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Dissolution of Plutonium Scrub Alloy and Anode Heel Materials in H-Canyon

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SUMMARY

H-Canyon has a "gap" in dissolver operations during the last three months of FY03 in which they can dissolve FB-Line legacy residues. One group of material to be processed during the gap is pre-existing scrub alloy material received from the Rocky Flats Plant in the early 1980's. There are 14 cans of material containing approximately 3.8 kilograms of plutonium. Of the 14 cans, it was anticipated that four cans contain salts from the Molten Salt Extraction (MSE) process, two cans contain anode heel materials, and eight cans contain scrub alloy buttons.

H-Canyon desires to process the materials using a flowsheet similar to the SS&C (sand, slag and crucible) dissolution flowsheet used in F-Canyon. The proposed flowsheet for this material will have a starting nitric acid (HNO_3) level of ~3M, an ending acid level of ~ 1.5M, 0.002M mercury, ~2 g/L boron, and 0.15M CaF_2 (calcium fluoride). The materials will be loaded into carbon steel cans and then placed into aluminum metal charging bundles.

Samples of 13 items were sent to Savannah River Technology Center (SRTC) for characterization and flowsheet testing -- four MSE salts, two anode heels, and seven scrub alloy buttons. SRTC dissolved and characterized each of the samples. Two of them, originally thought to be MSE salts, were found to be graphite mold materials and were unsuitable for processing in H-Canyon. Characterization studies confirmed that the identification of the remaining items as MSE salts, scrub alloy buttons, and anode heel materials was correct.

The MSE salts and anode heels solids are comprised primarily of plutonium, potassium, sodium and chloride. The solids dissolve readily in 4M HNO_3/0.3M HF (hydrofluoric acid) without any noticeable gas generation. Both the MSE salts and anode heels left behind small amounts of residual solids. The scrub alloy buttons are comprised primarily of plutonium and aluminum. The solids dissolve readily with light, effervescent gas generation at the material surface and only trace amounts of NOx generation. Of the seven button samples, four dissolved completely. Two button samples contained small amounts of tantalum that did not dissolve. The last of the seven scrub alloy samples left a trace amount of residual plutonium solids. It is anticipated that the presence of undissolved fissile material is a function of where the sample was located relative to the button surface.

Process simulation experiments followed characterization studies. The baseline flowsheet (starting HNO_3 ~3.0M) was tested along with an increased-acid flowsheet (starting HNO_3 ~5.5M) at a 1:10,000 scale. Experiments show that both flowsheets are effective in dissolving the scrub alloy buttons, MSE salts, and anode heel samples. The vigor of the reaction of nitric acid with the items is characterized as a gentle "fizz" at the surface of the scrub alloy button samples with only trace amounts of NOx generation. As a result, the aggressiveness of overall process is determined by the dissolution of the steel cans and aluminum charge bundles. If a starting acid concentration of 3.0M is used, the final baseline free nitric acid concentration will be approximately 1.7M, which is sufficiently high to avoid the formation of plutonium polymer. Processing of all 14 samples in H-Canyon using the baseline flowsheet is expected to produce about 1.3 wt.% residual solid containing about 1.3% of the plutonium.

When the characterization data for the individual samples are used to predict final anion and cation concentrations for the simulant experiments, good agreement is observed between the two data sets. However, for most samples, the plutonium assay values determined experimentally do not correspond with FB-Line assay values. It is unclear how much of the difference can be attributed to analytical techniques and sample preparation methods in SRTC versus inaccuracies in the original assay values or heterogeneity in the samples.

Three differences exist between the proposed baseline flowsheet and the as-tested flowsheet. First, the mercury catalyst, aluminum charge bundles, and steel cans were omitted and simulated by dissolved aluminum nitrate and iron nitrate. During the dissolution of charge bundles and steel cans, large amounts of NOx are released. Since the presence of NOx improves dissolution, the omission of the catalyst, charge bundles, and steel cans will not have a negative effect on overall dissolution behavior. Second, prior to sampling of the scrub alloy materials, a decision was made not to sample a can containing a plutonium/gallium alloy button. Because earlier work shows that plutonium/aluminum and plutonium/gallium behave similarly, the omission of the plutonium/gallium button from the SRTC experimental program is not expected to impact the recommended flowsheet. Last, the presence of nylon bag material in the experiments was omitted because of prior experience showing that dissolved nylon bag does not affect the dissolution process.

INTRODUCTION

During the last three months of FY03, H-Canyon has a "gap" in dissolver operations in which they can dissolve FB-Line legacy residues. One group of material to be processed during the gap is pre-existing scrub alloy material received from the Rocky Flats Plant (RFP) in the early 1980's.[1] There are 14 cans of material containing approximately 3.8 kilograms of plutonium. Of the 14 cans, it is believed that four are salts from the molten salt extraction (MSE) process, two are anode heels from the electrorefining process, one is a plutonium-gallium (Pu/Ga) button, and seven are plutonium/aluminum (Pu/Al) scrub alloy buttons. The scrub alloy buttons were produced at RFP to recover plutonium from MSE salts. SRS has processed scrub alloy materials in F-Canyon.[2,3]

H-Canyon plans to process these materials using a flowsheet similar to the one used to dissolve SS&C (sand, slag and crucible) in F-Canyon.[4] The proposed flowsheet for this material will have a starting nitric acid (HNO_3) level of ~3M, an ending acid level of ~ 1.5M, 0.002 M mercury, ~2 g/L boron, and 0.15M CaF_2 (calcium fluoride). The F-Canyon dissolver was operated at 90-95^{o}C to minimize corrosion and reduce residual ruthenium volatility. The materials will be charged into carbon steel cans that are placed in nylon bags and loaded into aluminum metal charging bundles. The carbon steel cans and aluminum charging bundles react with HNO_3, dissolve, and generate NOx gas as a reaction byproduct. Once dissolved, the material will be neutralized and discarded as waste.

Samples of the MSE salts, anode heels, and scrub alloy materials were sent to Savannah River Technology Center (SRTC) for characterization and flowsheet testing. The Pu/Ga button was not sampled because its composition and behavior for the proposed flowsheet conditions are known from earlier studies.[5] SRTC performed dissolution studies on each of the samples to individually characterize them. After the characterization tests, SRTC evaluated the proposed flowsheet to ensure that the materials will dissolve adequately in the H-Canyon dissolver.

EXPERIMENTAL DESCRIPTION

The experimental work was performed in two stages, 1) characterization of the samples and 2) simulated H-Canyon dissolution. Each stage will be discussed separately.

SAMPLE CHARACTERIZATION

SRTC received samples from 13 FB-Line items targeted for dissolution in H-Canyon. The samples are identified as MC03-17 through MC03-29. Information about the samples is listed in Table 1.

Acid solutions were prepared for dissolution of each sample. Hydrofluoric acid (HF) was used as a fluoride source for characterization to prevent cation interference during subsequent analyses. Deionized water was combined with 255 mL of 15.7M HNO_3 and 10.15 mL of 29.6M HF. The final concentration of the acid is calculated to be 4M HNO_3 and 0.3M HF. An additional 300 mL of 8M HNO_3/0.2M HF was prepared by combining 200 mL of 4M HNO_3/0.3M HF with 100 mL of 15.7M HNO_3.

The solid samples were opened and photographed. The first set of characterization tests was performed as follows. For each sample, an empty 150-mL beaker was weighed. Next, 0.5 grams of sample was added to the empty beaker and weighed. Thirty milliliters of 4M HNO_3/0.3M HF were added to the beaker, and the beaker was weighed again.

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[1] J. E. Therrell, "Evaluation of Processing Scrub Alloy Items in Material Characterization," NMM-EFL-03-028, March 2003.
[2] J. H. Gray. "Flowsheet for Processing Scrub Alloy Materials in Canyon Dissolvers," WSRC-TR-2000-00327, August 2000.
[3] J. H. Gray. "The Characterization and Dissolution of Scrub Alloy Buttons in F-Canyon," WSRC-TR-2000-00516, January 2001.
[4] D. G. Karraker, et. al. "Flowsheet Modifications for Dissolution of Sand, Slag, and Crucible Residues in the F-Canyon Dissolvers," WSRC-TR-97-00395, December 1997.
[5] J. H. Gray. "The Characterization and Dissolution of Scrub Alloy Buttons in F-Canyon, WSRC-TR-2000-00516, January 2001.

Each beaker was covered with a watch glass, and water was placed in each watch glass. The watch glass helps limit evaporation of acid during heating.

Each beaker was placed on a hot plate and heated to 55°C for 90 minutes. After 90 minutes, observations were made and recorded regarding the degree of dissolution. The beaker was then heated to 90-95°C for 90 minutes. Once again, observations were made and recorded. The samples may have been heated for longer times if it was judged beneficial to the characterization efforts. When heating was complete, the beakers were allowed to cool to ambient temperature. The watch glass was removed and the beaker was weighed again to determine how much liquid had evaporated.

