Low Temperature Dissolution Flowsheet for Pu Metal

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ABSTRACT

The Savannah River National Laboratory was requested to develop a Pu metal dissolution flowsheet at two reduced temperature ranges for implementation in the Savannah River Site H-Canyon facility. The dissolution and H_2 generation rates during Pu metal dissolution were investigated using a dissolving solution at ambient temperature (20-30 °C) and for an intermediate temperature of 50-60 °C. The Pu metal dissolution rate measured at 57 °C was approximately 20 times slower than at boiling (112 - 116 °C). The dissolution rate at ambient temperature (24 °C) was approximately 80 times slower than the dissolution rate at boiling Hydrogen concentrations were less than detectable (<0.1 vol %).

INTRODUCTION

Plutonium metal is dissolved in the H-Canyon 6.1D dissolver to prepare feed solution for PuO_2 production.(1) To prepare a dissolver charge, 3013 Pu storage containers are transferred to HB-Line where the inner containers are cut open and the contents transferred to dissolvable carbon steel cans (containing no polymeric gasket materials). The cans are then bagged out of the glovebox into dissolvable nylon bags and transferred to the Hot Crane Maintenance Area (HCMA). In the HCMA, the carbon steel cans are loaded into stainless steel charging bundles fitted with carbon steel endcaps for dissolution. Once loaded, a bundle is transferred to the 6.1D dissolver and charged to the 10-well insert. Under the current flowsheet, the dissolving solution is heated to boiling after complete charging of the dissolver until the Pu metal is dissolved.(1)

During charging of the 6.1D dissolver for the Batch 5 of Pu metal dissolution, the Savannah River Site (SRS) entered an operational pause. When deliberate operations in H Canyon resumed, the ambient-temperature solution in the dissolver was sampled and the analysis indicated that all the Pu metal had dissolved (without heating). Dissolving the Pu metal in the 6.1D dissolver at ambient conditions or at a reduced temperature has advantages. The highly oxidizing and corrosive environment from the use of boiling 10 M HNO_3 containing 0.1 M fluoride contributes to the oxidation of Pu(IV) to Pu(VI) and generates metallic impurities as a result of the dissolver corrosion. The use of less aggressive conditions (i.e., lower temperature) would minimize the amount of ferrous sulfamate required to reduce the Pu(VI) prior to anion exchange in HB-Line, reduce the amount of impurities which must be removed during anion exchange, and would extend the life of the 6.1D dissolver by reducing the corrosion rate during dissolution. However, the increased processing time from slower Pu metal dissolution rates at reduced temperatures would have to be considered.

The dissolution of Pu metal using HNO_3 solutions containing fluoride was investigated at both the Rocky Flats Environmental Technology Site (RFETS) and the SRS. However much of the testing was conducted at HNO_3 concentrations in the 3-5 M range and at elevated temperatures (80-100 °C) to limit the formation of PuO_2 and maximize the rate of dissolution.(2-5) Miner et al. performed lower temperature (23-69 °C) dissolution experiments; however, the Pu metal was dissolved using 1-5 M HNO_3 solutions containing 0.01-0.13 M hydrogen fluoride.(6) Holcomb performed dissolution experiments using both alpha and delta phase Pu metal. The alpha metal was dissolved using 3-5 M HNO_3 solutions containing fluoride ion as the catalyst; however, Al was also present in the solution at Al to fluoride molar ratios of 0, 0.5, 0.75, and 1.0. The dissolutions were performed at 90-100 °C.(7) In experiments with delta phase Pu metal, Holcomb demonstrated that a 2-3 M HNO_3 solution containing 0.1 M fluoride at 35-50 °C could be used to dissolve Pu metal in the SRS F-Canyon facility. The current H-Canyon flowsheet used to dissolve Pu metal for PuO_2 production utilizes the same dissolving solution as the desired low temperature flowsheet (10 M HNO_3, 0.1 M F, and 1.5 g/L B); but, the dissolution is performed at the boiling point of the solution (112 – 116 °C).(1)

Based on the merits of a low temperature flowsheet, SRNL was requested to perform a series of Pu metal dissolution experiments to develop and demonstrate the flowsheet for the 6.1D dissolver at temperatures below boiling. The dissolving chemistry utilized a 10 M HNO_3 solution, containing 0.1 M fluoride (as KF) and 1.5 g/L B (as boric acid) which is consistent with the dissolving solution used for previous 6.1D dissolutions.(1) The Pu metal dissolution and H_2 generation rates were measured at 20-30 °C (i.e., ambient conditions) and at an intermediate temperature (50-60 °C).

EXPERIMENTAL

The Pu metal used for the low temperature dissolution flowsheet demonstration experiments is from the same batch of material used to develop the flowsheet currently in use.(1) The samples were prepared from delta phase metal. A thin oxide coating was present on the surface. The thin sheet-like coupons were cut from larger pieces if necessary using tin snips. For each experiment, the Pu metal mass ranged between 2.5 and 3.3 g. A solution volume between 369 and 489 mL was used to target a final dissolved Pu concentration of 6.75 g/L Pu. The mass and dimensions of the metal pieces used in each of the four experiments are provided in Table 1. The dimensions of the metal pieces were measured using a micrometer. Using the measured dimensions, the calculated density of the metal pieces ranged from 13.4 to 15.1 g/cm^3.

The dissolution vessel and offgas collection system were fabricated from borosilicate glass by the SRNL Glass Shop. A photograph of the equipment is shown in Fig. 1. The dissolving vessel was made from a 500-mL round-bottom flask. Penetrations were added for a condenser, sample port, thermocouple, and N_2 purge, and the bottom was flattened slightly to facilitate heating and agitation using a hot plate/stirrer (with magnetic stir bar). The apparatus is similar to equipment previously used for Pu metal dissolutions and offgas measurements at SRNL.(1) The solution temperature was controlled using an external thermocouple monitored by the hot plate. A secondary thermometer inserted directly into the dissolving solution through a glass port was used to verify that the target temperature in solution was maintained.

