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Dissolution of Fissile Materials Containing Plutonium and Beryllium Metals

Tracy S. Rudisill and Mark L. Crowder

Savannah River National Laboratory
Westinghouse Savannah River Company
Aiken, SC 29808

Abstract

Scrap materials containing plutonium (Pu) metal were dissolved at the Savannah River Site (SRS) as part of a program to disposition nuclear materials during the deactivation of the FB-Line facility. Some of these items contained both Pu and beryllium (Be) metal as a composite material. The Pu and Be metals were physically separated to minimize the amount of Be associated with the Pu; however, a dissolution flowsheet was required to dissolve small amounts of Be combined with the Pu metal using a dissolving solution containing nitric acid (HNO_3) and potassium fluoride (KF). Since the dissolution of Pu metal in HNO_3/fluoride (F^-) solutions was well understood, the primary focus of the flowsheet development was the dissolution of Be metal.

Initially, small-scale experiments were used to measure the dissolution rate of Be metal foils using conditions effective for the dissolution of Pu metal. The experiments demonstrated that the dissolution rate was nearly independent of the HNO_3 concentration over the limited range of investigation and only a moderate to weak function of the F^- concentration. The effect of temperature was more pronounced, significantly increasing the dissolution rate between 40 and 105°C. The offgas analysis from three Be metal foil dissolutions demonstrated that the production of hydrogen (H_2) was sensitive to the HNO_3 concentration, decreasing by a factor of approximately two when the concentration was increased from 4 to 8 M. In subsequent experiments, complete dissolution of Be samples from a Pu/Be composite material was achieved in a 4 M HNO_3 solution containing 0.1-0.2 M KF. Gas samples collected during each experiment showed that the maximum H_2 generation rate occurred at temperatures below 70-80°C.

A Pu metal dissolution experiment was performed using a 4 M HNO_3/0.1 M KF solution at 80°C to demonstrate flowsheet conditions developed for the dissolution of Be metal. As the reaction progressed, the rate of dissolution slowed. The decrease in rate was attributed to the complexation of F^- by the dissolved Pu. The F^- became unavailable to catalyze the dissolution of plutonium oxide (PuO_2) formed on the surface of the metal which inhibited the dissolution rate. To compensate for the complexation of F^-, an increase in the concentration to 0.15-0.2 M was recommended. Dissolution of the PuO_2 was addressed by recommending an 8-10 h dissolution time with an increase in the dissolving temperature (to near boiling) during the final 4-6 h to facilitate the digestion of the solids. Dilution of the H_2 concentration below 25% of the lower flammability limit by purging the dissolver with air was also necessary to eliminate the flammability concern.

Introduction

Scrap materials containing Pu metal were dissolved at the SRS as part of a program to disposition nuclear materials during the deactivation of the FB-Line facility. Some of these items contained both Pu and Be metal as a composite material. The Pu and Be metals were physically separated to minimize the amount of Be associated with the Pu; however to be compatible with existing equipment, the dissolution flowsheet was required to dissolve small amounts of Be combined with Pu metal using a solution containing HNO_3 and KF. No data were available for the simultaneous dissolution of both materials using this type of flowsheet. Available data for the dissolution of pure Be and Pu in HNO_3-based flowsheets are summarized below.

Be Metal Dissolution

Beryllium metal dissolves very slowly in HNO_3 solutions. The dissolution rate in 10 and 70 wt% solutions was measured by Darwin et al.[1] The data are summarized in Table 1.

Table 1 Beryllium Metal Dissolution in HNO_3 Solutions

HNO_3 Concentration (wt%)	(M)	Temperature	Test Duration (h)	Mass Loss (mg/cm^2-h)
10	1.67	Room	60	2.8
10	1.67	Boiling	0.1	8
72	15.6	Room	60	0.03
72	15.6	Boiling	0.1	20

The slow rate of dissolution in concentrated HNO_3 at room temperature can be attributed to passivation of the Be surface due to the formation of a beryllium oxide coating. Dilute acid (at room temperature) has a slight, but measurable, rate of attack. The dissolution rate in boiling HNO_3 is much higher, but would still be an inefficient and time consuming means to dissolve Be metal. The data in Table 1 were generated by exposing small samples of massive extruded Be to reagent grade HNO_3. The reaction in boiling acid was described as far from violent; however, the authors speculated that the use of powdered Be could generate more energetic conditions. This behavior would likely be true, since the rate of dissolution of solids is generally proportional to the available surface area.

In a more detailed study, Hardy et al. [2] performed a series of dissolutions using both Be metal sheet and tubes. In most of the experiments, the rate of dissolution during the first 0.5 to 1 h was usually greater than the final constant value; however, this result was thought to be due to a surface effect associated with the sheet and tube fabrication methods. The final constant dissolution rates at 97°C for Be metal sheet and tubes as a function of the HNO_3 concentration are plotted on Figure 1. The rates for the tube are generally lower than for the sheet, but follow the same trends, being approximately independent of the HNO_3 concentration from 6 to 14 M. Beryllium dissolution rates were also reported to increase markedly with temperature.