Table 1. SRTC Sample Information

Item ID	Expected Fissile Wgt. (grams)	Net Wgt. (grams)	Sample Weight (grams)	Expected Material Type	Disposition Path
MC03-17/A	415	1732	28.8	MSE Salt	Send to H-Canyon
MC03-18/A	388	1665	26.7	MSE Salt	Send to H-Canyon
MC03-19	*4*	*990*	*28.9*	*MSE Salt*	*Disposed as Solid Graphite Waste*
MC03-20	*130*	*762*	*29.1*	*MSE Salt*	*Disposed as Solid Graphite Waste*
MC03-21	251	1390	2.1	Scrub Alloy Button	Send to H-Canyon
MC03-22	277	1462	2.0	Scrub Alloy Button	Send to H-Canyon
MC03-23	268	1540	1.9	Scrub Alloy Button	Send to H-Canyon
MC03-24	276	1374	2.1	Scrub Alloy Button	Send to H-Canyon
MC03-25	199	1040	3.4	Scrub Alloy Button	Send to H-Canyon
MC03-26	318	1197	3.7	Scrub Alloy Button	Send to H-Canyon
MC03-27	289	1156	2.3	Scrub Alloy Button	Send to H-Canyon
MC03-28	178	192	1.9	Anode Heel	Send to H-Canyon
MC03-29	181	194	2.7	Anode Heel	Send to H-Canyon
Total to Send to H-Canyon	**3040**	**12942**	---	---	---

If solids remained in the beaker, the solids were filtered through a weighed 0.45-μm filter. The filter paper was weighed again after drying in air overnight. The filter paper was then dried in air in an oven at 130°C for three hours. Once dry, the filter paper and dried solid were weighed again. Solid samples were submitted for analysis using scanning electron microscopy (SEM). At the time of sampling, x-ray diffraction (XRD) was not available for radioactive samples. Filtrate samples were submitted for analysis by ion chromatography (IC), inductively coupled plasma emission spectroscopy (ICPES), alpha pulse height analysis (alpha PHA), gamma pulse height analysis (gamma PHA), and gross alpha (Radscreen).

The process was repeated for samples MC03-19 and MC03-20 that were ground with a mortar and pestle prior to dissolution. When filtered and dried, these filter paper samples were dried at 100°C for three hours. The test samples are designated as MC03-19G and MC03-20G.

Because of the presence of residual solids in several samples, the above procedure was repeated using 0.25-grams samples in 30 mL of 8M HNO_3/0.2M HF. The samples dissolved in this manner included MC03-17, -18, -22, -23, -26, -28, and -29. The samples were only heated at 90-95°C for three hours. After dissolution, the solids were filtered and submitted for gamma PHA. Liquid samples were submitted for ICPES, alpha PHA, gamma PHA, and Radscreen.

Because of the lack of dissolution observed in samples MC03-19 and MC03-20 and data from SEM, it was judged that the samples contained large amounts (>75%) carbonaceous materials. Therefore, a magnesium oxide (MgO) crucible was weighed and charged with residual MC03-19 solids from the dissolution tests. The solids were dried in

a furnace at 150°C in air for three hours. The crucible and dried solids were weighed. The crucible and solids were then heated in air to 1025°C for three hours. Upon cooling, the crucible and residual solids were weighed again.

SIMULATED H-CANYON DISSOLUTION

The proposed flowsheet for H-Canyon dissolution of these plutonium-bearing materials is based on a flowsheet used in F-Canyon for dissolving sand, slag and crucible (SS&C).[4] A major departure from the SS&C flowsheet is the use of 3M HNO_3 instead of 9.3M HNO_3 to reduce the amount of acid that must be neutralized prior to sending the final solution to waste. The material processing will be performed in 7500 liters of solution. The targeted starting conditions are 3M HNO_3, 0.002 M mercury, ~2 g/L boron, and 0.15M CaF_2. Other process assumptions include:

- The materials will be dissolved into a single batch of acid in a series of three charges. The first charge will contain a Pu/Ga button, MC03-17 and MC03-18. The second charge will contain MC03-22, -25, -26, -28, and -29. The third charge will include MC03-21, -23, -24, and -27.
- Sixteen carbon steel cans at 250 grams each and 16 carbon steel cans at 120 grams each will be added more or less evenly over the three charges and produce a final iron concentration of ~0.79 g/L or 0.014M.
- Nine aluminum charging bundles at 6.8 kilograms each will be added evenly over the three charges and produce a final aluminum concentration of ~8.2 g/L or 0.303M.
- One mole of aluminum metal will react with 3.75 moles of HNO_3 in the presence of Hg^{2+} to yield aluminum nitrate, NO, N_2O, and N_2.[6] Calculations show that the reaction will deplete the dissolver nitric acid by approximately 0.5M per charge. This depletion will yield a final acid concentration in the dissolver of ~1.5M.
- For the SRTC tests, the addition of an appropriate amount of solid $Fe(NO_3)_3$-$9H_2O$ and $Al(NO_3)_3$-$9H_2O$ will simulate the dissolution of the aluminum charge tubes and steel cans. Solid sodium hydroxide (NaOH) is added and dissolved before the plutonium samples to account for the acid depletion associated with the charge tube and steel can dissolution reactions.
- For the SRTC tests, the nylon bag material is disregarded. Prior experiences shows that dissolved nylon bag material at low concentrations does not affect canyon processing.[7]

The dissolution was performed in a 2000-mL beaker with a specially designed cover to reflux vapors and maintain a constant liquid volume in the dissolver. The beaker was filled with 750 mL of starting solution (2.5M HNO_3, ~2 g/L B, 0.15M CaF_2, 0.101M $Al(NO_3)_3$, and 0.05M $Fe(NO_3)_3$). The matrix assumes that the steel cans and aluminum bundles of the first charge have dissolved and depleted the acid by 0.5M. The starting solution was heated to and controlled at 90-95°C.

Once at temperature, the first charge of material was added to the dissolver pot. The material was dissolved at temperature for 12 hours or until the material dissolved completely. As necessary, the dissolution time was spread over two days. When the first charge cycle was complete, $Fe(NO_3)_3$-$9H_2O$ (12.120 g) and $Al(NO_3)_3$-$9H_2O$ (28.418 g), were added to the dissolver to simulate the dissolution of steel cans and aluminum bundles. Sodium hydroxide (15.000 g) was also added to simulate the coinciding acid depletion of the material charge due to the aluminum and iron metal dissolution reactions. When the $Fe(NO_3)_3$-$9H_2O$, $Al(NO_3)_3$-$9H_2O$ and NaOH were dissolved, the second charge of Pu-bearing materials was added and dissolved at temperature for 12 hours or until the materials dissolved completely. The process chemical addition and sample dissolution were repeated for the third charge of materials.

Upon completion of dissolution, the liquid was cooled to ambient temperature. The liquid was then filtered through a 0.45-μm filter. Duplicate liquid samples were submitted for analysis by ICPES, IC, RadScreen, Alpha PHA, and Gamma PHA. The solids were analyzed using Gamma PHA.

A second simulation experiment was conducted at an elevated starting acid to determine if increased acid would decrease the amount and fissile content of any residual solids. For the second test, the assumed starting conditions were 5.5M HNO_3, ~2 g/L B, and 0.15M CaF_2. The test was conducted in the same manner as the first.

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[6] W. S. Durant and W. C. Perkins. "Systems Analysis – 200 Area, Savannah River Plant, H-Canyon Operations." DPSTSY-200-1H, Volume 1, p. F-10, October 1983.

[7] R. A. Pierce. "Testing of Acid-Soluble Plastics for SS&C Processing in F-Canyon," SRT-CTS-96-0120, November 1996.

A final experiment was conducted using a sealed vessel with only periodic venting to control evaporative losses of chloride. The vessel was charged with 250 mL of 5.0M HNO_3/0.3M HF. Samples of all materials targeted for H-Canyon dissolution (excluding MC03-19 and -20) were charged at the appropriate amounts to simulate anion and cation loading in the H-Canyon dissolver independent of the batch chemicals. The solution was heated to 90-95°C for eight hours and then cooled. Duplicate samples were submitted for analysis using IC and ICPES.

DISCUSSION OF RESULTS

SAMPLE CHARACTERIZATION

The discussion of sample characterization results will focus on one class of materials at a time to allow better understanding of all the samples of a certain class by comparison and contrast. According to expectations, there were three material types. In reality there ended up being four material types: MSE Salts (MC03-17 and -18), Scrub Alloy Buttons (MC03-21 through -27), Anode Heels (MC03-28 and -29), and Unidentified Carbonaceous Materials (MC03-19 and -20). Representative pictures of the as-received materials are in Attachment 1.

DISSOLUTION CHARACTERISTICS

MSE Salts: Both MSE salts behaved similarly in 4M HNO_3/0.3M HF and in 8M HNO_3/0.2M HF. In 4M HNO_3/0.3M HF, the bulk of the material dissolved readily and left behind a pink residue (see Figure 1). The weight percent residual solid for MC03-18 was calculated at 6.9%; a value for MC03-17 was not obtained. The second dissolution, occurring in 8M HNO_3/0.2M HF, yielded complete dissolution for both samples. Filtering yielded no visible solids.

Figure 1. MC03-17 Residue

Scrub Alloy Buttons: The seven scrub alloy buttons behaved similarly, in general, but did exhibit some noticeable differences. All seven samples reacted immediately with the 4M HNO_3/0.3M HF solution upon contact, and required heating to obtain complete dissolution. However, of the seven, three samples did not dissolve completely. Samples MC03-22, -23, and –26 all left a small amount of residue.

