uranium concentration.[3,5] The reaction rates observed for these experiments are well below what the rates are estimated by Eq. (7). A comparison of measured and calculated values is contained in Table 5.

Table 5. Experimental and Calculated Dissolution Rates

Solution	Expt. Rate (mg/min-cm^2)	Calc. Rate (mg/min-cm^2)	Percent Difference
2M HNO$_3$	0.051	0.092	44.6
2M HNO$_3$/2M NaNO$_3$	0.254	0.736	65.5
4M HNO$_3$	0.309	0.736	58.0
4M HNO$_3$/3M NaNO$_3$	1.258	3.944	68.1
7M HNO$_3$	1.285	3.944	67.4
10M HNO$_3$	4.057	11.500	64.7

Although rates seem to be a function of total nitrate concentration above 2M HNO_3, the difference between all measured and calculated values is very large, typically in the 58-68% difference range. There is not enough detail in the literature to understand why the data are different, but two reasons can be speculated. The first is that in the handling of SRTC samples prior to being added to the test vessel, a thin oxide coating is able to build up on the surface of the metal which can impede the reaction at the start of the tests, and perhaps throughout the tests. It is also possible that since the sample is oriented primarily in the horizontal position (see Figure 5), the presence of gases along the bottom surface of the samples restricts solution access to the metal surface.

Effect of Fluoride and Boron: The effects of boron and fluoride on uranium metal dissolution rate were not well documented in the available literature. The only relevant understanding is analogous work performed with plutonium. To obtain acceptable dissolution rates of plutonium metal in low concentrations of HNO_3 (for H-Canyon or HB-Line), the use of fluoride is required to dissolve the oxide coating that tends to form on the metal surface. Without fluoride, the oxide coating remains at the metal surface and impedes dissolution.[7] Boron is frequently added to Savannah River Site canyon dissolvers as a component of dissolution at 2 g/L to function as a neutron poison. It has the added effect of complexing some of the available fluoride.[8]

Comparable behavior was observed with uranium metal. The data from Table 2 are plotted in Figure 7 to show the effect of fluoride. The data show that dissolution rate is limited by the presence of the oxide coating for KF concentrations between 0 and 0.05M KF. The effect of HNO_3 concentration appears negligible until there is sufficient KF (0.1M) to remove the oxide coating, especially when considering that the dissolution temperature for the 2M HNO_3 tests is only 5^oC lower than the 4M HNO_3 tests.

The addition of KF to the system accelerates the dissolution rates by removing the oxide barrier to HNO_3 dissolution. In effect, the data indicates that an oxide coating inhibits HNO_3 dissolution at lower KF concentrations. The data also suggest that the oxide coating persists or continually reforms at the material surface in the presence of 0-0.05M KF and 2 g/L boron. It is only at higher KF concentrations (>0.1M) that the oxide coating has been sufficiently removed to see an effect from HNO_3 concentration.

This behavior is consistent with both the comparative dissolution rates and empirical data showing the metal surfaces to be dull when withdrawn from solutions at lower KF concentrations and shiny when KF concentrations are higher (see Figure 4). Only samples dissolved in 0.1M KF had a level of shine that suggests the absence oxide. When a sample was not pickled to remove the oxide coating prior to rate testing, the dissolution rate increased in comparison to the rate of a pickled sample (0.323 vs. 0.137 mg/min-cm^2) because of rapid oxide dissolution. The change in rate should not be confused with an increase rate in metal dissolution, rather the quick dissolution of oxide from the sample surface, which is on the order of five weight percent. In addition, the sample surface color changed from charcoal gray to dull silver. This indicates that pickling is not required prior to dissolving samples in 2M HNO_3/0.025M KF and 2 g/L boron.