To perform the Pu metal dissolution rate experiments (Pu-Diss-1 and Pu-Diss-2), the Pu metal was initially placed in a perforated glass basket. The basket was suspended in the dissolver by a glass rod held in place by a compression fitting. The compression fitting allowed adjustment of the basket height. The

Pu metal was held above the dissolving solution until the desired solution temperature was reached. Water was not circulated through the condenser during the experiments because the targeted solution temperatures were well below boiling. The dissolving solution consisted of a 10 M HNO_3 solution containing 0.1 M fluoride (from KF) and 1.5 g/L B (from boric acid) which is consistent with the dissolving solution used for the current H-Canyon dissolver flowsheet. The solution was stirred at 250 RPM using the magnetic stir bar. During dissolution rate measurements, the vessel top and basket assembly were detached to periodically remove, weigh and measure the Pu metal coupon. One milliliter solution samples were also taken using a pipette for analysis at that time. The solution samples were analyzed for ^{239}Pu and ^{241}Am by gamma pulse height analysis (GPHA). Samples of the initial and/or final dissolving solutions were also analyzed for metals by inductively-coupled plasma emission spectroscopy (ICPES), ammonium by ion chromatography (IC), and for free and total acid by titration.

The offgas generated from the dissolution of the Pu metal coupon during Experiments Pu-Offgas-1 and Pu-Offgas-2 exited through the condenser (Fig. 1). Viton® tubing was used to connect a 40-mL sample bulb and a 2-L Tedlar® gas-collection bag to the condenser (Fig. 2). The sample bulb was connected to the tubing using quick-disconnect fittings which allowed easy replacement of the bulb during dissolution. A final gas sample was also taken by opening an evacuated sample bulb that was connected directly to the dissolver vessel via a sample port using a quick-disconnect fitting. The bulbs were fabricated using glass stopcocks at both ends to prevent leakage following removal from the dissolving system. The Tedlar® bag was placed in a water-filled vessel with a graduated cylinder incorporated into the top which allowed measurement of the gas volume by water displacement. The Tedlar® bag system is capable of measuring offgas generation as small as 3 ml up to about 580 ml. Water was not circulated through the condenser.

Before the offgas experiments began, air was initially purged from the dissolver and condenser using N_2. A penetration in the dissolver (obscured by the condenser in Fig. 1) equipped with a quick-disconnect fitting was provided to attach the N_2 supply line. Nitrogen gas (estimated at 200-400 mL/min) was used to purge the dissolver system including gas bulbs with about 2-3 Liters of N_2 prior to lowering the coupon into the HNO_3 solution. Once the N_2 purge was complete, one of the purged gas sample bulbs was put in line with the Tedlar® bag to collect the gas sample for analysis by GC. Agitation was then started at 250 RPM. For the moderate temperature (50-60 °C) experiment, the hot plate set point was programmed to 55 °C. The volume of water displaced by the offgas was recorded periodically by the rising water column height in the graduated cylinder of the Tedlar® bag system during the experiment. When the desired solution temperature was reached, the glass basket containing the Pu metal was lowered into the solution and the water height in the graduated cylinder of the Tedlar® bag system was recorded periodically to track the offgas generation. The dissolving solution consisted of a 10 M HNO_3 solution containing 0.1 M fluoride (from KF) and 1.5 g/L B (from boric acid) which is consistent with the dissolving solution used in previous 6.1D dissolutions.

The final solution samples were analyzed for ^{239}Pu and ^{241}Am by gamma pulse height analysis (GPHA) and the gas samples were analyzed by GC. Samples of the final solution following each dissolution were also analyzed for metals by ICPES and free acid by titration. IC-Cation analysis was also performed to investigate the possibility of ammonium formation.

RESULTS AND DISCUSSION

General Observations

Prior to starting the dissolution experiments, a Pu metal coupon was placed in the glass dissolver basket as described in the experimental section. Based on the mass of the Pu coupon, the dissolver vessel was filled with the appropriate amount of dissolver solution targeting a final Pu concentration of 6.75 g/L when the coupon was completely dissolved. The stirrer was turned on and the coupon was lowered into the solution representing time zero. At regular intervals (based on the expected dissolution rate for the conditions being tested), the coupon was removed from the vessel to measure the mass and physical dimensions. The solution was sampled at each interval to measure the Pu concentration by GPHA. The offgas measurements were performed in the same fashion without removing the coupon or sampling except the condenser was connected to the Tedlar® bag making a sealed system. No visible gas generation was observed from the Pu metal coupons as they dissolved. The plutonium metal dissolved slowly to produce a green opaque solution. After a period of time, light brown gas was observed in the reactor vessel. No visible solids were observed in the vessel following any of the dissolutions.

Sample Analysis

The activities for both ^{239}Pu and ^{241}Am were measured by GPHA. The ^{239}Pu activities were converted to total Pu values by assuming the metal coupons were weapons grade Pu containing 94 wt % ^{239}Pu. Before the concentrations were correlated with the dissolution time, they were corrected for the small change in volume which occurred due to the removal of samples and evaporation losses; although a small concentrating effect would be expected in the 6.1D dissolver due to evaporation. The volumes of solution at the conclusion of Experiments Pu-Diss-1 and Pu-Diss-2 only decreased by 1 and 7 mL respectively as a result of the low temperature of the dissolutions. A small correction was also made for the amount of material removed in samples prior to completing the experiment. The mass of Pu removed in each 1-mL sample ranged from <0.1 mg to approximately 7 mg. The magnitude of the corrections ranged from <1% to approximately 3%.

The corrected Pu and Am concentrations as functions of the dissolution time are plotted in Fig. 3 and Fig. 4 for Experiments Pu-Diss-1 and Pu-Diss-2, respectively. The error bars in the figures reflect the one sigma uncertainty in the GPHA. The uncertainties associated with the volume measurements used to calculate the corrected actinide concentrations were found to be insignificant compared to the uncertainties in the radiochemical analyses.

The Pu and Am concentrations (Fig. 3 and Fig. 4) are consistent with the observation that complete dissolution was accomplished in each experiment. Each figure shows a steady increase in the actinide concentrations with time which approaches a constant value at the end of the experiment. Table 2 provides a comparison of the maximum corrected concentration (at the end of each experiment) to the concentration calculated from the mass of Pu metal and the volume of the dissolving solution used in the experiment. The uncertainties in the Pu concentrations calculated from the metal masses and initial volumes of solution were based on a 1% relative standard deviation in each of the measurements.

The Pu concentrations for each experiment show good agreement between the concentration measured by GPHA and the concentration based on the mass of Pu metal dissolved and the volume of the dissolving solution. Differences in the values are likely attributed to uncertainties in the radiochemical analyses and to some extent, impurities in the Pu metal.

To calculate the amount of Pu and Am metal dissolved as a function of time, the estimated solution volume and the Pu and Am concentrations at each sample time were used to calculate the mass of Pu and Am in solution. The calculated mass was expressed as a percentage of the total mass dissolved based on the final mass of Pu and Am in solution at the end of the experiment. Fig. 5 and Fig. 6 show the mass percent of Pu and Am dissolved as a function of time for Experiments Pu-Diss-1 and Pu-Diss-2, respectively. The error bars in the figures were calculated using the one sigma uncertainties in the GPHA and propagation of error techniques. The uncertainties associated with the volume measurements used to calculate the amounts of the metals dissolved were found to be insignificant compared to the uncertainties in the radiochemical analyses.