Figure 2. MC03-23 Undissolved Solids

The solids from MC03-22 and –23 were fine black powders and appeared to be the same. The filtered solids represented 9.5 and 7.3 weight percent, respectively, of the initial sample weight. Extended contact in excess of five hours with the acid at 90-95°C did not cause further dissolution. The residue from MC03-26, accounting for about 4.5 weight percent, was tan colored. A picture of the residue in the beaker from MC03-23 is shown in Figure 2. A picture of the MC03-26 solids is not included because the solids are not visible in the pictures. Solids were submitted for SEM analysis. Dissolution of MC03-22, -23, and -26 in 8M HNO_3/0.2M HF yielded similar results. In all three cases, solids remained after 90 minutes at 90-95°C. The solids were once again filtered. However, the solids from these dissolution tests were sent for gamma radiation counting instead of drying and weighing them.

Anode Heels: The two anode heel samples behaved similarly. Both dissolved some in 4M HNO_3/0.3M HF, but left behind a visible amount of fine black solids even though they were heated for five hours at 90-95°C. MC03-22 and –23, respectively, left behind 5.2 and 12.0 weight percent residue. A picture of undissolved residue from MC03-28 is shown in Figure 3.

Unidentified Carbonaceous Materials: Samples MC03-19 and -20, originally thought to be MSE salts, behaved similarly, but nothing like the MSE salts of MC03-17 and -18. Both samples dissolved sparingly in either 4M HNO_3/0.3M HF or 8M HNO_3/0.2M HF. Dissolution of MC03-19 could not be visibly detected in the dissolution acid. Figure 4 shows that the dissolving acid remains colorless after contact with the sample at 90-95°C for three

hours. MC03-20 exhibits some color change upon dissolution, but still much less than the other samples. Attempts to calculate the percent of undissolved solids were not successful.

Because sample MC03-20 was a finer material (see Attachment 1) and dissolved better than MC03-19, the dissolution in 4M HNO_3/0.3M HF was repeated with sample that had been ground with a mortar and pestle to increase surface area. However, the dissolution behavior remained essentially unchanged. Calculations show that the weight percent undissolved sample for MC03-19G and –20G were 95.8% and 87.2%, respectively.

Figure 3. MC03-28 Undissolved Solids

Figure 4. MC03-19 Undissolved Solids

CHEMICAL CHARACTERISTICS

The analytical data from ICPES are contained in Attachment 2 (ICPES). A review of the data in conjunction with what is known about the samples leads to several considerations when assessing the ICPES data. First, the presence of boron (B) and silicon (Si) in the samples are the result of borosilicate glass (from the beaker) dissolution by HNO_3/HF. Second, the indicated presence of both cerium (Ce) and uranium (U) in all of the samples is almost certainly an artifact of spectral interference caused by plutonium (Pu). A comparison of both Ce and U concentrations with Pu shows a strong linear relationship for both Ce and U across all 13 samples. Subsequent conclusions made about the composition of each sample assume that the B, Si, Ce, and U data are false positives with respect to the sample composition. .

Measured potassium (K) data are not reported for all samples because a different ICPES technique was needed due to the presence of carbonaceous materials in some samples, particularly in MC03-19 and MC03-20, which created an interference with potassium. However, because it is known that MSE salts have nearly equimolar ratios of KCl and NaCl, a derived potassium value could be estimated from the sodium data. An average of the nine measured potassium values in Attachment 2 shows a KCl:NaCl molar ratio of 0.836 (the ratio varies between 0.76 and 0.92). This average value has been used in conjunction with the sodium data to estimate potassium values for the other samples. The calculated potassium values in Attachment 2 are listed as red-bold-italicized text.

The analytical data from IC are contained in Attachment 3. As a reference point, unheated 4M HNO_3 /0.3M HF solutions contain 248,000 mg/L NO_3^- and 5700 mg/L F^-. In general, the samples show good agreement with the calculated NO_3^- concentration. The fluoride values are all low and the difference from the projected value varies greatly. The measured fluoride data indicates that either fluoride evaporation or reaction with the glass beaker is occurring, which would not be surprising. If evaporation is the reason, those samples that had a thermocouple in them would have been more susceptible to evaporation. The watch glass cover on top of the thermocouple does not seal the beaker top as effectively as without the thermocouple. In a similar manner, it is possible that the samples may have exhibited chloride losses due to evaporation.

Radiochemical data (alpha and gamma) are contained in Attachment 4. Although both alpha and gamma data are available, it is general practice to use alpha values in calculating Pu-239 values and gamma values for calculating Am-241 levels. As such, assay values for each material are determined accordingly. The recorded alpha values are the average of measurements taken using Alpha PHA and Alpha Radscreen. In general, more deviation was

observed in the first data set (4M HNO_3/0.3M HF) than in the second set (8M HNO_3/0.2M HF). It is thought that solids may have been present in some of the samples from the 4M HNO_3/0.3M HF that were not filtered. Furthermore, since 8M HNO_3/0.2M HF should yield better sample dissolution for characterization, and because the alpha and gamma values show good agreement, the second data set, whenever available, was used to calculate assay values. The only exception is for MC03-28 where there is an apparent error in the measured alpha value. For assay of solids, only Gamma PHA is used because self-shielding distorts alpha measurements. Although dissolved in 4M HNO_3/0.3M HF, samples MC03-19G and -20G were tested as part of the second sample set.

The differences in experimental assay values between the first and second sample sets are cause for concern, but a path for resolution is not immediately obvious. It is possible that the variances are caused by heterogeneity within the individual samples. The radiochemical data for the simulated process experiments diminishes the concern from a programmatic perspective. Those results provide good, repeatable characterization of the expected final H-Canyon dissolution product apart from the individual characterization tests and are discussed in a subsequent section.

A composite table of the liquid and solid data is contained in Table 2 as weight percent of original sample. The data do not account for any oxygen that might be associated with compounds in solution, which may affect the overall material balances. The material balance data show that the analyses account for most of the solid added to the experiment (typically 80-100%). For some of the 4M HNO_3/0.3M HF samples, the quality of the mass balance data is hindered by the lack of potassium data or inaccuracy of the potassium data due to carbon interference.

The residual solids data in Table 2 for the 4M HNO_3/0.3M HF samples are based on estimates using SEM data. The residual solids data in Table 2 for the 8M HNO3/0.2M HF samples are based on a combination of the RadChem data and the SEM analyses of the 4M HNO_3/0.3M HF samples. The composite data for the dissolution of carbonaceous solids reflects that very few solids dissolved into solution.

It is worth noting that of the seven MSE, scrub alloy, and anode heel samples that had residual solids after dissolution in 4M HNO_3/0.3M HF, those seven samples had high chloride concentrations. Similarly, of the four samples that dissolved completely in 4M HNO_3/0.3M HF, those four samples had little or no chloride. In light of the generally soluble nature of plutonium chlorides, and since SEM characterizations do not show the presence of chloride in the residual solids, a correlation of the effect of chloride on dissolution performance is not immediately understood.

MSE Salts: Analysis of the residual solids using SEM revealed that the only material detectable was plutonium. Because of the light pink color (see Figure 1) and the presence of fluoride in solution, and since SEM can detect chloride but not fluoride, it is anticipated that the residue is a hydrated plutonium fluoride (PuF_4-nH_2O).[8] Upon dissolution in 8M HNO_3/0.2M HF, no residual solids were observed. The concern that plutonium fluoride solids will form during H-Canyon processing is minimal. The literature states the PuF_4 dissolves with comparative ease in aqueous solution that form stable complexes with fluoride solutions such as Fe (III), Al (III), and BO_3^-.[8]

Liquid analyses show that the two samples are similar. The composition of Table 2 identifies the primary components as Pu, K, Na, and Cl, which is expected. Sampling also indicates relatively high (compared to the other 11 samples) amount of Am. This is expected because the MSE process concentrates americium. The material balances for the 4M HNO_3/0.3M HF tests appear better than the 8M HNO_3/0.2M HF tests. The reason for difference is unknown.

Scrub Alloy Buttons: SEM analyses of the residual solids show that the MC03-22 and -23 solids are about two-thirds tantalum compound and one-third plutonium compound (probably oxide). SEM analysis of MC03-26 shows almost exclusively unidentified plutonium compound. The tan color of the MC03-26 solids suggests they are PuO_2. Residual solids after dissolution in 8M HNO_3/0.2M HF show very little undissolved plutonium with sample MC03-22 having the most at 0.05 wt %.

[8] J.J. Katz, G.T. Seaborg, and L.R. Morss (eds). The Chemistry of the Actinide Elements, Second Edition. Chapman and Hall (London, 1986), p. 732-735.