Figure 7. Effect of KF/Boron on Dissolution Rates
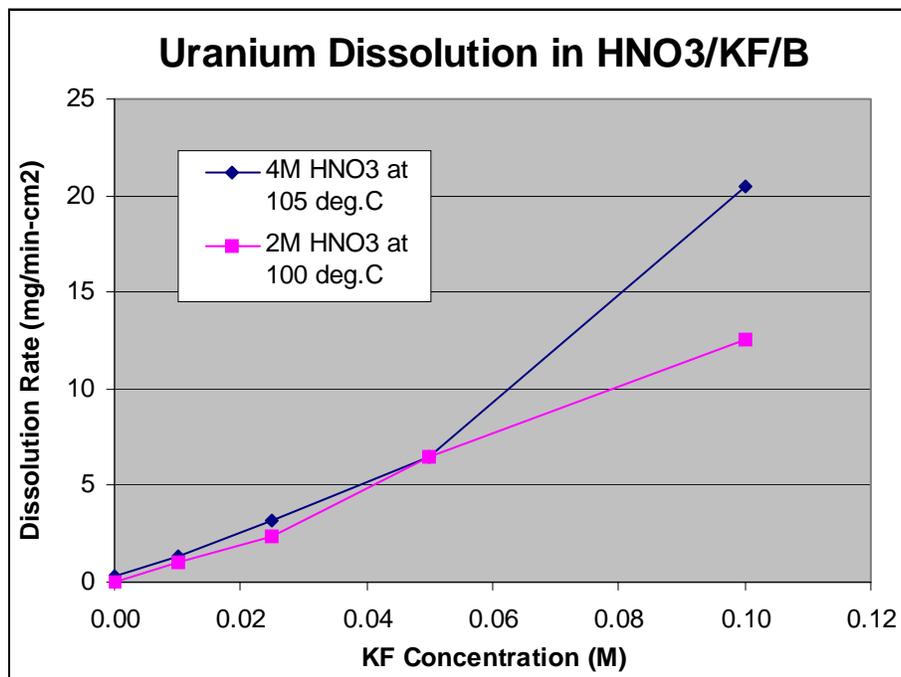
Effect of Temperature: The literature shows that increases in temperature produce increases in dissolution rate. This behavior is as expected. Treatment of the data in the literature indicates that the effect on reaction rate is essentially linear within the temperature range of interest.[3] This behavior seems questionable since an exponential type relationship is typically expected.

Two plots of the data are shown in Attachment 3 for the tests containing only HNO_3 and those with HNO_3/KF and boron. Since the rate data are plotted in a semi-log manner, linearity of the data will indicate whether or not there is an exponential type relationship with respect to temperature.   The data plots indicate a high degree of linearity and, as a result, an exponential relationship with respect to temperature consistent with what should be expected.

Of the seven data sets, the trendlines for six of the data sets yield an R^2 value of 0.97 or greater, thereby indicating a high degree of linearity. Only one data set, 10M HNO_3 (R^2 = 0.87), exhibits less linearity. The data of Reference 3 at 10.4M HNO_3 possesses a linearity of 0.93 but has a slope comparable to that of the 10M HNO_3 data. The decrease in linearity in 10M and 10.4M HNO_3 may be caused by a high gas generation rate at 105^oC, which interferes with the ability of solution to access the surface of the metal.

The data also agree with what was observed in Figure 7. In 0-0.025M KF, the reaction rate as a function of temperature is independent of whether the HNO_3 concentration is 2M or 4M. The lines for 2M or 4M HNO_3 in 0.01M KF and 2 g/L boron are essentially identical; the behavior in 0.025M KF and 2 g/L boron shows little difference between 2M and 4M HNO_3.

Proposed Chemical Reactions:

The above data in conjunction with the literature[3,4,5] make it possible to propose a series of chemical reactions at $100\text{-}105^oC$ to describe uranium metal dissolution under varying acid conditions. The reactions are proposed (not explicitly in the literature except Eqs. (10)[9] and (11)[3]) to facilitate a better understand of the system chemistry as a function of acid concentration. The reactions parallel those of Eqs.(2)-(6).

$$U \; + \; 6HNO_3 \; \rightarrow \; UO_2(NO_3)_2 \; + \; 3NO_2 \; + \; NO \; + \; 2H_2O \qquad (8)$$

$$2U \; + \; 10HNO_3 \rightarrow 2UO_2(NO_3)_2 \; + \; 3NO_2 \; + \; 3NO \; + 5H_2O \quad (9)$$

[HNO_3]
Increase

$$U + 4.5HNO_3 \rightarrow UO_2(NO_3)_2 \; + \; 1.57NO + \; 0.84NO_2 \; + \qquad (10)$$
$$0.005N_2O \; + \; 0.043N_2 \; + \; 2.25\,H_2O$$

$$U \; + \; 4HNO_3 \; \rightarrow UO_2(NO_3)_2 \; + \; 2NO \; + \; 2H_2O \qquad\qquad (11)$$