The percentages of Pu and Am dissolved at each sample time during the experiments were very close in magnitude which indicates that the metal dissolved uniformly. The data for each experiment show that complete dissolution essentially coincided with the removal of the final sample. The dissolution times for the two experiments are given in Table 3.

Dissolution Rate Measurements

The mass loss from the Pu metal coupons as a function of time used to calculate the dissolution rates for the ambient (Pu-Diss-1, 24 °C) and intermediate temperature (Pu-Diss-2, 57 °C) experiments are listed in Table 4 and Table 5, respectively.

The calculated mass to surface area ratio for each sample time is shown for the ambient (Pu-Diss-1, 24 °C) and intermediate temperature (Pu-Diss-2, 57 °C) dissolution experiments in Fig. 7 and Fig. 8, respectively, where the fitted slope is equal to the dissolution rate in mg/min/cm^2.

Based on a review of the Pu mass to surface area ratio versus dissolution time data at 24 °C in Fig. 7, there was a small induction period of approximately 2 h due to PuO_2 on the surface of the coupon when it was initially placed in the dissolving solution. This conclusion was based on the reduced values for the first two data points. The final data point was not used due to complete dissolution of the Pu metal coupon. A linear fit of the remaining data is shown as equation 1:

$$\frac{M_{Pu}}{S} = 500 - 0.24D_t \tag{1}$$

where $\frac{M_{Pu}}{S}$ is the mass to surface area ratio and D_t is the dissolution time. This fit has an adjusted R^2 of 0.997, indicating the dissolution rate at ambient temperature is fairly linear or constant (not including the induction period). Using the slope from the fit, the dissolution rate at ambient temperature or 24 °C is 0.24 ± 0.01 mg/min/cm^2.

Inspection of the Pu mass to surface area ratio versus dissolution time data at 57 °C shows there is a smaller induction period, estimated to be approximately 20 minutes based on the first two data points. The last point was also not used to calculate the dissolution rate due to complete dissolution of the Pu metal coupon. A linear fit of the remaining data is shown as equation 2.

$$\frac{M_{Pu}}{S} = 477 - 0.96D_t \qquad (2)$$

This fit has an adjusted R^2 of 0.999 indicating the dissolution rate at 57 °C is also fairly linear or constant (not including the induction period). Using the slope from the fit, the dissolution rate at 57 °C is 0.96 ± 0.02 mg/min/cm^2.

Relationship of Pu Metal Dissolution Rate to H-Canyon Processing

The overall dissolution rate of Pu metal is directly proportional to exposed surface area in contact with the dissolving solution. The calculated specific surface area (SSA) of the Pu metal coupons used in this work ranged from 2.1-2.2 cm^2/g. The SSA of the coupons is greater than two times larger than the DOE 3013 Standard packaging requirement for Pu metal of less than 1 cm^2/g. Therefore, the H_2 generation rates that are reported on a Pu mass basis are conservative for all Pu metal that was packaged in 3013 containers.

Holcomb reported the dissolution time of a nominal SRS Pu button as a function of dissolution rate.(8) The nominal Pu button had a SSA of 0.076 cm^2/g. However, Pu metal dissolved in H Canyon that originates from 3013 containers may have larger SSA's. Plutonium metals and alloys packaged to meet the 3013 Standard have a surface area less than 1 cm^2/g. Since the overall dissolution rate is proportional to the Pu metal surface area, the estimated time to completely dissolve a Pu metal charge could range significantly. Assuming a bounding upper SSA of 1 cm^2/g for the Pu metal, the overall dissolution rate would be about 13 times faster than the nominal button.

Based on process knowledge using the current flowsheet at boiling (112 - 116 °C), a Pu metal charge was estimated to dissolve in the H-Canyon 6.1D dissolver in 24-36 h. (1) The Pu metal dissolution rate measured at 57 °C is approximately 20 times slower than at boiling, and the dissolution rate at ambient temperature (24 °C) is approximately 80 times slower. Therefore, a Pu metal charge dissolved at 57 °C is estimated to dissolve in the 6.1D dissolver in approximately 20-30 days, and a Pu metal charge dissolved at ambient conditions (24 °C) is estimated to dissolve in about 80-120 days; although, higher ambient temperatures or increased SSAs of the Pu metal will result in shorter dissolution times.

To further evaluate the impact of dissolving temperature, dissolution rates at a broad range of temperatures were compared from available data for similar dissolving solutions in Table 6. The estimated H Canyon processing times are provided for each dissolving temperature.

Pu Metal Offgas Generation

The offgas generation rate during the dissolution of the Pu metal was measured by water displacement in a Tedlar® bag system. A leak check was initially performed by adding sufficient Ar or N_2 to the Tedlar® bag system to generate a column of water about 16-cm tall. The Tedlar® bag system was then closed and monitored for any observable decrease in the water column height over approximately 3 minutes. After the system integrity was confirmed, the experiment was started. Samples of the offgas were analyzed by GC. The volume correction due to the water pressure on the Tedlar® gas bag varied linearly with the amount of gas collected. The volume was also corrected for the tubing volume that was submerged in the water column. The generated offgas volumes measured during Experiments Pu Offgas-1 (performed at

24 °C) and Pu-Offgas-2 (performed at 57 °C) as a function of the cumulative dissolution time are given in Table 7 and Table 8, respectively.

The overall offgas generation rates based on the data in Table 7 and Table 8 are 0.004 mL/min for the ambient temperature (24 °C) experiment and 0.15 ml/min for the experiment performed at 57 °C. In earlier work(1) (see Table 9, Experiment Pu-5) the offgas generation rate at 100 °C with a similar dissolving solution was 1.6 mL/min. The offgas generation rates at the lower temperatures are orders of magnitude less than at 100 °C. Since the total surface area of the Pu metal pieces dissolved in the offgas experiments was approximately the same, the offgas generation rates should be proportional to the metal dissolution rates if the dissolution mechanisms are the same. The negligible offgas generation rate observed at 24 °C is consistent with previous observations made by Rudisill et al., where no visible gas generation was observed evolving from Pu metal coupons dissolving in HNO_3 at 20 and 35 °C.(1)

The offgas generation rate per mole of dissolved Pu was calculated for Experiment Pu-Offgas-1 and Pu Offgas-2 since the metal completely dissolved during the offgas collection. The values were calculated using the ideal gas law by assuming the pressure of the gas was 1 atm and the gas was at the temperature of the glovebox. The calculated offgas generation rates are given in Table 9. Rudisill et al., using a similar dissolving solution, reported the offgas generation rate per mole of Pu at 100 °C was 0.6 mole offgas/mol Pu.(1) The difference in offgas rate at 100 °C and this work may be indicative of different reaction mechanisms taking place at the lower temperature ranges and perhaps increased solubility of the gas species in the dissolving solution.