Table 2. Composite Sample Characterization Data in Weight Percent

DISSOLUTION IN 4M HNO_3/0.3M HF

	Weight Percent in the Filtrate																	Weight Percent in Residual Solids				% Material Balance
	Al	Ca	Cu	Fe	K	La	Mg	Mn	Mo	Na	Ni	P	Sb	Sn	Cl-	Pu	Am	Pu	O	F	Ta	
MC03-17	0.49	0.08	0.08	0.07	9.42	0.04	3.27	0.02	0.03	7.34	0.04	0.01	0.04	0.05	37.61	32.62	1.47	5.56	---	1.77	---	93.3
MC03-18	0.44	0.06	0.08	0.05	6.72	0.04	3.01	0.02	0.04	4.60	0.04	0.02	0.04	0.04	24.80	52.65	0.68	5.07	---	1.61	---	102.9
MC03-19	0.85	0.54	0.01	0.05	3.44	0.00	0.42	0.00	0.01	2.42	0.00	0.01	0.07	0.05	0.00	81.35	0.00	---	---	---	---	27.9
MC03-20	3.05	2.13	0.18	1.02	2.74	0.07	0.15	0.05	0.08	1.92	0.28	0.01	0.09	0.11	0.00	78.16	0.12	---	---	---	---	30.0
MC03-21	73.46	0.10	0.07	0.10	0.21	0.03	0.10	0.02	0.08	0.14	0.06	0.04	0.20	0.08	0.00	25.29	0.03	---	---	---	---	95.8
MC03-22	53.50	0.84	0.09	0.11	1.90	0.02	0.20	0.01	0.06	1.34	0.03	0.03	0.15	0.07	5.88	26.61	0.06	2.70	1.49		5.09	104.3
MC03-23	54.93	2.09	0.09	0.14	1.94	0.03	0.33	0.01	0.06	1.37	0.03	0.04	0.16	0.07	11.28	21.15	0.05	1.85	1.02		3.49	116.5
MC03-24	73.24	0.01	0.08	0.16	0.14	0.03	0.01	0.02	0.09	0.10	0.04	0.05	0.20	0.08	0.00	25.65	0.10	---	---	---	---	90.0
MC03-25	78.90	0.00	0.10	0.15	0.21	0.02	0.05	0.01	0.07	0.15	0.02	0.04	0.21	0.08	0.00	19.91	0.08	---	---	---	---	91.4
MC03-26	33.56	0.94	0.05	0.08	6.46	0.02	7.04	0.01	0.05	4.55	0.03	0.02	0.11	0.05	23.13	17.93	0.91	4.77	0.64			89.4
MC03-27	42.93	0.16	0.13	0.07	0.56	0.06	4.13	0.03	0.08	0.39	0.04	0.05	0.16	0.09	2.08	46.76	2.27	---	---	---	---	88.4
MC03-28	1.00	0.04	0.61	1.24	1.80	0.08	0.16	0.10	0.19	1.27	1.27	0.07	0.10	0.11	12.15	73.53	0.08	5.56	0.74	---	---	83.6
MC03-29	0.80	0.04	0.17	0.11	5.05	0.07	0.39	0.04	0.07	3.56	0.08	0.03	0.07	0.08	15.71	61.03	0.12	11.69	1.56	---	---	95.6
MC03-19G	0.23	0.07	0.01	0.06	0.94	0.00	0.02	0.00	0.00	0.66	0.01	0.00	0.02	0.02	0.00	0.01	0.00	0.62	---	---	---	97.8
MC03-20G	0.79	0.63	0.02	0.82	0.97	0.01	0.06	0.04	0.02	0.68	0.03	0.01	0.01	0.02	0.00	4.72	0.03	0.47	---	---	---	95.7

-Tests indicate that Samples MC03-19 and MC03-19G contain at least 90.5 weight % graphite; MC03-20 and MC03-20G are similar sample

DISSOLUTION IN 8M HNO_3/0.2M HF

	Weight Percent in the Filtrate																	Weight Percent in Residual Solids				% Material Balance
	Al	Ca	Cu	Fe	K	La	Mg	Mn	Mo	Na	Ni	P	Sb	Sn	Cl-	Pu	Am	Pu	O	F	Ta	
MC03-17	0.76	0.05	0.09	0.08	13.61	0.04	4.74	0.02	0.04	8.94	0.03	0.01	0.05	0.08	44.12	25.66	1.68	---	---	---	---	79.6
MC03-18	0.84	0.38	0.10	0.07	14.01	0.05	5.39	0.03	0.05	10.22	0.03	0.04	0.06	0.07	38.65	29.28	0.74	---	---	---	---	84.7
MC03-22	54.30	1.66	0.12	0.15	5.30	0.03	0.29	0.02	0.07	3.35	0.03	0.04	0.17	0.08	6.94	20.34	0.07	0.05	1.13	---	5.09	88.4
MC03-23	46.43	5.21	0.09	0.15	5.93	0.03	0.35	0.01	0.07	4.16	0.03	0.04	0.15	0.08	16.65	15.40	0.04	0.02	0.77	---	3.49	82.1
MC03-26	32.89	1.24	0.06	0.11	9.19	0.03	9.6	0.02	0.06	6.45	0.04	0.01	0.12	0.07	24.33	14.69	1.09	0.01	0.00	---	---	79.0
MC03-28	1.67	0.13	0.68	1.14	10.82	0.09	0.43	0.09	0.29	8.31	1.28	0.07	0.12	0.17	14.67	59.99	0.08	0.03	0.00	---	---	69.2
MC03-29	1.26	0.09	0.23	0.17	8.27	0.09	0.70	0.06	0.07	5.84	0.11	0.04	0.09	0.13	18.46	64.22	0.16	0.01	0.00	---	---	81.4

Analysis of liquid samples show that all of the scrub alloy samples are primarily plutonium and aluminum. Six of the seven scrub alloy samples contain 15-27 wt. % plutonium. Only sample MC03-27 contains a significantly different amount (46.8 wt. %), but the overall material balance does not indicate any analytical problem.

Also worth noting, three of the scrub alloy samples contain greater than 5 wt.% chloride while three others have no measurable chloride. The three samples also have correspondingly higher values for sodium and potassium. What makes the difference between samples worth noting is that the three samples with greater than 5 wt.% chloride left residual solids while the four samples with little or no chloride dissolved completely. The differences in chloride levels may indicate that the samples with high chloride levels are closer to the button surface, hence higher KCl and NaCl concentrations. This is consistent with SRTC experience that scrub alloy buttons have higher chloride levels near the surface than toward the center of the button.[9,10] It is anticipated that the presence of undissolved material is more a function of where the sample was located relative to the button surface. The presence of tantalum in samples MC03-22 and MC03-23 is likely from the stirrer used when the button was made

Anode Heels: An attempt to identify the solids from the 4M HNO_3/0.3M HF tests using SEM was unsuccessful because the high radiation field associated with the solids overwhelmed the detector. It is expected that the high radiation field is caused by the presence of Am-241. Dissolution of both samples in 8M HNO_3/0.2M HF yielded similar dissolution behavior. Analysis of residual solids identified very few plutonium solids. The amount of plutonium in the residual solids, because it is so small, suggests that another solid is present as a residual solid. However, neither an accurate weight nor identification are available. Based on the proposed composition of the can material (Table 1) – approximately 180 grams of Pu in about 193 grams of bulk – the amount of unidentified solid is expected to be very small.

Filtrate analyses show that the anode heel materials contain the types of compounds expected – Pu, K, Na, and Cl. The levels of Na and K are higher than would be expected from Table 1. The presence of higher levels of Na and K is consistent with the lower-than-expected experimental assay values (Attachment 4). The composite analyses for both samples (MC03-28 and MC03-29) indicate that the two samples are similar, although MC03-28 has some other metal in it (such as steel alloy) as evidenced by its higher levels of Fe, Cu, Mo, and Ni.

Unidentified Carbonaceous Materials: Attempts to identify the undissolved MC03-19 and –20 solids using SEM found that the SEM could not identify the bulk of the material. This means that the bulk material had an atomic number less than 11 (sodium). The most likely candidate was carbon. Minor amounts of plutonium, iron, tantalum, neptunium, and silicon were noted in the SEM analyses. Radiochemical analyses (using Gamma PHA) of the residual solids from the ground-up samples indicated that most of the plutonium in sample MC03-19 does not dissolve, but that it can be dissolved from sample MC03-20.

Analyses of the filtrates confirm the lack of sample dissolution. The data in Table 2 show that very little of the solid can be accounted for as dissolved. A poor material balance was obtained for the "as-is" samples (MC03-19 and MC03-20) because the filter paper containing the solids was overheated. Although a good material balance was obtained for the ground-up samples (MC03-19G and MC03-20G), the bulk of the solid is unidentified material.

In attempt to confirm the SEM result, the undissolved solids were dried and then subjected to conditions that would be able to oxidize carbon. When the undissolved solids were dried and heated in a MgO crucible inside a furnace at 1025^{o}C for 3 hours, the dried solid lost 90.5% of its bulk weight. The residual solids were predominantly black, but some pink residue was observed on the crucible wall. This result, in conjunction with the SEM analysis and the dissolution characteristics, suggests very strongly that these two samples are primarily carbonaceous materials (graphite molds) instead of MSE salts. They are not suitable candidates for dissolution in H-Canyon.