Beryllium metal is soluble to a greater extent in other solvents. The relative dissolution rates for common acids are compared below.

$$HF > H_2SO_4 \approx HCl > HNO_3$$

The metal dissolves rapidly in 3 M sulfuric acid (H_2SO_4) and 5 M ammonium fluoride (NH_4F).[1] Beryllium like aluminum (Al), dissolves in strong bases, forming the beryllate (BeO_2^{2-}) ion (equation 1).[1,3]

$$Be + 2\ KOH \rightarrow K_2BeO_2 + H_2 \tag{1}$$

Metallic Be is also rapidly dissolved by ammonium bifluoride (NH_4HF_2). The reaction (equation 2) has been used as the basis for scrap recovery on an industrial scale.[1]

$$2\ NH_4HF_2 + Be \rightarrow (NH_4)_2BeF_4 + H_2 \tag{2}$$

The rate of Be dissolution in HNO_3 solutions containing F^- has also been evaluated. Hardy et al. [2] performed a series of experiments in 14 M HNO_3 at 50°C with hydrofluoric acid (HF) concentrations that varied between 0 and 0.5 M. Above 0.1 M HF, the reaction became very vigorous and caused the temperature to rise almost to the boiling point. The rate of dissolution in solutions containing greater than 0.01 M HF was initially fast but became constant at approximately 0.04 mg/cm^2-min. The initial dissolution rates were much higher, increasing linearly from nominally 0.2 to 1.5 mg/cm^2-min as the HF concentration was increased from 0.05 to 0.25 M. A reduction in the dissolution rate did not occur until enough Be dissolved to produce a Be:HF molar ratio which exceeded 3:1.

A dissolution flowsheet for ^{238}Pu scrap containing Be and brass was developed at the SRS.[4] Dissolution rate data for cylinders of Be-containing $^{238}PuO_2$ scrap as a function of HNO_3 and HF concentrations are reproduced on Figure 2. The dissolution rates were measured under reflux conditions. The rates increase with both the addition of F^- and as the HNO_3 concentration increases in the same general manner as the data presented on Figure 1.

Pu Metal Dissolution

The dissolution of Pu metal using a HNO_3/KF flowsheet was investigated at both the Rocky Flats Plant and the SRS. Miner et al. performed a series of experiments in which unalloyed (alpha phase) Pu metal was dissolved in solutions containing 1-5 M HNO_3 and 0.01-0.13 M HF at 26-69°C.[5] The maximum rate of dissolution occurred at approximately 3 M HNO_3 in combination with an HF concentration of 0.13 M (the highest investigated) at any temperature between 26 and 69°C. Additional dissolution experiments with alpha and delta-stabilized metal were performed by Holcomb at the SRS.[6-7] The focus of these experiments was the effect of the Al^{3+} concentration on the dissolution rate. The experiments verified the optimal flowsheet recommended by Miner et al. and demonstrated that the dissolution rate was sensitive to the presence of Al^{3+} and other elements which complex F^-. Complexation of F^- decreases its activity in solution and effectiveness as a catalyst for the dissolution of PuO_2. The dissolution of both alpha and delta-stabilized metal in HNO_3 requires a small amount of free F^- to inhibit the formation of a PuO_2 layer on the surface of the metal due to oxidation by HNO_3. Generally, the rate of dissolution increases with the F^- concentration and is only constrained by plutonium tetrafluoride (PuF_4) precipitation. The HNO_3 concentration must also remain dilute to reduce the surface oxidation rate. This requirement is even more important for delta-stabilized metal. Karraker reported that the surface of delta-stabilized Pu metal was much more reactive toward nitrate (NO_3^-) oxidation than that of alpha phase metal.[8]

Based on the work of Miner et al. and Holcomb, the use of a dissolving solution containing nominally 3 M HNO_3-0.1 M F^- was considered optimal for the dissolution of both alpha and delta-stabilized Pu metal at temperatures ranging from 25-90°C. Under these conditions, dissolution rates in the range of 5-10 mg/cm^2-min would be expected.[5-7]

Hydrogen Generation

The dissolution of both Be and Pu metals result in the generation of offgases containing H_2. During the development of the dissolution flowsheet for ^{238}Pu scrap containing Be and brass, [4] offgases containing 12 vol% H_2 were produced by boiling 10 M HNO_3 containing ≤ 0.01 M F^-. The balance of the offgas was reported as nitric oxide (NO). In those experiments, the production of H_2 was attributed almost entirely to the dissolution of Be; gases evolved during the dissolution of brass contained less than 0.01 vol% H_2. In that study, 0.69 mole of offgas was produced for every mole of Be dissolved. The H_2:NO ratio was also reported to be independent of the HNO_3 concentration. In a subsequent study, Thompson [9] analyzed the gases produced when Be metal was dissolved in 1-15 M HNO_3 solutions containing 0.1 M F^-. At each HNO_3 concentration, the evolved gas contained 75 vol% H_2 and 25 vol% NO. The increase in the H_2 concentration shows that the additional F^- shifts the Be dissolution mechanism from HNO_3 oxidation to a typical metal-acid reaction (equation 3).

$$Be + 2\,HNO_3 \rightarrow Be(NO_3)_2 + H_2 \tag{3}$$

In those experiments, 0.88 mole of offgas was produced for every mole of Be dissolved.