The mechanisms that impact dissolution and offgas behavior when dissolving Pu metal in HNO_3 between ambient and boiling temperatures are complex and are not well understood. The total offgas rate observed is related to the moles of Pu metal dissolved, the Pu metal dissolution rate, and composition of the gas produced. The primary gases observed during Pu metal dissolution are H_2 , NO, NO_2, and N_2O. Kyser et al. summarized multiple reactions that can take place when dissolving Pu metal in HNO_3.(10)

$$Pu(s) + 8HNO_3 \rightarrow Pu(NO_3)_4 + 4NO_{2(g)} + 4H_2O \tag{3}$$

$$Pu(s) + \frac{16}{3}HNO_3 \rightarrow Pu(NO_3)_4 + \frac{4}{3}NO_{(g)} + \frac{8}{3}H_2O \tag{4}$$

$$Pu(s) + 5HNO_3 \rightarrow Pu(NO_3)_4 + \frac{1}{2}N_2O_{(g)} + \frac{5}{2}H_2O \tag{5}$$

$$Pu(s) + \frac{24}{5}HNO_3 \rightarrow Pu(NO_3)_4 + \frac{2}{5}N_{2(g)} + \frac{12}{5}H_2O \tag{6}$$

$$Pu(s) + 5HNO_3 \rightarrow Pu(NO_3)_4 + \frac{1}{2}NH_4NO_3 + \frac{3}{2}H_2O \tag{7}$$

$$Pu(s) + 4HNO_3 \rightarrow Pu(NO_3)_4 + 2H_2 \tag{8}$$

Kyser et al. also showed that a complex series of solution and gas phase reactions can occur once the NOx gases are produced (10). The subsequent reactions, such as NO_2 reacting with water to reform HNO_3 and HNO_2 (equation 15), can reduce the net volume of offgas measured in the offgas collection system.

$$2NO + HNO_3 + H_2O \leftrightarrow 3HNO_2 \tag{9}$$

$$NO_{(g)} + \frac{1}{2}O_{2(g)} \leftrightarrow NO_{2(g)} \tag{10}$$

$$3NO_{(g)} \leftrightarrow N_2O_{(g)} + NO_{2(g)} \tag{11}$$

$$2NO_{2(g)} \leftrightarrow N_2O_{4(g)} \tag{12}$$

$$NO_{(g)} + NO_{2(g)} \leftrightarrow N_2O_{3(g)} \tag{13}$$

$$3NO_{2(g)} + H_2O \leftrightarrow 2HNO_{3(l)} + NO_{(g)} \tag{14}$$

$$2NO_{2(g)} + H_2O_{(g)} \leftrightarrow HNO_{3(g)} + HNO_{2(g)} \tag{15}$$

Furthermore, increased solubility of gases in the dissolving solution at lower temperatures would lead to a reduced amount of observed offgas. Final solutions from the two offgas experiments were analyzed for ammonium, a possible non-gaseous product from Pu metal dissolution in HNO_3.(10) Samples from Experiments Pu-Offgas-1 and Pu Offgas-2 contained only 21 and 5 ppm ammonium, respectively.

Therefore, ammonium formation does not significantly account for the decrease in offgas generation at the lower temperatures when compared to boiling conditions.

Pu Dissolution Offgas Composition

Since the offgas generation was low for the ambient (24 °C) and moderate temperature (57 °C) dissolution experiments, only one in-line gas bulb was collected at the end of each experiment. A second gas sample was also taken by opening an evacuated sample bulb that was attached directly to the headspace of the dissolver.

The concentrations of H_2, N_2, and O_2 in the offgas samples collected during Experiments Pu-Offgas-1 and Pu-Offgas-2 were obtained by GC. The compositions from the analysis are shown in Table 10. Since the H_2 concentrations for both the ambient (24 °C) and moderate temperature (57 °C) dissolution experiments were less than detectable (<0.1 vol %), there was no need to adjust the concentrations to account for dilution from gas initially present in the system.

Oxygen concentrations above the detection limit in the ambient temperature dissolution gas sample bulbs taken at 45.5 h were unexpected as the system was initially purged with N_2 and leak checked. The O_2 is most likely due to a small amount of air in-leakage over the course of the 52.4 h experiment, which was much longer than past experiments performed with the dissolver system. Conversely, the experiment at 57 °C (Pu-Offgas-2) lasted approximately 8 h and the O_2 concentrations were below the GC detection limit.

Although there was visual evidence of NO_2 from the light brown gas discussed earlier, the GC was not configured to properly quantify NO_2.

Formation of Pu(VI)

Crapse et al. recently performed Pu metal dissolution experiments at temperatures ranging from 95 to 108 °C using 7 to 8.5 M HNO_3 while monitoring the oxidation of Pu(IV) to Pu(VI) using UV-vis spectroscopy.(9) The dissolutions were performed with Fe, Cr, and Ni in the solution to simulate the presence of corrosion products during the dissolution of Pu metal in the 6.1D dissolver. Formation of Pu(VI) was presumed to be facilitated by the presence of Cr(VI) formed in the highly oxidizing HNO_3 solutions. It was determined that lowering the temperature to 95 °C from near boiling dramatically decreased the rate of Pu(VI) formation. The rate of formation of Pu(VI) has also been shown to decrease as HNO_3 molarity increases. Therefore, Pu metal dissolutions performed using 10 M HNO_3 and at more reduced temperatures (24 and 57 °C) would be expected to generate even less Pu(VI).

Solution samples from the Pu-Offgas-1 and Pu Offgas 2 experiments were analyzed by UV-vis spectroscopy to determine if Pu(VI) is present in the solutions. However, it is unlikely that Pu(VI) will be observed. Rudisill et al. sampled and analyzed the solutions from a series of flowsheet demonstration experiments and reported that the estimated Pu(VI) concentration was significantly less than 1 wt %; although, the actual detection limit was not established.(1) The UV-vis spectra were recorded within approximately one week of the dissolution experiments. From these results, it appears that the presence of Cr(VI) (or another strong oxidant) is likely required to oxidize Pu(IV) to Pu(VI) during metal dissolutions. The Pu metal dissolutions in this study were performed using glassware without the presence of potential corrosion products (e.g., Cr) in the solution (similar to the experiments performed by Rudisill et al.); therefore, the absence of Pu(VI) would not be indicative of what to expect during the dissolution of Pu metal in the 6.1D dissolver.