[9] J.H. Gray. "Dissolution Flowsheet for Plutonium Anode Heel Dissolution," DPST-85-346, March 1985.
[10] J. H. Gray. "Plutonium Anode Heel Metal Dissolution," DPST-85-516, June 1985

SIMULATED H-CANYON DISSOLUTION

BASELINE FLOWSHEET

Experimental work with the baseline flowsheet showed the samples behaving similar to the characterization tests. The first charge contained proportional amounts of MC03-17 and -18. The samples dissolved quickly (within one hour) and leave no visible solids. Although the reaction is quick, a light "fizz" at the surface of the samples with only trace NOx generation characterizes the reaction. In H-Canyon, the overall vigor of the reaction will be determined primarily by the reaction of nitric acid with the aluminum charge bundles and steel cans. Furthermore, any potential contribution of hydrogen generation from sample dissolution will be negligible compared to the aluminum charge tube dissolution reaction. A low generation rate for Pu/Al alloy dissolution is expected to be analogous with what has been observed for the dissolution of U/Al alloy fuel.[11]

Visual inspection indicates complete dissolution, which is not completely unexpected considering the much lower mass-to-volume sample ratio. It is possible that some residue from MC03-17 and -18 was present because a smaller amount of residue (0.35 g combined sample in the simulation test vs. 0.50 g in each characterization test) in a larger volume (750 mL vs. 30 mL) would be difficult to see. Furthermore, the color of the solid, light pink, would make seeing the solids even more difficult.

The second charge, containing samples MC03-22, -25, -26, -28, and -29, also exhibited good dissolution in comparison to the characterization tests. The bulk of the solids dissolved quickly. A small amount of black residue was still visible even after 12 hours dissolution at 90-95^{o}C. However, the amount of residue seemed small when considering that four of the five samples did not dissolve completely during characterization tests. This behavior may also be attributable to mass-to-volume ratio being much lower. The mass-to-volume ratio effect is not as clear, though, because other solids have been added (iron nitrate, aluminum nitrate, boric acid, and sodium hydroxide) during the simulated dissolution that were not part of the characterization studies.

The third charge, containing samples MC03-21, -23, -24, and -27, behaved similar to the second charge. The bulk of the scrub alloy buttons dissolved quickly with little gas generation, and a small amount of black residue remained. Even after an additional 12 hours of dissolution at 90-95^{o}C, some black solids remain. However, it is not clear whether the black solids are only from the second charge or from both the second and third charges. The amount of undissolved solids is approximately 1.3 weight percent of the total sample added.

INCREASED-ACID FLOWSHEET

Experimental work with the increased-acid flowsheet (5.5M HNO_3 starting vs. 3.0M HNO_3) showed the sample dissolution behavior to be similar to the characterization tests. The first charge contained proportional amounts of MC03-17 and -18. The samples dissolved quickly (within one hour) with visual inspection indicating complete dissolution.

The second charge, containing samples MC03-22, -25, -26, -28, and -29, also exhibited good dissolution in comparison to the characterization tests. The bulk of the solids dissolved quickly. Although a small amount of black residue was still visible even after 12 hours dissolution at 90-95^{o}C, the amount of residue was much less than that of the baseline flowsheet.

The third charge, containing samples MC03-21, -23, -24, and -27, behaved similarly to the second charge. The bulk of the scrub alloy buttons dissolved quickly and a small amount of black residue remained. After about four hours of dissolution at 90-95^{o}C, very few, if any, solids were visible in the dissolver. The dissolution was run for a total of 12 hours. The solutions were filtered and the rate of filtration was slow. The slow rate suggests the presence of silica solids (from etching of glass vessel) in solution. A light coating of gray solids was observed on the filter. The amount of undissolved solids could not be accurately measured because it was less than 0.5 weight percent of the total sample charge (based on visual comparison with the baseline flowsheet solids).

[11] M. L. Hyder, et.al. "Processing of Irradiated, Enriched Uranium Fuels at the Savannah River Plant," DP-1500, April 1979, p. 5.5.

CHEMICAL ANALYSES

Chemical data for both simulation tests show good agreement between Test #1 and Test #2. A compilation of the data is contained in Table 3. The consistency between the two experiments is expected because there were very few residual solids for each test. The test was run as a 1:10,000-scale experiment and the concentrations of anions and cations closely reflect what can be expected after dissolution in H-Canyon. One exception is sodium, which was added as NaOH to neutralize HNO_3. Another exception is iron, which was accidentally added at a concentration 10X higher than the baseline flowsheet level. None of these exceptions is expected to have affected either the rate or completeness of the dissolution reactions.

Experiments show that both flowsheets are effective in dissolving the Table 1 materials. The baseline flowsheet produced only 1.3 wt.% residual solids with 0.0037 grams of undissolved plutonium. The undissolved plutonium represents 1.3% of the total plutonium charged to the dissolver. The increased-acid flowsheet yielded less than 0.5 wt.% residual solids with 5.04E-05 grams of undissolved plutonium or 0.02% of the total plutonium charged to the dissolver. Although SEM analyses were not performed on either sample, based on the characterization SEM data, it is assumed that the residual solids also contain small amounts of tantalum. The addition of the Pu/Ga button would be expected to increase the total undissolved solids proportionally without changing the percentage of undissolved solids. The Pu/Ga button contains approximately 600 grams of Pu compared to 3000 grams for the other samples. Therefore, a proportional increase in total residual solids would project a total residual solids increase of 20%. However, the residual solids would still comprise about 1.3 wt.% total undissolved solids for the baseline flowsheet (3.0M) and less than 0.5 wt.% for the increase-acid flowsheet (5.5M)

Using the filtrate data from Table 2, calculations were made to predict element concentrations for the simulation tests. Where available, the calculations use 8M HNO_3/0.2M HF characterization data instead of the 4M HNO_3/0.3M HF data on the assumption that more solids were dissolved in the higher acid. The calculated values are listed in Table 3 as "Predicted Test #3." The predicted values show good agreement with the data measured in Test #3.

Most of the elements in Table 3 were added as feed chemicals during the experiment (Al, B, Ca, Fe, Na, F^-, and NO_3^-). The cation data for feed chemicals show good agreement with what is expected. These results provide a measure of data validation. Boron was added at 2000 mg/L (measured at 1900-2000 mg/L). Iron was added at 0.13M or 7260 mg/L (measured at 7230-7420 mg/L). Sodium was added at 1.0M or 23000 mg/L (measured at 22400-23200 mg/L). Aluminum was added at 0.303M or 8180 mg/L, not counting aluminum from scrub alloy buttons (measured at 8200-8360 mg/L). The main exception is calcium. Calcium was added at 0.15M or 6010 mg/L. However, it was measured at 1610-1650 mg/L for the baseline test and 1800-1840 mg/L for the increased-acid flowsheet. The difference may be attributable to incomplete dissociation of calcium fluoride.[12] Because of incomplete dissociation, ICPES cannot accurately measure calcium.

The anion data exhibit some agreement with expected values. Nitrate values agree fairly well. A total of 238,000 mg/L nitrate (3.86M) was added to Test #1 and of 393,000 mg/L nitrate (6.34M) was added to Test #2. Both samples for Test #1 and Sample B for Test #2 agree with the expected values. The amount of fluoride charged to the dissolver was 0.3M or 5700 mg/L. However, Test #1 measured 3870 mg/L fluoride and Test #2 measured 4930 mg/L. This result compares to 4955 mg/L for Test #3, which minimized evaporative losses. Differences in fluoride values may be attributable to both evaporation and reactions with the glass vessel. Chloride values for Tests #1 and #3 show reasonable agreement with the calculated value of 219 mg/L. In the data for Test #2, the high nitrate concentration interferes with and flattens the chloride peak in ion chromatography. As a result, the chloride value for Test #2 is not reliable. Test #3 best reflects the expected H-Canyon flowsheet chloride value.

Test #3 also depicts which cations are added as feed chemicals and which are associated with the samples. In Test #3, the only compounds added as feed chemicals were F^- and NO_3^-. The data show that Mo, Ni, P, Sb, Sn, and Sr in Tests #1 and #2 are either introduced as impurities in the feed chemicals or are the result of analytical issues (ICPES) caused by spectral interference with plutonium.

One element that can be used to compare the simulant data from Test #1 and Test #2 with the characterization data is plutonium. The average plutonium measured in Test #1 (Samples A and B) and Test #2 (Sample A) in the

[12] J. D. Christian, "Dissolution of Sand, Slag, and Crucible Residues," Report Prepared for WSRC, January 1998.

residual solid and filtrate is 0.294 grams. Since the experiment is a 1:10,000 scale test, the amount of plutonium that is expected in the H-Canyon final solution is 2940 grams. This result compares favorably with the assay values shown in Table 1 (3040 grams) and with the characterization data of Attachment 4 (2903 grams). Because of the sizeable differences between the item-specific plutonium assay values in Table 1 and Attachment 4, the agreement with Attachment 4 is more significant. Similar agreement is seen with the filtrate values for Am-241 in Table 3.