Only limited data are available concerning the concentration of H_2 and other gases produced during the dissolution of Pu metal using solutions containing HNO_3 and F^-. Miner et al. reported that gas samples withdrawn from just above the surface of the dissolving solution at various times during dissolution always contained ≤ 0.3 vol% H_2. The gas produced in the highest concentration was nitrous oxide (N_2O). The gases were analyzed by gas chromatography. The minimum detection limit for H_2 was 0.05 vol%.

Experimental Objectives

Since the dissolution of Pu metal in HNO_3/F^- solutions is well understood, the primary focus of this experimental program was the dissolution of Be metal. A series of small-scale experiments was performed in which dissolution rates of Be metal foils were measured using dissolving conditions effective for the dissolution of Pu metal. As part of these experiments, the composition and quantity of offgas produced were measured during several demonstrations of aggressive dissolving conditions. In subsequent experiments, optimal flowsheet conditions were demonstrated for the dissolution of samples of contaminated Be metal removed from a composite material and a sample of scrap Pu metal. The composition and quantity of offgas generated during the demonstration experiments were also measured. The experimental methods used to perform these experiments and a discussion of the results and observations are presented in the following sections.

Experimental

Dissolution Rate of Be Metal Foil

A series of small-scale experiments was completed in which dissolution rates of Be metal were determined. The dissolution rates were measured using 25 mm x 25 mm x 0.5 mm Be metal foils containing nominally 0.6 g of metal; the Be assay was 99.5%. The dissolutions were performed in a 500 mL three-neck flask using a porous glass basket attached to the center stopper to hold and allow access to the foil. A water-cooled condenser was attached to the flask to reduce the evaporation of the dissolving solution. The dissolving solution was heated and stirred using a heating mantle equipped with a magnetic stirrer. The temperature of the dissolving solution was monitored using an alcohol-filled thermometer.

Dissolutions were performed using solutions containing 3-8 M HNO_3/0.0135-0.2 M KF at 40°C to boiling (105°C). The experiments were performed by initially preheating the dissolving solution to the desired temperature, inserting the Be foil into the flask using the glass basket, and periodically removing the foil to measure the mass and surface area (i.e., length, width, and thickness of the foil). Dissolution rates were calculated as the rate of change of the mass to surface area ratio as a function of time.

Offgas Characterization from Be Metal Foil Dissolution

In subsequent experiments, the volume and composition of the offgas generated during the dissolution of Be metal foils were measured. The experiments were performed in the same manner as the experiments used to measure the dissolution rates. To sample and collect the offgas, the exit from the condenser on the dissolver was connected with ¼ inch plastic tubing to an approximate 25 mL sample bulb and 1 L Tedlar® bag. The sample bulb was fabricated with glass stopcocks on the ends to provide a means to isolate the sample. Quick disconnects (which seal upon disconnection) were used to attach and remove the sample bulbs and Tedlar® bags from the plastic tubing.

To perform an experiment, the Be metal foil was loaded into the glass basket and suspended in the flask above the level of the dissolving solution. The solution was preheated to the desired temperature and air was removed from the system by purging with argon for nominally 10 min. The argon supply was attached to the dissolving vessel using a glass stopper fabricated with a quick disconnect. Following the argon purge, an evacuated Tedlar® bag was connected to the sample bulb exit. The dissolution was initiated by lowering the glass basket containing the Be foil into the dissolving solution. The offgas was collected until the Be foil was completely dissolved. The volume of gas collected during a dissolution was determined by the difference in the amount of water displaced by the empty (evacuated) and filled bag. Gas analyses were performed by gas chromatography.

Three dissolution experiments were performed in which the volume and composition of the offgas were measured. Dissolving solutions containing 4 M HNO_3/0.1 M KF, 4 M HNO_3/0.2 M KF, and 8M HNO_3/0.1 M KF were used during dissolution experiments. A dissolution temperature of 80°C was targeted for the experiments; although, the heat of reaction from the metal dissolution raised the temperature to 90-100°C during each experiment.

Contaminated Be Metal Dissolution

A series of dissolution experiments was performed using nominally 2.5 g samples of contaminated Be metal physically separated from a composite material. The objectives of the experiments were to compare the dissolution of the contaminated material to the dissolution of the Be metal foils and to characterize the offgas produced during the dissolution. A 1 L, three-neck flask was used for the dissolutions; other laboratory equipment was essentially the same as used for the Be metal foil dissolutions. During the experiments, 2-5 gas samples were taken to characterize the offgas throughout the dissolution process. Air was initially removed from the dissolving vessel and plastic tubing by purging with nitrogen (N_2). The sample bulbs were also purged with N_2 for nominally 10 min prior to use. Tedlar® bags used to collect the offgas were evacuated by vacuum pump. The volume of gas collected in each bag was determined as the difference in the amount of water displaced by the filled and evacuated bags. Gas analyses were performed by gas chromatography.