H-Canyon Dissolver Purge

Without controls, the volume of H_2 generated during the dissolution of Pu metal in the H-Canyon dissolver must be maintained below 25% of the Lower Flammability Limit (LFL). When automatic instrumentation with safety interlocks is provided, the combustion concentration is permitted to be maintained at or below 60% of the LFL. Since the ambient and moderate temperature Pu dissolution experiments generated no detectable H_2 gas, the purge requirements for the 6.1D dissolver were evaluated by assuming the H_2 concentration was conservatively at the detection limit of the gas chromatograph (0.1 vol %). The comparison of the maximum H_2 concentrations with the appropriate LFL shows that a dissolver purge is not required for Pu metal dissolutions performed at ambient temperature or 50-60 °C. However, if the dissolver is heated or used to dissolve a full charge at ambient temperature, SRNL recommends the continued use of the sparge to provide agitation in the dissolver.

Conclusions

The current H-Canyon flowsheet used to dissolve Pu metal for PuO_2 production utilizes boiling HNO_3. The SRNL was requested to develop a complimentary dissolution flowsheet at two reduced temperature ranges. The dissolution and H_2 generation rates of Pu metal were investigated using a dissolving solution at ambient temperature (20-30 °C) and at an intermediate temperature of 50-60 °C.

The dissolving solution for each experiment consisted of 10 M HNO_3, 0.1 M KF, and 1.5 g/L B. The Pu metal dissolving rates were constant throughout the dissolution up to 6.75 g/L Pu, except initially, when the rates were reduced due to the passivation of the metal surface by PuO_2. The Pu metal dissolution rate measured at 57 °C was approximately 20 times slower than at boiling (112 - 116 °C). The dissolution rate at ambient temperature (24 °C) was approximately 80 times slower than the dissolution rate at boiling.

The total dissolution time required in H-Canyon to completely dissolve the Pu metal is dependent upon the dissolving solution temperature as well as the surface area of the Pu metal being dissolved. Based on process knowledge and the current flowsheet at boiling, a Pu metal charge was estimated to dissolve in the H-Canyon 6.1D dissolver in 24-36 h. Therefore, a Pu metal charge dissolved at 57 °C is estimated to dissolve in the 6.1D dissolver in approximately 20-30 days, and a Pu metal charge dissolved at ambient conditions (24 °C) is estimated to dissolve in about 80-120 days; although, higher ambient temperatures or increased SSAs of the Pu metal will result in shorter dissolution times.

Hydrogen concentrations measured by GC in the off-gas from the Pu metal dissolutions at the two temperatures were less than detectable (<0.1 vol %). Dissolution and offgas generation rates were observed to decrease as the temperature decreased. The moles of offgas generated per mole of Pu dissolved also decreased with temperature.

Using a conservative H_2 concentration of 0.1 vol % and total offgas generation rates measured during Pu metal dissolutions performed at 24 °C and 57 °C, maximum H_2 concentrations were estimated for an H Canyon dissolver charge of 46 kg of Pu metal. Comparison of the maximum H_2 concentrations with the appropriate LFL showed that a dissolver purge is not required for Pu metal dissolutions performed at ambient temperature or 50-60 °C.

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References

1. T. S. Rudisill and R. A. Pierce, Dissolution of Plutonium Metal in 8-10 M Nitric Acid, SRNL-STI-2012-00043, Rev. 1, Savannah River National Laboratory, Aiken, SC (July 2012).
2. T. S. Rudisill and M. L. Crowder, Dissolution of FB-Line Residues Containing Beryllium Metal, WSRC-TR-2005-00042, Rev. 1, Westinghouse Savannah River Company, Aiken, SC (October 2005).

3. T. S. Rudisill, M. L. Crowder, and M. G. Bronikowski, Dissolution of FB-Line Metal Residues Containing Beryllium in H-Canyon, WSRC-TR-2005-00329, Westinghouse Savannah River Company, Aiken, SC (July 2005).
4. T. S. Rudisill, M. L. Crowder, and M. G. Bronikowski, Dissolution of Fissile Materials Containing Vanadium and Tantalum Metals, WSRC-TR-2006-00159, Westinghouse Savannah River Company, Aiken, SC (May 2006).
5. T. S. Rudisill, M. L. Crowder, M.G. Bronikowski, Dissolution of Fissile Materials Containing Tantalum Metals, WSRC-STI-2007-00285, Westinghouse Savannah River Company, Aiken, SC (May 2007).
6. F. J. Miner, J. H. Nairn, and J. W. Berry, Dissolution of Plutonium in Dilute Nitric Acid, I&EC, Ind Eng Chem Prod RD, 8, pp. 402-405 (1969).
7. H. P. Holcomb, Dissolving Alpha-phase Plutonium Metal, WSRC-RP-89-00616, Westinghouse Savannah River Company, Aiken, SC (July 1989).
8. H. P. Holcomb, Laboratory-scale Dissolution of Delta-phase Plutonium Metal, WSRC-TR-90-0101, Westinghouse Savannah River Company, Aiken, SC (March 1990).
9. K. P. Crapse, T. S. Rudisill, P. E. O'Rourke, and E. A. Kyser, III, AFS-2 Flowsheet Modifications to Address the Ingrowth of Pu(VI) during Metal Dissolution, 2013, SRNL-STI-2013-00709, Savannah River Nuclear Solutions, Aiken, SC (July 10, 2014).
10. E. A. Kyser, Follow-up to EOC Question on Generation of Soluble Ammonium during the Dissolution of AFS-2 Iron Metal Cans and Pu Metal for the AFS-2 Flowsheet, SRNL-L3100-2015-00177, Savannah River Nuclear Solutions, Aiken, SC (October 7, 2015).