Table 3. Simulation Test Data Compilation

A and B are duplicate samples
Only compounds consistently above 5 mg/L listed

Analyte (mg/L)						Filtrate Total Pu239 (grams)	Filtrate Total Am241 (grams)	Solid Total Pu239 (grams)	Solid Total Am241 (grams)	Total Pu239 (grams)	Total Am241 (grams)
Sample	Cl-	F^-*	NO_3^-*	Pu**	Am**						
Test #1A	270	3870	238000	386	9.4	0.290	0.0070	3.68E-03	1.24E-05	0.294	0.0070
Test #1B	272	3870	216000	384	9.5	0.288	0.0072	---	---	0.292	0.0072
Test #2A	*1020*	4880	600000	392	9.8	0.294	0.0074	5.04E-05	3.34E-07	0.294	0.0074
Test #2B	*890*	4980	369000	460	9.9	0.345	0.0074	---	---	0.345	0.0074
Test #3A	183	4980	285000	---	---	---	---	---	---	---	---
Test #3B	184	4930	213000	---	---	---	---	---	---	---	---
Predicted Test #3	219	5700	304000	386	9.7	0.290	0.0072	---	---	---	---

Analyte (mg/L)												
Sample	Al*	B*	Ca*	Fe*	Mg	Mo	Na***	Ni	P	Sb	Sn	Sr
Test #1A	8360	1900	1650	7420	47.2	17.9	23200	5.9	33.5	36.8	22.7	361
Test #1B	8210	2000	1610	7290	47.2	17.9	22800	5.4	35.3	36.8	22.5	352
Test #2A	8330	1910	1800	7300	44.0	19.6	22500	5.3	32.9	37.8	23.2	387
Test #2B	8200	1920	1840	7230	43.8	17.7	22400	5.3	28.2	37.4	23.4	398
Test #3A	630	143	17.0	5.8	43.6	1.4	167	1.0	<0.7	<3.8	4.3	3.6
Test #3B	632	143	17.4	5.8	43.3	1.8	170	1.1	0.7	<3.8	4.6	3.7
Predicted Test #3	626	---	14.5	1.9	38.1	1.0	60.4	0.8	0.5	2.1	1.2	---

* For Tests 1 and 2: Al, B, Ca, F^-, Fe, and NO_3^- added as batch chemicals and simulants for dissolved cans/tubes
** Pu determined using Alpha PHA; Am determined using Gamma PHA
*** For Tests 1 and 2: Na added as NaOH to neutralize acid and simulate acid depletion

DEPARTURES FROM THE H-CANYON FLOWSHEET

Several differences exist between the flowsheets used in the SRTC experiments and the process conditions that will be used in H-Canyon. The first of these is the presence of 0.002M Hg^{2+} ion for dissolution of the aluminum charge tubes. The second difference is the lack of a Pu/Ga button sample in the SRTC experiments. The expected impacts of the differences are as follows.

Mercury Addition: Mercury is added in H-Canyon as a catalyst to facilitate the dissolution of the aluminum metal charge tubes. This dissolution reaction is:[13]

$$Al + 3.75\ HNO_3 \xrightarrow{Hg^{2+}} Al(NO_3)_3 + 0.225\ NO + 0.15\ N_2O + 0.11\ N_2 + 1.9\ H_2O \qquad (1)$$

Mercury is omitted from SRTC experiments because 1) aluminum charge tubes are not used and 2) it avoids the unnecessary generation of a mixed-hazardous waste. The significance of this variation is seen in the byproducts of the aluminum dissolution reaction. During the dissolution of aluminum, large amounts of NOx are released. The

[13] W. S. Durant and W. C. Perkins. "Systems Analysis – 200 Area, Savannah River Plant, H-Canyon Operations." DPSTSY-200-1H, Volume 1, p. F-10, October 1983.

presence of NOx, an oxidant, improves dissolution. Therefore, the absence of NOx generated by aluminum metal dissolution will tend to cause the SRTC experimental results to be conservative – the materials will dissolve better in the H-Canyon flowsheet than in the SRTC variant flowsheet.

Omission of the Pu/Ga Button: Prior to sampling of the scrub alloy materials, a decision was made to not sample a can containing a Pu/Ga alloy button. The decision was based on the assumption that the dissolution characteristics of the Pu/Ga alloy button would be comparable to the Pu/Al alloy buttons. The decision is based on earlier work with the dissolution of Pu/Ga scrub alloy button material showing that Pu/Al and Pu/Ga behave similarly under like dissolution conditions.[5] As a result, the omission of the Pu/Ga button from the SRTC experimental program is not expected to impact the program's conclusions because seven Pu/Al button samples are incorporated in the test program.

Omission of the Nylon Bag Material: Although iron and aluminum were added to experimental dissolver solutions to simulate the presence of the steel cans and aluminum charging bundles, the addition of nylon bag material was omitted. Nylon was chosen because it dissolves readily in acid and does not leave a residue. Lab tests and calculations showed that the dissolved nylon did not affect the dissolution, solvent extraction, and evaporation operations of F-Canyon.[6]

PROPOSED FLOWSHEET

The proposed flowsheet for the materials of Table 1 is the baseline flowsheet – starting solution of 3.0M HNO_3, 0.002 M Hg, ~2 g/L B (as H_3BO_3), and 0.15M CaF_2. The use of 0.3M fluoride will provide sufficient free fluoride to dissolve the plutonium samples.[4] Preparation of the starting solution will require the dissolution of boric acid into solution before calcium fluoride can be dissolved into the nitric acid. SRTC experiments have shown that at least 1.5 g/L boron as H_3BO_3 are required to dissolve 0.15M CaF_2 into 3M HNO_3 at room temperature; at least 0.75 g/L of boron is required for CaF_2 dissolution is at 60°C.[14]

The solution will be heated to 55-60°C and charged with the materials contained in steel cans, acid-soluble nylon bags, and aluminum charge bundles. The reaction of nitric acid with the steel cans and charge bundles is an exothermic reaction that will help raise the dissolver temperature. Additional heating will be required to heat the dissolver to at least 95°C. The dissolver should be held above 95°C for at least 24 hours. The F-Canyon dissolver was operated at 90-95°C to minimize corrosion and reduce residual ruthenium volatility. Once the dissolution cycle is complete, the dissolver temperature is reduced, as needed, to load the next charge and the dissolution cycle is repeated starting at 55-60°C. The presence of both boron and aluminum in solution as fluoride complexing agents will prevent the formation of insoluble plutonium fluoride compounds.[8] Plutonium fluoride dissolution in HNO_3 appears to be analogous to calcium fluoride discussed in the previous paragraph.

The vigor of the reaction with nitric acid of the materials in Table 1 is characterized as a gentle "fizz." As a result, the aggressiveness of the reaction is determined by the reaction of the steel cans and aluminum charge bundles with nitric acid. Furthermore, the reaction products generated from the dissolution of the steel cans and aluminum charging bundles will overwhelm any potential generation of hydrogen by the scrub alloy samples.

An Al:HNO_3 ratio of 3.75 (Eq. 1) describes acid consumption for the dissolution of the aluminum charge bundles. In the absence of a comparable reaction for carbon steel, a Fe-HNO_3 ratio of 3.75 is also assumed for steel can (Fe) dissolution in calculating overall acid consumption. The resulting reactions will consume approximately 0.25 moles per liter HNO_3 as NOx, and an additional 1.05 moles per liter HNO_3 in nitrate salt formation. Starting with a nitric acid concentration of 3.0M, the final baseline free nitric acid concentration will be approximately 1.7M. The final acid concentration is well above the 0.22M ambient-temperature limit calculated for preventing the formation of plutonium polymer in Pu(IV) solutions of 7 g/L or less.[15]

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[14] R. A. Pierce. "Actinide Technology Laboratory Notebook," WSRC-NB-2003-00107, p. 17.
[15] M. G. Bronikowski, M. L. Crowder, and M. C. Thompson. "Technical Basis for Safe Operations with Pu-239 Polymer in NMS&S Operating Facilities (F & H Areas)," WSRC-TR-99-00008, January 1999.

CONCLUSIONS

Simulation and characterization experiments have been conducted to validate a variation of the F-Canyon SS&C flowsheet for use in H-Canyon. Testing was performed with 13 samples – two MSE salts, seven scrub alloy buttons, two anode heel materials, and two unidentified carbonaceous materials originally thought to be MSE salts. Of the 13 materials, eleven are judged suitable for processing in H-Canyon. Two of the samples, originally thought to be MSE salts, are graphite mold materials which will be disposed as solid waste.

Characterization of the individual samples confirmed the identification of the remaining MSE salts, scrub alloy buttons, and anode heel materials. The MSE salts dissolved readily without any noticeable gas generation. The primary components of the MSE salts are Pu, K, Na, and Cl. When dissolved in 4M HNO_3/0.3M HF, they left a small about 7 wt.% light pink residue assumed to be PuF_4-xH_2O. In 8M HNO_3/0.2M HF, the MSE salts dissolved completely. The anode heels dissolve more slowly than the MSE salts, but also dissolve without any noticeable gas generation. Filtrate analyses show the primary components of Pu, K, Na, and Cl. The levels of K, Na, and Cl are higher than would have been expected based on FB-Line assay values. When dissolved in 4M HNO_3/0.3M HF or 8M HNO_3/0.2M HF, the anode heels left behind 5-12 wt.% of a residue that could not be identified using SEM because of its dose rate.