$$5U \; + \; 14HNO_3 \; \rightarrow \; 5UO_2(NO_3)_2 \; + \; 2N_2O \; + \; 7H_2 \qquad\quad (12)$$
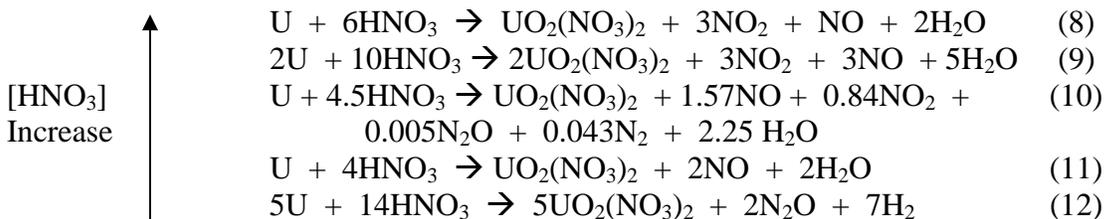
System Mixing:

The mixing study data reveal the type of mixing behavior that can be expected at room temperature or 100°C for either 2M or 4M HNO$_3$ with 0.025M KF and 2 g/L boron. At 2M HNO$_3$, dissolution at room temperature generated a visible gas stream of extremely fine bubbles. The gas stream was able to mix the liquid in the dissolver insert and prevent the formation of a uranium layer around the metal (Attachment 1). The gas generation rate for 2M HNO$_3$ at room temperature is only a fraction (~4-6% based on Table 2) of what it will be at 100°C for either 2M or 4M HNO$_3$ with KF and boron. Therefore, thorough mixing will also be present in the dissolver insert at 100°C in either 2M or 4M HNO$_3$.

In 4M HNO$_3$/0.025M KF and 2 g/L boron at room temperature, very little gas generation is observed at first and almost none is visible after about six hours. Nonetheless, uranium dissolves at a rate comparable to 2M HNO3/0.025M KF and 2 g/L boron. As the uranium dissolved, the more-dense liquid settled to the bottom of the vessel away from the sample (Attachment 2). The uranium (blue due to U(IV)) spreads evenly throughout the solution below the sample even though no mixing was present. Although this shows that the use of 4M HNO$_3$ in boron and KF does not present a criticality hazard at room temperature, it produces a less desirable condition than that of 2M HNO$_3$.

Use of an intermediate-acid case (3M HNO$_3$) and a lower-acid case (1M HNO$_3$) both showed reaction characteristics comparable to the 2M HNO$_3$ test. A steady stream of small gas bubbles provides adequate mixing in the dissolver insert at room temperature. Based on the reaction characteristics in conjunction with gas generation studies, 2M HNO$_3$ with 0.025M KF and 2 g/L boron will be recommended as the preferred solution for H-Canyon processing.

CONCLUSIONS/RECOMMENDATIONS

Uranium metal dissolution experiments have shown that acceptable dissolution rates can achieved for the Pu-contaminated scrap program using either high HNO$_3$ concentrations (>7M) or low HNO$_3$ concentrations (1-4M) in the presence of fluoride (0.025M) and boron (2 g/L). During dissolution in the presence of little or no fluoride, an oxide coating forms on the surface of the uranium metal and impedes the reaction rate. At low acid concentrations in the absence of fluoride, the reaction rates are unacceptably slow for the Pu-contaminated scrap program. Tests have shown that samples with thick oxide coatings dissolve readily in 2M HNO$_3$/0.025M KF and 2 g/L boron. The observed behavior of dissolution rates as a function of acid concentration and temperature are in general agreement with what is expected based on the literature.

Gas generation tests have demonstrated that hydrogen generation is not an issue at the conditions being proposed for plant operations. At HNO$_3$ concentrations above 2M, the hydrogen component of the offgas is less that 0.1% by volume. When the HNO$_3$ is reduced to 1M in the presence of KF and boron, the hydrogen concentration (corrected)

rises above the LFL to 5.4% by volume. Sparging and the operation of the dissolver offgas system will dilute this concentration below the LFL.

Mixing studies have shown that criticality is not a likely event in the dissolver insert either at room temperature or at $100^{o}C$. In 2M HNO_3/0.025M KF and 2 g/L boron at room temperature, a steady gas stream is generated from the surface of uranium metal. The gas generation rate is sufficient to mix the contents of the dissolver insert. In 4M HNO_3/0.025M KF and 2 g/L boron, minimal gas generation and mixing occurs. Instead of mixing the uranium, the more-dense uranium solution drops down out of the dissolver insert and away from the metal being dissolved. Variations in acid concentration away from 2M HNO_3 should not be a problem since dissolution in both 1M or 3M HNO_3 (with KF and boron) at room temperature produces gas generation comparable to that of 2M HNO_3. When the temperature is raised to $100^{o}C$, the gas generation at 1-4M HNO_3 exceeds that of 2M HNO_3 at room temperature and provides excellent mixing in the dissolver insert.