The contaminated Be metal dissolutions were performed using a 4 M HNO_3 solution containing 0.1-0.2 M KF. Dissolution temperatures of 70 and 80°C were targeted for the experiments; although, the heat of reaction from the metal dissolutions raised the temperatures above these values. A 650 mL aliquot of the dissolving solution was used in each experiment which simulated the dissolution of 50-60 g of Be in a 15 L dissolver. This amount of Be was approximately 10% of the normal Pu charge and was expected to represent a typical amount of Be associated with the Pu/Be composite material. For experiments performed using 0.1 M KF, this volume of solution also resulted in an approximate 4:1 mole ratio of Be to F^- (upon complete dissolution) which was the highest ratio investigated during the Be dissolution rate measurements. When the Be metal was added to the dissolver, the glass basket was suspended above the solution during the N_2 purge. Once the purging was complete, the glass basket was lowered into the solution, the heating mantle and stirrer were energized, and the gas sample bulb and Tedlar® bag were connected to the plastic tubing attached to the offgas condenser. When the first and subsequent gas samples were taken, the sample bulb and Tedlar® bag were disconnected from the condenser exit and a new bulb and bag were connected. The volume of gas collected in each bag was determined by water displacement and analysis was performed by gas chromatography.

Pu Metal Dissolution

To demonstrate the dissolution of Pu metal using a HNO_3/KF flowsheet, an experiment was performed in which 23 g of scrap metal were added to a 650 mL aliquot of a 4 M HNO_3/0.1 M KF solution. A dissolution temperature of 80°C was selected as the target value. These conditions were expected to generate a dissolution rate of nominally 10 mg/cm^2-min based on previous studies at the Rocky Flats Plant.[5] The solid to liquid ratio in this experiment was equivalent to dissolving 500 g of Pu in the 15 L working volume of the dissolver. The experiment was performed in the same equipment as used for the contaminated Be metal dissolution. During the experiment, two gas samples were taken to characterize the offgas from the dissolution. The mass of Pu dissolved during each sample time was determined by removing the Pu metal and measuring the mass before and after the collection period. Air was purged from the dissolving vessel and plastic tubing using N_2 prior to sampling. The sample bulbs were purged with argon prior to use. The Tedlar® bags used to collect the offgas were evacuated by vacuum pump. The volume of gas collected in each bag was determined by water displacement and analysis was performed by gas chromatography.

Results and Discussion

Dissolution Rate of Be Metal Foil

Dissolution rates were calculated as the rate of change of the mass to surface area ratio of the Be metal as a function of the dissolving time. A summary of the conditions and measured rate for each dissolution is given in Table 2.

Table 2 Be Metal Foil Dissolution Rates

Experiment No.	HNO_3 (M)	KF (M)	Temperature (°C)	Rate (mg/cm^2-min)
Be-1	3	0.1	40	0.47
Be-2	4	0.1	40	0.52
Be-3	4	0.15	40	0.67
Be-4	4	0.1	60	1.1
Be-5	4	0.1	80	2.5
Be-6	4	0.1	105	7.7
Be-7	8	0.1	40	0.41
Be-8	4	0.2	40	0.71
Be-9	4	0.2	105	9.2
Be-12	4	0.0135	40	0.21

Inspection of the data in Table 2 show that the Be metal dissolution rate was nearly independent of the HNO_3 concentration in the range of investigation and only a moderate to weak function of the F^- concentration. However, the effect of temperature was significantly more pronounced, increasing the rate of dissolution by a factor of approximately 15 between 40 and 105°C. These observations are generally consistent with the work by Hardy et al. [2] and the work performed at the SRS [4] in which the Be metal dissolution rate was not a strong function of either the HNO_3 or F^- concentrations, but increased markedly with temperature.

Temperature Dependence of Rate Constant

If the mechanism for the dissolution of Be metal in HNO_3/F^- solutions was known, an expression for the reaction rate in terms of the HNO_3 and F^- concentrations and a temperature dependent rate constant could be written. However, if one assumes the rate of dissolution is independent of the HNO_3 concentration over the range of investigation, the reaction becomes pseudo zero order for a constant F^- concentration and is only a function of temperature (equation 4).

$$\text{Rate} = k(T) \tag{4}$$

The temperature dependence of the rate constant can be calculated from the data in Table 2 (at 0.1 M KF) by assuming the dependence is represented by Arrhenius' Law:

$$k(T) = k_0 e^{-\frac{E}{RT}} \tag{5}$$

where E is the activation energy of the reaction and k_0 is the frequency factor. Equations 4 and 5 illustrate that a plot of log(Rate) versus 1/T should be linear with a slope of $-E/\ln(10)R$ and a y-intercept of $\log(k_0)$. The 0.1 M KF data from Table 2 are plotted on Figure 3 and generally show a linear relationship between the two variables. For comparison, the two data points at 0.2 M KF are also shown on the figure. The calculated activation energy and frequency factor for each KF concentration are given in Table 3.

Table 3 Parameters for Arrhenius Temperature Dependence

KF (M)	E (KJ/mole)	K_0
0.1	41.6	3.89×10^6
0.2	39.3	2.55×10^6

An activation energy of nominally 40 KJ/mole would be described as moderately temperature sensitive (i.e., the reactants must be heated to achieve a significant dissolution rate).[10] Predictably, the activation energy for the data at 0.2 M KF is lower than the activation energy at 0.1 M due to the increased KF concentration.

Offgas Characterization from Be Metal Foil Dissolution

Three experiments were performed in which the volume and composition of the offgas produced from the dissolution of a Be metal foil were measured. The raw data from the gas analyses were adjusted to account for dilution from gas in the freeboard region of the dissolution vessel, condenser, plastic tubing, and sample bulb. The adjusted concentrations and a summary of the conditions for each dissolution are given in Table 4. The dissolution temperature for each experiment was 90-100°C.