TABLE 1

Mass and Dimensions of Pu Metal Used in Flowsheet Demonstration Experiments

Experiment	Mass	Length	Width	Thickness	Surface Area
	(g)	(mm)	(mm)	(mm)	(cm^2)
Pu-Diss-1	2.4844	29.41	8.28	0.74	5.43
Pu-Diss-2	2.6998	18.26	15.12	0.73	6.01
Pu-Offgas-1	3.1203	20.68	14.95	0.67	6.67
Pu-Offgas-2	3.3031	20.04	17.03	0.71	7.35

TABLE 2

Comparison of Pu Concentrations Based on Corrected Value and Metal Mass

Experiment	Temperature	(Corrected) Pu Concentration	(Mass-based) Pu Concentration	Difference
	(°C)	(g/L)	(g/L)	(%)
Pu-Diss-1	24	6.44 ± 0.32	6.73 ± 0.10	4.35
Pu-Diss-2	57	6.85 ± 0.34	6.75 ± 0.10	-1.49

TABLE 3

Time Required for Complete Dissolution of Pu Metal Coupons

Experiment	Temperature (°C)	Dissolution Time (h)
Pu-Diss-1	24	33.4
Pu-Diss-2	57	8.2

TABLE 4

Pu-Diss-1 Dissolution Time and Weight Measurements (24 °C)

Time (min)	Mass (g)
0	2.4844
117.3	2.4600
294.6	2.2585
470.1	2.0282
590.2	1.8252
770.4	1.5895
950.7	1.3422
1072.9	1.1478
1253.0	0.9236
1434.0	0.6884
1554.0	0.5202
1734.1	0.3155
1914.2	0.0988
2002.8	0.0000

TABLE 5

Pu-Diss-2 Dissolution Time and Weight Measurements (57 °C)

Time (min)	Mass (g)
0	2.6998
20.1	2.5981
40.5	2.4667
60.1	2.3311
104.4	2.0597
164.5	1.7022
224.3	1.3691
288.5	1.0051
345.2	0.7083
405.1	0.4001
465.0	0.1090
491.0	0.0000

TABLE 6

Estimated H-Canyon Processing Times from Dissolution Rate Data

Temperature	HNO_3	KF	B	Fe	Dissolution Rate	Est. Processing Time
(°C)	(M)	(M)	(g/L)	(g/L)	(mg/min/cm^2)	(day)
112	10	0.1-0.2	1-2	–	20*	1-1.5
100	10	0.1	1.0	1.9	13.8	1-2
95	6	0.1	1	3.5**	5.1	4-6
57	10	0.1	1.5	–	0.96	20-30
24	10	0.1	1.5	–	0.24	80-120

* Estimated dissolution rate(1)

**Dissolving solution also contained 0.4 g/L Ni and 0.6 g/L Cr

TABLE 7

Pu-Offgas-1 Offgas Generation at 24 °C

Cumulative Dissolution Time	Total Offgas Generated
(min)	(mL)
0.0	0.0
120.6	0.0
240.0	2.7
379.8	2.7
1293.0	5.5
1415.4	5.5
1474.8	11.0
1595.4	11.0
1836.0	11.0
2164.2	11.0
2724.0	11.0
2730.0	11.0

TABLE 8

Pu-Offgas-2 Offgas Generation at 57 °C

Cumulative Reaction Time (min)	Total Offgas Generated (mL)
0.0	0.0
61.7	8.2
133.1	22.0
191.4	30.2
252.1	38.5
308.2	46.7
370.4	55.0
428.0	66.0
489.4	74.3
549.4	82.6
578.4	85.4

TABLE 9

Offgas Generation per Mole of Dissolved Pu

Exp.	Reaction Temp. (°C)	HNO_3 (M)	KF (M)	B (g/L)	Fe (g/L)	Glovebox Temp. (°C)	Offgas Gen. (mol offgas/mole Pu)
Pu-Offgas-1	24	10	0.1	1.5	–	24	0.035
Pu-Offgas-2	57	10	0.1	1.5	–	25	0.25
Pu-5(1)	100	10	0.05	1	1.9	18.5	0.6

TABLE 10

Composition of Offgas from Pu Metal Dissolutions in 10 M HNO3

Exp.	Temperature (°C)	H_2 (vol %)	O_2 (vol %)	N_2 (vol %)	Comment
Pu-Offgas-1	24	<0.1	1.7	98	In line with Tedlar® Bag and System for whole dissolution
Pu-Offgas-1	24	<0.1	6.5	93	Pulled from reactor head space at end of dissolution
Pu-Offgas-2	57	<0.1	<0.1	99	In line with Tedlar® Bag and System for whole dissolution
Pu-Offgas-2	57	<0.1	<0.1	99	Pulled from reactor head space at end of dissolution