The scrub alloy buttons dissolved readily with light gas generation at the material surface. Of the seven button samples, four dissolved completely. Two button samples contained small amounts of tantalum that did not dissolve. Characterization of the scrub alloy buttons confirms that the main components are aluminum and plutonium. The compositions of the seven samples are fairly uniform with six samples containing 15-27 wt.% plutonium; the seventh sample contained 47 wt.% plutonium. The three samples that did not dissolve completely had chloride concentrations in excess of 5 wt.% while the four samples that dissolved had little or no chloride. It is anticipated that the presence of undissolved material is more a function of where the sample was located relative to the button surface and not directly related to chloride concentration.

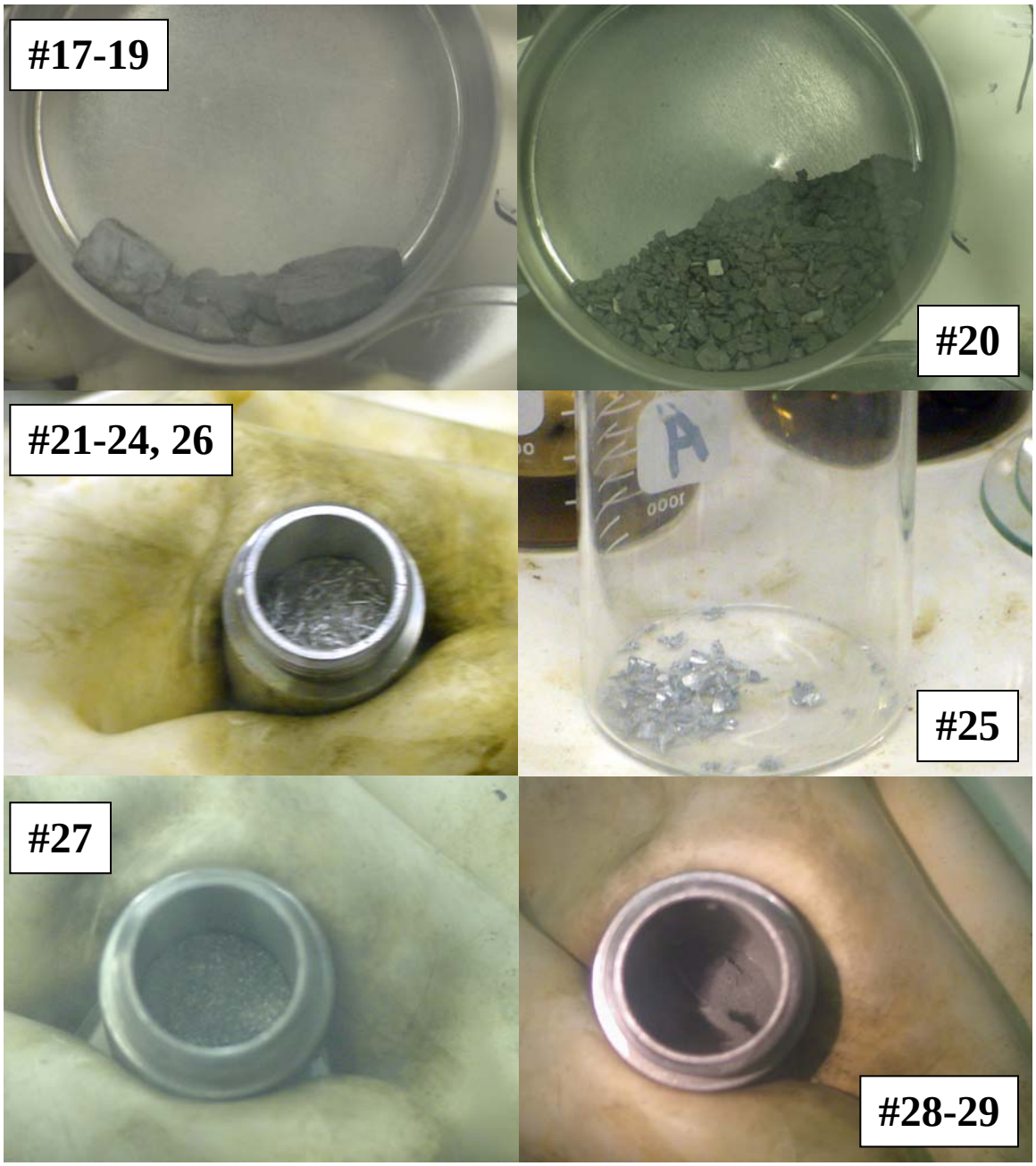
The baseline flowsheet (starting nitric acid level of ~3.0M) was tested along with an increased-acid flowsheet (starting acid level increased to ~5.5M) at a 1:10,000 scale. Experiments show that both flowsheets are effective in dissolving the scrub alloy buttons, MSE salts, and anode heel samples. The baseline flowsheet produced 1.3 wt.% residual solids with 3.68E-03 grams of undissolved plutonium (37 grams in H-Canyon). The undissolved plutonium represents 1.3 wt.% of the total plutonium charged to the dissolver. The increased-acid flowsheet yielded less than 0.5 wt.% residual solids with 5.04E-05 grams of undissolved plutonium (0.5 grams in H-Canyon). The undissolved plutonium represents 0.02% of the total plutonium charged to the dissolver. The addition of the Pu/Ga is expected to proportionally increase the total residual solids by about 20% or 44 grams in H-Canyon for the baseline flowsheet and 0.6 grams for the increased-acid flowsheet.

The vigor of the reaction with nitric acid of the items is characterized as a gentle “fizz” at the surface of the scrub alloy button samples. As a result, the aggressiveness of the reaction will be determined by the reaction of the steel cans and aluminum charge bundles with nitric acid. The processing of the materials will consume approximately 1.3M of nitric acid -- 0.25 moles per liter as NOx and an additional 1.05 moles per liter HNO_3 in nitrate salt formation. The final baseline free nitric acid concentration, assuming a starting concentration of 3.0M, will be approximately 1.7M, which is sufficiently high to avoid the formation of plutonium polymer.

When the characterization data for the individual samples are used to calculate final anion and cation concentrations for the simulant experiments, good agreement is observed between the two data sets. The presence of plutonium and high concentrations of nitrate can cause analytical issues in the measurement of Mo, Ni, P, Sb, Sn, Sr (using ICPES) and Cl (using IC). For most samples, the plutonium assay values determined experimentally do not show good agreement with FB-Line assay values. It is unclear how much of the difference can be attributed to analytical technique and sample preparation in SRTC versus inaccuracies in the FB-Line assay value or heterogeneity of the samples.

ATTACHMENTS

ATTACHMENT 1. SRTC As-Received Samples



ATTACHMENT 2. Sample Characterization ICPES Data

DISSOLUTION IN 4M HNO3/0.3M HF

Analyte (mg/L) [Only compounds consistently above 5 mg/L listed]																		
Sample	Al	B*	Ca	Ce*	Cu	Fe	K	La	Mg	Mn	Mo	Na	Ni	P	Sb	Si*	Sn	U*
MC03-17	89.5	129	13.7	57	14.4	13.0	1720	6.6	598	4.2	6.0	1340	6.5	2.0	7.4	1340	9.5	169
MC03-18	95.3	128	13.4	66	16.8	10.9	1450	7.8	649	4.5	8.2	993	8.1	3.8	8.3	1320	9.7	197
MC03-19	43.8	151	27.6	0.9	0.68	2.8	***176***	0.14	22	<0.1	<0.53	124	0.14	<0.7	<3.8	1500	2.8	4.1
MC03-19G	42.1	139	13.0	2.6	1.05	11.3	***158***	0.32	2.9	0.13	0.86	119	1.9	<0.7	<3.8	1250	3.4	9.1
MC03-20	176	131	123	34	10.1	58.7	***31.6***	4.1	8.5	2.7	4.8	111	16.1	<0.7	5.4	1380	6.1	107
MC03-20G	264	269	211	21.8	7.0	274	***360***	2.64	20.1	13.1	5.11	229	9.54	2.71	4.33	1780	6.2	77
MC03-21	11300	13.9	16	35	11.0	15.5	***397***	4.0	16	2.5	11.6	22	9.2	5.4	31.1	na	12.1	112
MC03-22	10100	15.0	159	39	17.0	20.1	***20.5***	4.5	37	2.6	11.8	253	4.8	5.6	29.2	na	12.5	129
MC03-23	11200	16.5	426	43	17.5	27.8	***33.3***	5.6	68	3.0	11.5	279	5.9	8.7	32.7	na	13.5	160
MC03-24	11000	14.6	2	42	12.0	24.4	***972***	4.8	1.6	3.2	13.0	14	5.6	7.4	30.2	na	12.7	125
MC03-25	12400	18.3	0	32	15.5	22.8	***89.8***	3.6	7.4	2.3	11.0	23	3.6	5.7	33.1	na	12.9	97
MC03-26	5050	30.4	141	27	7.1	12.5	***266***	3.4	1060	2.0	6.8	684	4.5	3.0	16.2	na	7.8	88
MC03-27	6870	12.4	25	79	20.1	11.2	***817***	9.1	661	5.4	12.9	63	6.9	8.1	25.1	na	14.8	240
MC03-28	148	88.6	5	108	89.5	182	***169***	12.3	23	15.1	27.9	187	187	11.0	15.1	na	15.9	547
MC03-29	130	92.3	6	93	27.0	17.2	***325***	10.6	63	6.8	10.8	575	13.5	5.6	11.8	na	13.4	327
- ***Red-bold-italicized*** text indicates calculated potassium values instead of analytically-measured data																		