Table 4 Characterization of Offgas from Be Metal Foil Dissolutions

Expt. No.	HNO_3 (M)	KF (M)	Offgas:Be (mole:mole)	H_2 (mol%)	NO (mol%)	N_2O (mol%)
Be-13	4	0.1	0.31	42	28	5.1
Be-14	8	0.1	0.31	26	45	20
Be-15	4	0.2	0.30	46	28	4.2

The data in Table 4 show that the production of H_2 was sensitive to the HNO_3 concentration. When the HNO_3 was increased from 4 to 8 M, the concentration of H_2 in the offgas was reduced by a factor of approximately two. This result is consistent with the dissolution mechanism shifting away from a typical metal/acid reaction (equation 3) toward increased production of nitrogen oxides (by equations 6-8). The presence of NO_2 in the offgas was identified based on the light brown color of the collected gas; however the gas chromatograph configuration was not capable of this analysis.

$$\mathrm{Be} + 2\ \mathrm{HNO_3} \rightarrow \mathrm{Be(NO_3)_2} + \mathrm{H_2} \tag{3}$$

$$\mathrm{Be} + 4\ \mathrm{HNO_3} \rightarrow \mathrm{Be(NO_3)_2} + 2\ \mathrm{NO_2} + 2\ \mathrm{H_2O} \tag{6}$$

$$3\ \mathrm{Be} + 8\ \mathrm{HNO_3} \rightarrow 3\ \mathrm{Be(NO_3)_2} + 2\ \mathrm{NO} + 4\ \mathrm{H_2O} \tag{7}$$

$$4\ \mathrm{Be} + 10\ \mathrm{HNO_3} \rightarrow 4\ \mathrm{Be(NO_3)_2} + \mathrm{N_2O} + 5\ \mathrm{H_2O} \tag{8}$$

The ratio of offgas produced to the amount of Be dissolved during each experiment was essentially constant at 0.31 mole/mole. This ratio is considerably less than the values (0.69 and 0.88 mole/mole) measured during previous work at the SRS.[4,9] The lower value could be attributed to the adsorption of nitrogen oxides by the dissolving solution with oxidation back to HNO_3 and potentially to changes in the dissolution path (i.e., reaction) as a function of temperature.

Contaminated Be Metal Dissolution

The time required to completely dissolve the contaminated Be metal samples is summarized in Table 5.

Table 5 Time to Dissolve Contaminated Be Metal Samples

Expt. No.	Be Metal Mass (g)	Solution HNO_3 (M)	Solution KF (M)	Target Temperature (°C)	Maximum Temperature (°C)	Dissolution Time (min)
Be-17	2.3043	4	0.1	80	101	75
Be-18	2.2973	4	0.1	70	77	150
Be-19	2.7097	4	0.1	70	91	100
Be-20	2.5308	4	0.2	70	87	100

The dissolution times given in Table 5 are approximate; the times were based on visual observations that no metal remained in the dissolving vessel. In each experiment, the dissolution proceeded slowly at first based on the observed gas collection rate. When the temperature reached 60-70°C, gas generation increased and the appearance of the gas collected in the Tedlar® bag became browner in color. The brown gas indicated changes in the dissolution path at the higher temperatures which resulted in the production of more NO_2 (equation 6). In experiments Be-18, Be-19, and Be-20, an effort was made to minimize the temperature increase above 70°C by turning the heating mantle off (at approximately 65°C) prior to reaching the target temperature. However, in each experiment the heat produced by the Be dissolution and the insulating capacity of the heating mantle was sufficient to increase the temperature 10-20°C above the target values.

In general, the contaminated Be samples and the Be metal foils dissolved in a consistent manner; although, the volume of offgas generated by the sample dissolved in experiment Be-18 was considerably less than the volume generated in the other experiments (see following discussion). The dissolving solution was filtered (using medium porosity paper, > 2.5 μm particle retention) following each experiment; however, very few residual solids were collected. Samples of the solution from experiments Be-17 and Be-18 were analyzed for ^{238}Pu and $^{239/240}$Pu by thenolytrifluoroacetone (TTA) extraction/alpha pulse height analysis (APHA) and trace metal constituents by Inductively Coupled Plasma Emission Spectroscopy (ICP-ES). The ratios of Pu to Be in the samples were 0.003 and 0.008 g Pu/g Be, respectively.

The analyses of the solutions used for the dissolution of the two samples showed that the Be metal was very pure. Impurities other than potassium (K, from the KF used in the dissolving solution) which had the highest concentrations include silicon (Si), sodium (Na), and antimony (Sb). The Si is likely from the corrosion of the dissolving vessel during the dissolution and the Na could be present as an impurity in the KF. It is unclear whether the Sb was present as an impurity in the Be metal or the concentration was biased high due to interferences between elements during the ICP-ES analyses.

During the contaminated Be dissolutions, multiple gas samples were collected to characterize the offgas. The raw data from the gas analyses were adjusted in the same manner as the analyses from the dissolution of the Be metal foils to account for dilution from gas in the dissolution vessel, condenser, plastic tubing, and sample bulb. The adjusted concentrations, sample time interval, temperature range, and volume of offgas collected are shown in Table 6.