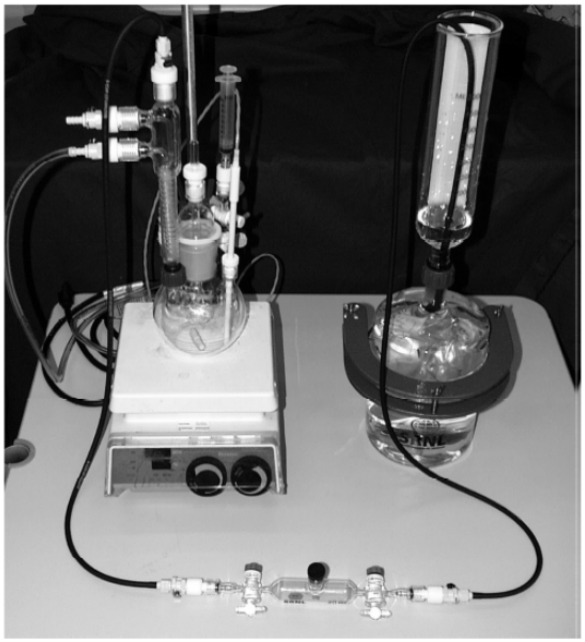

Fig. 1. Pu Metal Dissolving and Offgas Measurement System

Fig. 2. Tedlar® Gas-collection Bag

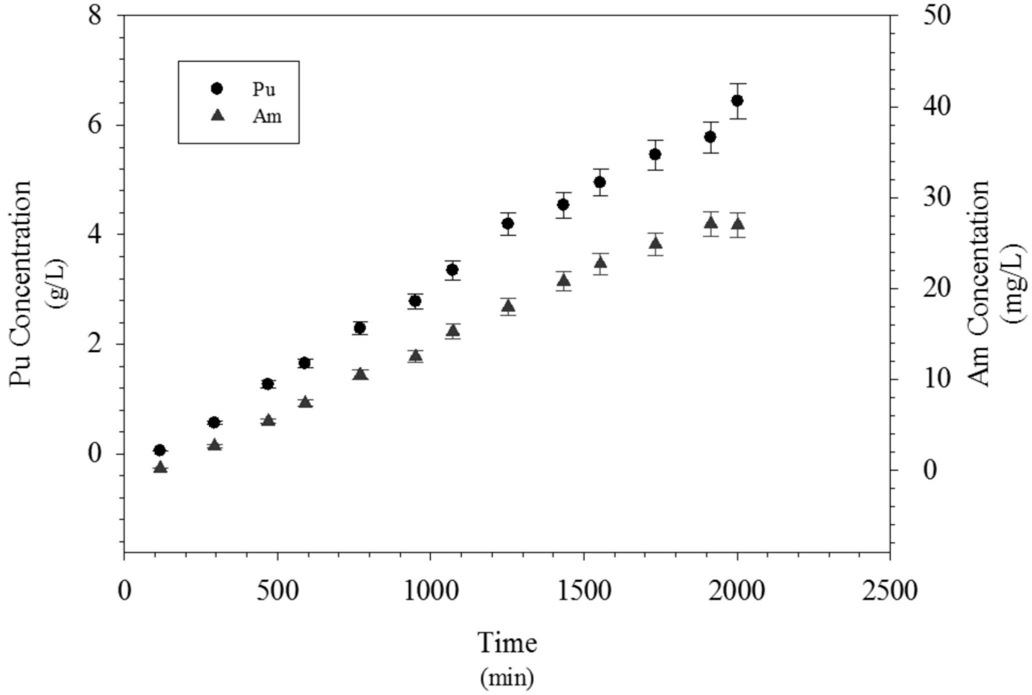

Fig. 3. Corrected Actinide Concentrations in Experiment Pu-Diss-1

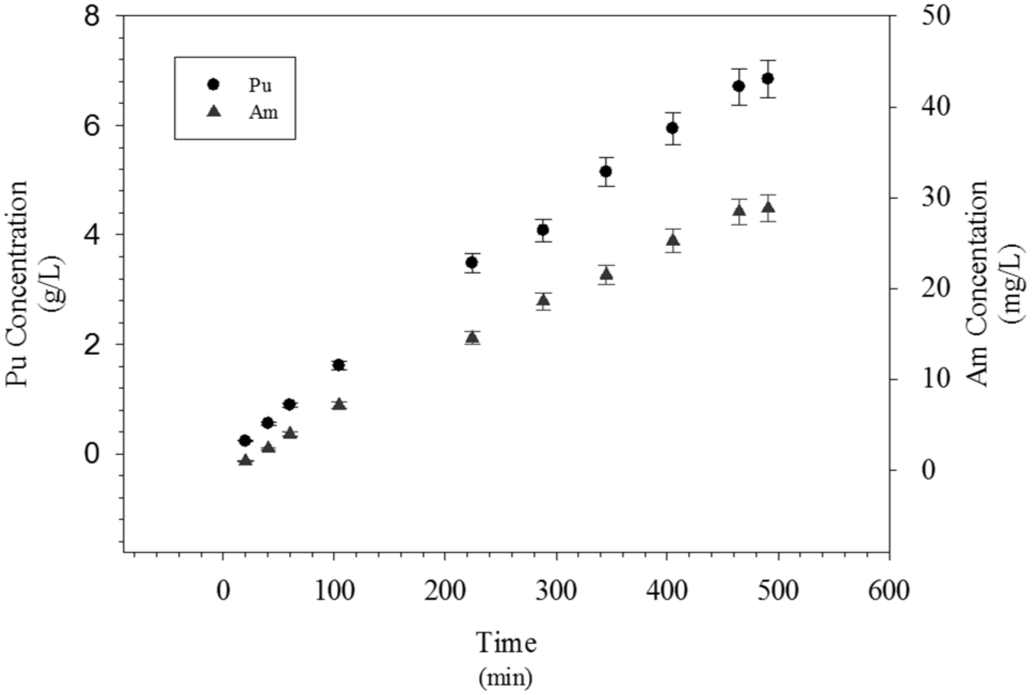

Fig. 4. Corrected Actinide Concentrations in Experiment Pu-Diss-2

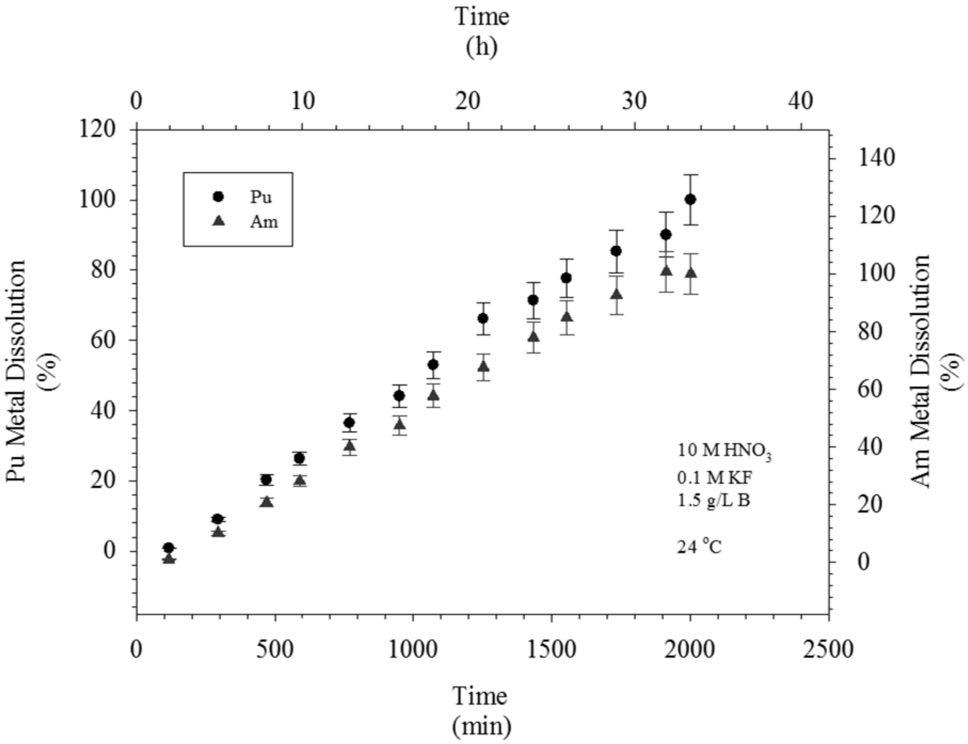