Based on reactions at room temperature and boiling, and the rates of reaction at $100^{o}C$, SRTC recommends the use of 2M HNO_3/0.025M KF and 2 g/L boron at boiling in H-Canyon to process the Pu-contaminated scrap material.

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ATTACHMENT 1. 2M HNO$_3$/0.025M KF and 2 g/L Boron Mixing Study Pictures
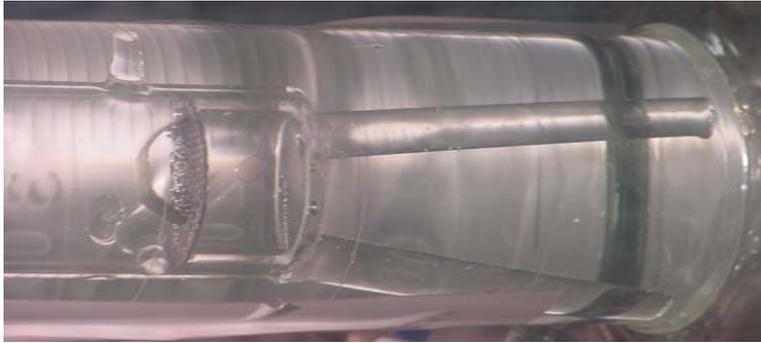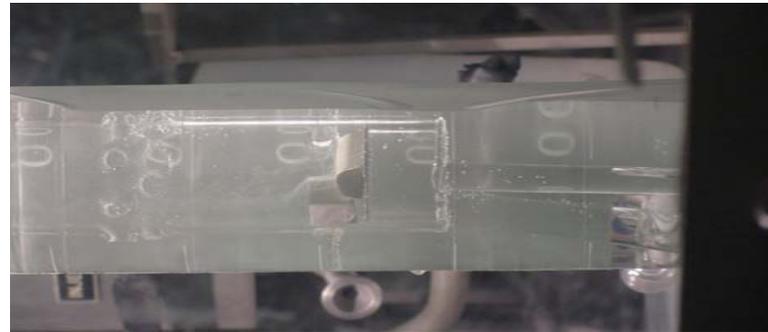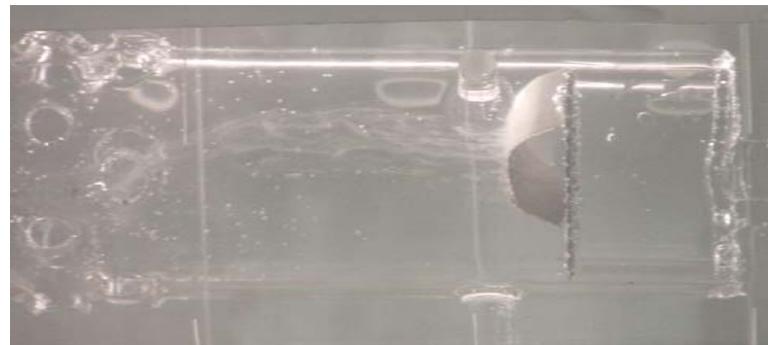
ATTACHMENT 2. 4M HNO_3/0.025M KF and 2 g/L Boron Mixing Study Pictures
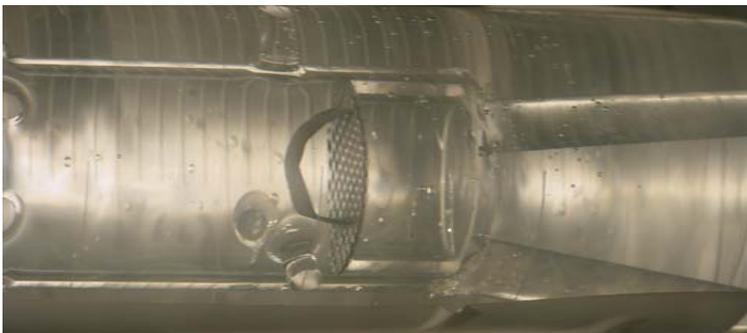
ATTACHMENT 3. Uranium Dissolution Rate Temperature Dependence