Table 6 Characterization of Offgas from Contaminated Be Metal Dissolutions

Expt./Sample No.	Time Interval (min)	Temperature Range (°C)	Offgas Collected (mL)	Adjusted H_2 (vol%)	Adjusted N_2O (vol%)
Be-17/1	0-30	23-79	233	31	BDL
Be-17/2	30-36	79-96	259	NR	2.7
Be-17/3	36-41	96-100	608	3.2	NR
Be-17/4	41-53	100-101	737	9.7	0.46
Be-17/5	53-75	101-97	18	17	10.6
Be-18/1	0-70	24-71	411	76	0.35
Be-18/2	70-150	71-77-68	31	NR	BDL
Be-19/1	0-60	24-75	428	19	0.11
Be-19-2	60-70	75-83	342	8.8	4.6
Be-19/3	70-75	83-87	193	NR	NR
Be-19/4	75-100	87-91-82	487	1.2	0.21
Be-20/1	0-60	24-71	373	55	BDL
Be-20/2	60-73	71-80	265	NR	1.7
Be-20/3	73-82	80-85	598	NR	0.67
Be-20/4	82-87	85-87	504	3.9	1.3
Be-20/5	87-100	87-82	213	1.3	NR

NR – not reported
BDL – below detection limit

The data in Table 6 show that the maximum H_2 generation rate occurred at temperatures below 70-80°C. At lower temperatures, the dissolution of the Be by a metal/acid dissolution mechanism (equation 3) was apparently maximized. As the temperature increased above this range, the dissolution proceeded to a greater extent by NO_3^- oxidation (equations 6-8). This assertion is supported by the color of the offgas observed in the Tedlar® bags. The offgas collected during the initial sample interval generally had less color than the offgas collected during the remainder of the experiments. A number of adjusted concentrations in Table 6 were not reported due to a low bias in the measured concentration which gave inconsistent results when adjusted to account for dilution from gases in the dissolution system.

The amount of offgas collected as a function of the amount of Be dissolved during each experiment is summarized in Table 7.

Table 7 Ratio of Offgas Produced to Amount of Be Dissolved

Experiment No.	Offgas:Be Ratio (mole/mole)
Be-17	0.30
Be-18	0.07
Be-19	0.20
Be-20	0.28

The offgas:Be ratios for experiments Be-17 and Be-20 are consistent with the 0.31 mole/mole collected during the dissolution of the Be metal foils. The ratio for experiment Be-19 was biased low due to a leak from the dissolution system when the quick disconnect on one of the Tedlar® bags was not properly seated and flow was obstructed. The low value obtained for experiment Be-18 cannot be completely explained. The Be metal used in this experiment was different in appearance from the other three samples. The sample was thicker and the edges were rougher in appearance where the material was broken. The elemental analysis of the dissolving solutions for experiments Be-17 and Be-18 do not show a significant difference; therefore, the difference in the offgas generation rates cannot be attributed to differences in composition. Hardy et al. reported differences in the dissolution (rate) behavior of Be metal for materials which were fabricated using different methods. [2] Therefore, it is possible that the fabrication history of the Be metal sample could have influenced its dissolution behavior resulting in the generation of less offgas. The Be metal samples used in experiments Be-17, Be-19, and Be-20 were similar in appearance and generally dissolved in the same manner.

Pu Metal Dissolution

The conditions selected for the Pu metal dissolution were expected to generate a dissolution rate of nominally 10 mg/cm^2-min based on work performed at Rocky Flats.[5] At the beginning of the experiment, the dissolution rate was probably consistent with this value; however, as the dissolution progressed, the rate of dissolution slowed. The first 72% of the metal was dissolved/oxidized in approximately 5 h. The last 18% of the metal required 7.5 h for complete dissolution/oxidation. The steady decrease in the dissolution rate was attributed to the complexation of F^- by the dissolved Pu. The F^- became unavailable to catalyze the dissolution of PuO_2 which formed on the surface of the metal and inhibited the dissolution rate. A reduction in the final Pu concentration and/or an increase in the F^- concentration would improve the overall dissolution rate; however, precipitation of PuF_4 must be avoided.

Complete solubilization of the Pu was not achieved. Plutonium oxide solids generated during the dissolution were collected by filtration (using medium porosity paper, > 2.5 μm particle retention). No Pu metal was observed in the solids. The filter paper and solids were calcined at 600°C, ground, and dissolved in boiling 8 M HNO_3/0.1 M KF for 3 h. The resulting solution was then filtered upon cooling. Essentially all of the solid material dissolved. The filter paper collected a small amount of very fine white powder which was probably silica from corrosion of the dissolution vessel. Samples of the solutions from the Pu metal and residue dissolutions were analyzed for ^{238}Pu and $^{239/240}$Pu by TTA extraction/APHA and for ^{241}Pu and americium-241

(^{241}Am) by gamma pulse height analysis (GPHA). An elemental analysis was performed by ICP-ES.

The radiochemical analyses indicated that 90% of the Pu metal dissolved during the initial dissolution. As noted above, the decrease in the dissolution rate and formation of PuO_2 was probably due to a reduction in the free F^- concentration from complexation with Pu. An increase in the F^- concentration to 0.15-0.2 M was recommended to increase the dissolution rate and decrease the amount of PuO_2 which forms during dissolution. An increase of this magnitude would not be expected to cause the precipitation of PuF_4. The ICP-ES analysis showed that the Pu metal was relatively pure. The presence of the small amount of impurities had essentially no influence on the dissolution characteristics of the metal.