Fig. 5. Actinide Metal Dissolution in Experiment Pu-Diss-1

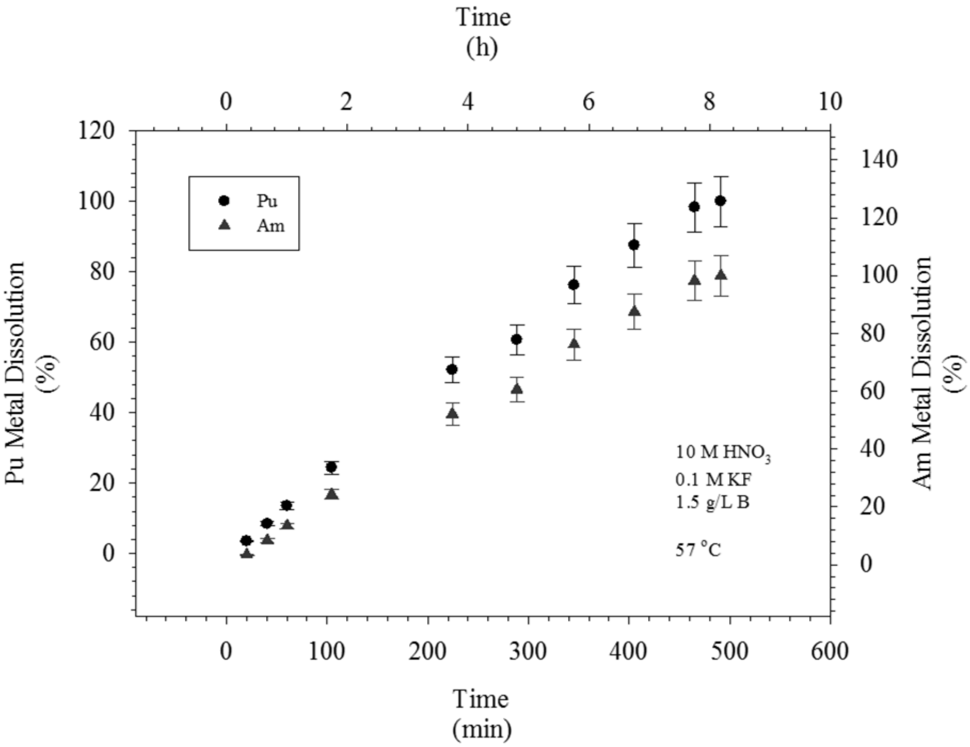

Fig. 6. Actinide Metal Dissolution in Experiment Pu-Diss-2

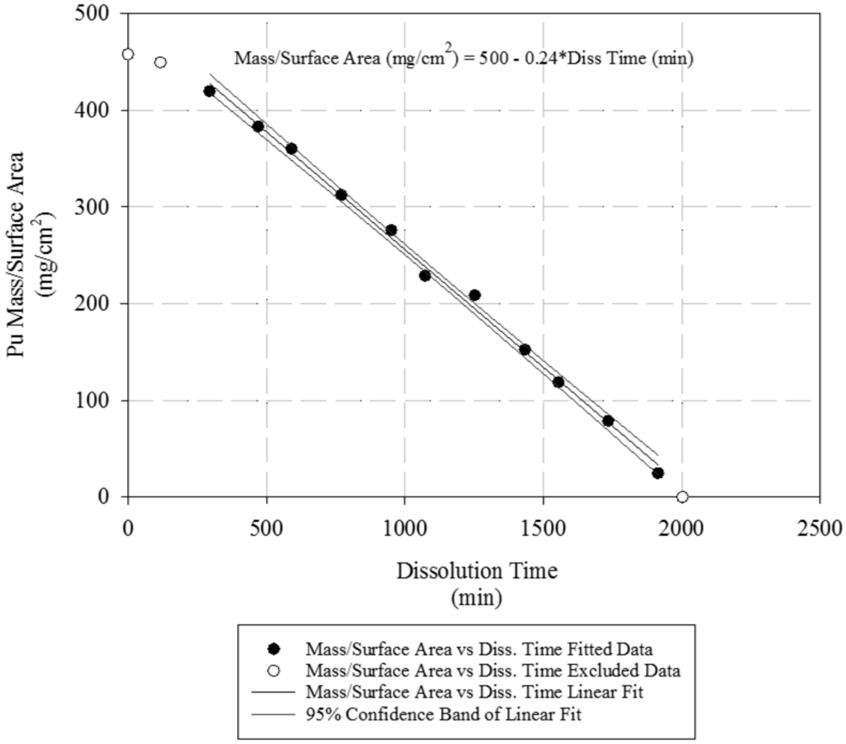

Fig. 7. Pu Mass to Surface Area versus Dissolution Time at 24 °C (Pu-Diss-1)

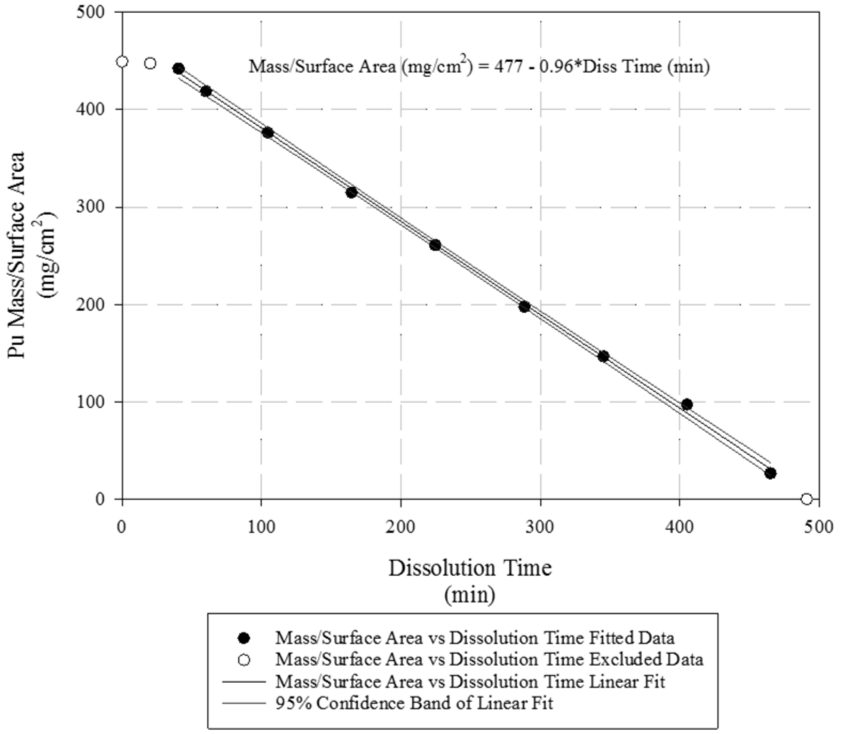

Fig. 8. Pu Mass to Surface Area versus Dissolution Time at 57 °C (Pu-Diss-2)