DISSOLUTION IN 8M HNO3/0.2M HF

Analyte (mg/L) [Only compounds consistently above 5 mg/L listed]																		
Sample	Al	B*	Ca	Ce*	Cu	Fe	K	La	Mg	Mn	Mo	Na	Ni	P	Sb	Si*	Sn	U*
MC03-17	58.2	101	3.95	26.2	6.83	6.1	1040	3.0	362	1.79	3.3	683	2.13	0.7	3.8	668	5.86	78.2
MC03-18	58	103	26.1	27.5	7.22	4.71	972	3.21	374	1.81	3.78	709	2.27	2.44	3.98	855	5.04	82.3
MC03-22	4130	21.9	126	20.8	9.0	11.3	403	2.5	22	1.4	5.4	255	2.6	3.1	12.9	103	6.13	72
MC03-23	3250	31.0	365	16.5	6.1	10.2	415	2.4	24	1.0	4.7	291	2.2	2.5	10.8	208	5.32	66
MC03-26	2100	50.3	78.9	14.1	3.8	7.3	587	1.8	614	1.0	3.8	412	2.3	0.7	7.56	362	4.17	45
MC03-28	93.6	87.8	7.2	43.6	38.0	64	608	5.0	24	5.1	16.1	467	72	4.0	6.55	657	9.29	242
MC03-29	82.6	88.3	5.9	50.7	15.1	11.4	541	6.0	46	3.7	4.8	382	7.0	2.6	6.12	655	8.26	168

* B and Si likely from borosilicate glass beaker dissolution; Ce and U likely from Pu spectral interference

ATTACHMENT 3. Sample Characterization Ion Chromatography (IC) Data

	Analyte (mg/L)						
Sample	F	Cl	NO2	NO3	PO4	SO4	C2O4
MC03-17	4960	6870	<100	285000	<100	31	78
MC03-18	4840	5350	<100	354000	<100	99	111
MC03-19	3460	<20	<100	178000	<100	34	43
MC03-20	4250	<20	<100	257000	<100	67	85
MC03-21	4070	<20	<100	258000	<100	30	<100
MC03-22	4570	1110	<100	270000	<100	29	<100
MC03-23	5220	2300	<100	272000	<100	49	27
MC03-24	4490	<20	<100	246000	<100	30	<100
MC03-25	4130	<20	<100	261000	<100	29	<100
MC03-26	4820	3480	<100	252000	<100	99	<100
MC03-27	4800	333	<100	256000	<100	47	<100
MC03-28	4640	1790	<100	238000	<100	64	41
MC03-29	4360	2540	<100	259000	<100	55	28

ATTACHMENT 4. Sample Characterization Radiochemical Data

LIQUIDS FROM TESTS IN LOW ACID (4M HNO_3/0.3M HF)

SAMPLE	Volume (mL)	Expt Sample (grams)	Alpha (dpm/mL)	Alpha Pu239 (dpm/mL)	Alpha % Pu239	Alpha % Am241	Alpha % Std Dev.	Alpha Am241 (dpm/mL)	Gamma Am241 (dpm/mL)	Gamma Pu239 (dpm/mL)	Can Weight (grams)	FBLine Assay Pu239	Expt Assay Pu-239*	Expt Assay Am-241*
MC03-17	25.4	0.497	3.49E+09	9.77E+08	28	72	15.7	2.51E+09	2.04E+09	na	1732	415	527.3	23.7
MC03-18	23.6	0.495	4.14E+09	1.86E+09	45	55	16.7	2.28E+09	1.12E+09	na	1665	388	901.6	11.7
MC03-19	27.2	0.500	1.29E+09	6.84E+08	53	47	147.2	6.06E+08	1.11E+06	na	990.4	4	224.9	0.0
MC03-19G	29.5	0.544	3.40E+05	1.80E+05	53	47	n/a	1.60E+05	1.11E+06	na	990.4	4	0.1	0.0
MC03-20	26.4	0.508	8.40E+08	7.39E+08	88	12	36.2	1.01E+08	5.39E+07	na	761.7	130	178.6	0.3
MC03-20G	16.0	0.560	2.91E+08	2.59E+08	89	11	5.9	3.21E+07	5.39E+07	na	761.7	130	34.4	0.2
MC03-21	29.6	0.476	7.25E+08	6.38E+08	88	12	16.7	8.70E+07	3.58E+07	na	1390	251	336.7	0.4
MC03-22	27.3	0.494	1.03E+09	8.24E+08	80	20	18.7	2.06E+08	7.97E+07	na	1462	277	405.9	0.8
MC03-23	28.4	0.496	8.13E+08	7.07E+08	87	13	19.3	1.06E+08	7.97E+07	6.17E+07	1540	268	379.6	0.9
MC03-24	29.5	0.493	7.80E+08	6.32E+08	81	19	11.3	1.48E+08	1.11E+08	4.38E+08	1374	276	317.1	1.2
MC03-25	29.1	0.500	6.66E+08	5.13E+08	77	23	10.5	1.53E+08	9.37E+07	na	1040	199	189.2	0.7
MC03-26	29.3	0.493	1.58E+09	4.42E+08	28	72	14.5	1.14E+09	1.04E+09	na	1197	318	191.8	9.7
MC03-27	27.3	0.495	4.09E+09	1.23E+09	30	70	9.1	2.86E+09	2.77E+09	9.34E+08	1156	289	477.6	23.2
MC03-28	28.1	0.495	1.91E+09	1.78E+09	93	7	3.9	1.34E+08	9.39E+07	1.71E+09	192	178	118.0	0.1
MC03-29	29.4	0.497	1.86E+09	1.62E+09	87	13	1.6	2.42E+08	1.48E+08	1.18E+09	194	181	113.2	0.2

LIQUIDS FROM TESTS IN HIGH ACID (8M HNO_3/0.2M HF)

SAMPLE	Volume (mL)	Expt Sample (grams)	Alpha (dpm/mL)	Alpha Pu239 (dpm/mL)	Alpha % Pu239	Alpha % Am241	Alpha % Std Dev.	Alpha Am241 (dpm/mL)	Gamma Am241 (dpm/mL)	Gamma Pu239 (dpm/mL)	Can Weight (grams)	FBLine Assay Pu239	Expt Assay Pu-239*	Expt Assay Am-241*
MC03-17	28.6	0.275	1.15E+09	3.22E+08	28	72	3.1	8.27E+08	9.75E+08	2.70E+08	1732	415	353.6	23.1
MC03-18	28.7	0.235	6.94E+08	3.33E+08	48	52	0.3	3.61E+08	3.89E+08	3.17E+08	1665	388	413.1	10.4
MC03-22	29.3	0.252	2.95E+08	2.54E+08	86	14	8.3	4.13E+07	4.26E+07	2.48E+08	1462	277	262.6	0.9
MC03-23	29.4	0.251	1.99E+08	1.77E+08	89	11	0.8	2.19E+07	2.13E+07	1.77E+08	1540	268	194.6	0.5
MC03-26	29.8	0.241	6.41E+08	1.54E+08	24	76	2.8	4.87E+08	5.32E+08	1.02E+08	1197	318	138.8	10.3
MC03-28	29.6	0.240	3.57E+05	3.21E+05	90	10	na	3.57E+04	3.25E+07	5.53E+08	192	178	79.7	0.1
MC03-29	28.2	0.227	7.74E+08	6.89E+08	89	11	0.8	8.52E+07	8.03E+07	6.12E+08	194	181	101.4	0.3

* Shaded values represent those used for assay calculations

ATTACHMENT 4 (cont'd). Sample Characterization Radiochemical Data

RESIDUAL SOLID SAMPLES										
SAMPLE	Expt Sample (grams)	Gamma Pu-239 (uCi)	Gamma Pu-241 (uCi)	Gamma Am-241 (uCi)	Sample Pu-239 (grams)	Sample Pu-241 (grams)	Sample Am-241 (grams)	Can Pu-239 (grams)	Can Pu-241 (grams)	Can Am-241 (grams)
MC03-19G	0.544	210.2	493.6	231.8	3.38E-03	4.79E-06	1.44E-04	6.16	8.72E-03	2.62E-01
MC03-20G	0.560	163.8	38.5	46.7	2.64E-03	3.73E-07	1.12E-05	3.59	5.08E-04	1.53E-02
MC03-22	0.252	7.218	20.7	1.981	1.16E-04	2.01E-07	5.78E-07	0.674	1.17E-03	3.35E-03
MC03-23	0.251	2.598	---	1.085	4.18E-05	---	3.16E-07	0.257	---	1.94E-03
MC03-26	0.241	1.194	---	2.094	1.92E-05	---	6.10E-07	0.095	---	3.03E-03
MC03-28	0.240	3.777	---	0.577	6.08E-05	---	1.68E-07	0.049	---	1.35E-04
MC09-29	0.227	1.604	---	0.259	2.58E-05	---	7.55E-08	0.022	---	6.45E-05