During the analysis of the offgas samples from the Pu dissolution, one of the samples was contaminated with air. The H_2 concentration in the remaining offgas sample when adjusted for dilution was 2.6 vol%. A small amount (1.4 vol%) of N_2O was detected. The presence of NO_2 was also identified based on the light brown color of the collected offgas. The total volumes of gas collected during the two sample periods were 0.17 and 0.48 mole of offgas per mole of Pu dissolved.

Conclusions

A series of small-scale experiments was used to measure the dissolution rate of Be metal foils in (3-8 M) HNO_3 solutions containing (0.0135-0.2 M) KF at 40-105°C. The experiments demonstrated that the dissolution rate was nearly independent of the HNO_3 concentration over the range of investigation and only a moderate to weak function of the F^- concentration. The effect of temperature was more pronounced, increasing the dissolution rate by a factor of approximately 15 between 40 and 105°C. In subsequent experiments, the offgas from three Be metal foil dissolutions was collected and analyzed to characterize the composition. The production of H_2 was found to be sensitive to the HNO_3 concentration decreasing by a factor of approximately two when the concentration was increased from 4 to 8 M. Complete dissolution of Be samples from a Pu/Be composite material was achieved using a 4 M HNO_3 solution containing 0.1-0.2 M KF. Multiple gas samples collected during each experiment showed that the maximum H_2 generation rate occurred at temperatures below 70-80°C. Lower temperatures favored the production of H_2 by a metal/acid dissolution mechanism. As the temperature increased above this range, the dissolution proceeded to a greater extent by NO_3^- oxidation.

A Pu metal dissolution experiment was performed using a 4 M HNO_3/0.1 M KF solution at 80°C to demonstrate flowsheet conditions developed for the dissolution of Be metal. As the reaction progressed, the rate of dissolution slowed. The decrease in rate was attributed to the complexation of F^- by the dissolved Pu. The F^- became unavailable to catalyze the dissolution of PuO_2 formed on the surface of the metal which inhibited the dissolution rate. An increase in the F^- concentration to 0.15-0.2 M was recommended to increase the dissolution rate and decrease the amount of PuO_2 solids which form during dissolution. Offgas analysis performed following the metal dissolution showed the presence of 2.6 vol% H_2 and a small amount of N_2O. The presence of NO_2 was also identified based on the light brown color of the collected offgas.

Flowsheet Recommendations

The use of a 4 M HNO_3 solution containing 0.15-0.2 M KF at 70-80°C was recommended for the dissolution of approximately 500 g of Pu metal containing minor amounts (~ 50 g) of Be in nominally 15 L of solution. As the Pu metal dissolves, the dissolution rate will slow due to a reduction in the free F^- by complexation. The reduction in the free F^- will result in the formation of increased amounts of PuO_2 on the metal surface which further inhibits the dissolution. For this reason, an 8-10 h dissolution time was recommended to digest any PuO_2 solids with an increase in the dissolving temperature (to near boiling) during the final 4-6 h to facilitate the digestion of the solids. Dilution of the H_2 concentration below 25% of the lower flammability limit by purging the dissolver with air is necessary to eliminate the flammability concern.

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Figure 1 Dissolution of Be Metal in HNO_3[2]

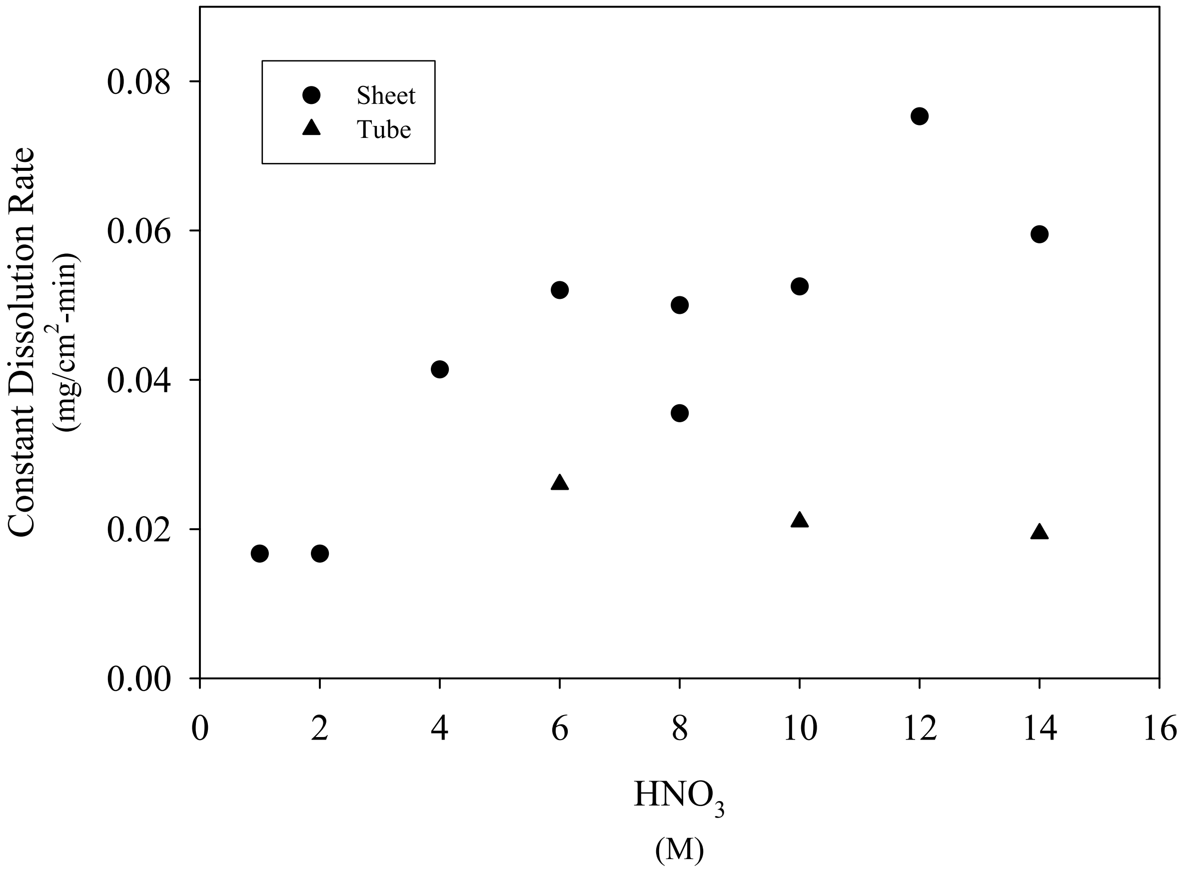

Figure 2 Dissolution Rate of Cylinders of Be-containing $^{238}PuO_2$ Scrap[4]

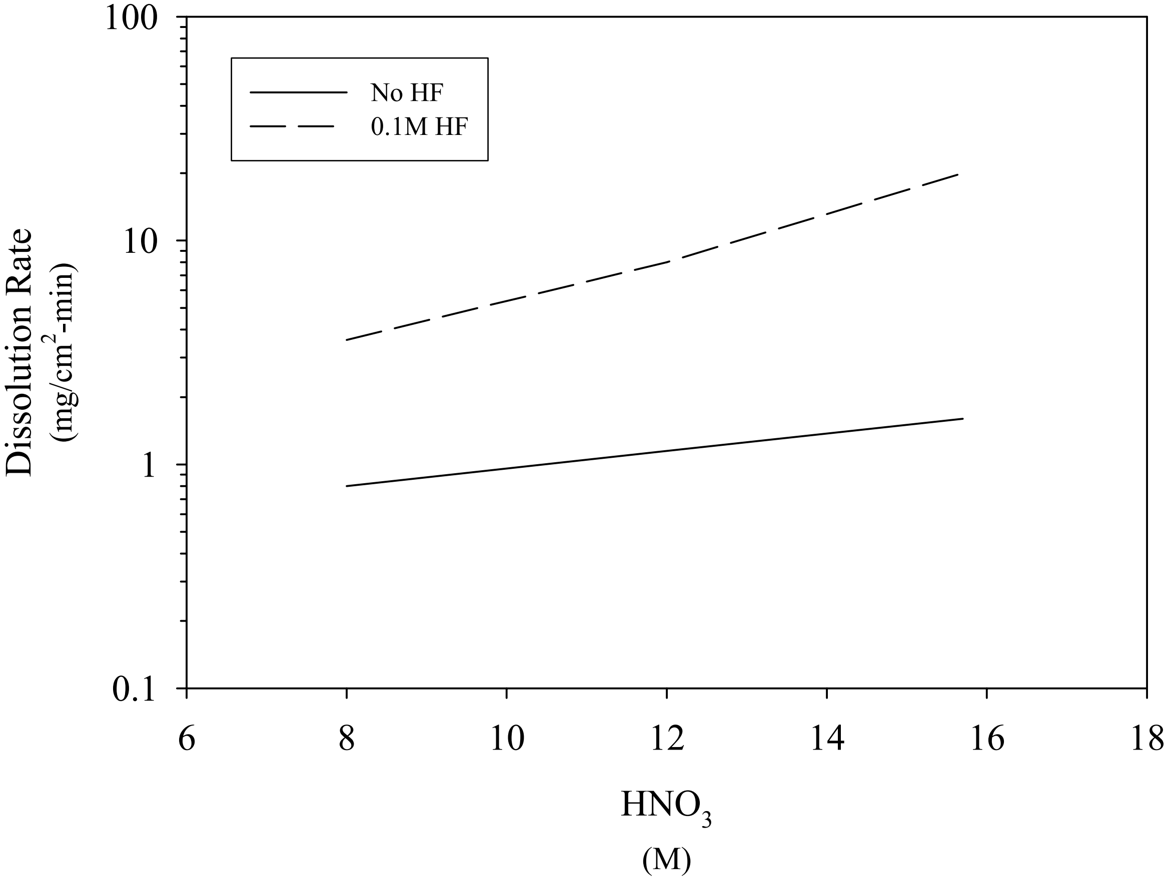

Figure 3 Arrhenius Temperature Dependence of Dissolution Rate Constant