Flow Sheet Development for the Dissolution of Unirradiated Mark 42 Fuel Tubes in F-Canyon, Part II

by

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Executive Summary

Two sets of tests were done to establish dissolution conditions for the unirradiated Mark 42 fuel tubes. Extended dissolution tests were done using 0.15 M and 0.20 M fluoride/8 M nitric acid/0.20 M boron solutions. Higher fluoride concentrations were used (i.e., 0.25 M, 0.275, and 0.30 M) in another set of tests. Reject Mark 42 compact material was used as the surrogate for the Mark 42 fuel tube cores. Aluminum nitrate nonahydrate was used as the surrogate for the aluminum from the can and cladding.

The extended dissolution tests were premised on a flow sheet in which 10.3 kilograms of plutonium and 96.3 kilograms of aluminum would be dissolved per batch in 6500 liters of solution. Potassium fluoride was used as the fluoride source, and the fluoride concentrations were 0.15 M and 0.20 M. The extended-dissolution tests showed that about 96-98% of the plutonium was dissolved after 195 hours at 85°C.

A different processing scheme for the unirradiated Mark 42 fuel tubes was used for the next set of tests. In that scheme, 6.2 kilograms of plutonium and 80.2 kilograms of aluminum would be dissolved per batch. Tests were done with 0.25 M, 0.275 M, and 0.30 M fluoride with calcium fluoride as the fluoride source. There were two tests using 0.30 M fluoride. Those two tests simulated dissolutions that were done in 6500 liters and in 10,000 liters. Dissolution of the reject Mark 42 compact material was completed in seven to 25 hours, depending on the fluoride concentrations and on the dissolver solution volume.

The most effective dissolution conditions used 0.30 M fluoride based on a dissolver solution of 10,000 liters. Under those conditions, the reject Mark 42 compact material dissolved in less than six hours. A parallel experiment was done based on 6500 liters in the dissolver solution. That dissolution was completed within 14 hours. The rapid dissolution of the 10,000-liter test conditions is not unexpected because the aluminum:fluoride mole ratio was 1:1.

The dissolution of the unirradiated Mark 42 fuel tubes is expected to be longer than the reject compact material. Although the Mark 42 reject compact material is chemically similar to the fuel core in the fuel tubes (i.e., plutonium oxide and aluminum), the compact material is crushed whereas the fuel core is a bulk material. That physical difference favors the dissolution of the compact material compared to the bulk material. Furthermore, the tests on the Mark 42 reject compact material did not assess the time required for the dissolution of the bulk aluminum in the can and the cladding.

No mercury was used in these tests. The aluminum dissolution proceeded rapidly anyway. Initially, that behavior was attributed to the physical form of the Mark 42 reject compact material; it was crushed. The higher surface area of the crushed material would facilitate dissolution compared to bulk material. An article in the literature indicated that there might be an alternate reason: the presence of HBF_4 in the solution might serve to enhance the dissolution. The dissolution of an aluminum coupon was tested in a nitric acid solution to which HBF_4 was added, in the dissolver solution (nitric acid, boric acid, and calcium fluoride), and in a nitric acid solution. Those tests showed that aluminum dissolution in the HBF_4 solution and in the dissolver solution proceeded readily and to completion within a few hours whereas the aluminum dissolution in the nitric acid solution was very slow and incomplete after 10 hours. The presence of HBF_4 in the dissolver solution is not an unreasonable expectation because of the equilibria among the boron, fluoride, and acid species. Mercury should continue to be used to promote the dissolution of aluminum in the unirradiated Mark 42 material because these tests do not provide sufficient information to recommend not using mercury. However, as the use of the mercury catalyst poses environmental issues, continued work on the use of the HBF_4 instead of a mercury catalyst for aluminum dissolution should be pursued.

The corrosive effect of the higher-fluoride concentrations is important to the acceptance of those fluoride concentrations for F-Canyon processing solutions. A study is being done by the Materials Applications and Technology Group to determine the corrosion effects of fluoride concentrations in the range of 0.2 to 0.4 M using the Mark 42 dissolution flow sheet. Those results will be published in a separate report. As part of that corrosion study, the effective free-fluoride concentrations will be measured.

Recommendation

The flow sheet recommendation is based on the addition of 6.2 kilograms of plutonium and 80.2 kilograms aluminum from the unirradiated Mark 42 fuel tubes to the dissolver solution per batch. Under those conditions, a 6500-liter dissolver solution of 8 molar nitric acid, 2.2 grams boron per liter, and 0.125 to 0.15 M calcium fluoride (fluoride concentration is 0.25 to 0.30 M) should dissolve the plutonium oxide in the unirradiated Mark 42 fuel tubes. Mercury should be added for the aluminum dissolution.

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1 Introduction

Two dissolution flow sheets were tested for the dissolution of unirradiated Mark 42 fuel tubes. Both the aluminum (from the can, cladding, and fuel core) and the plutonium oxide (PuO_2) are dissolved simultaneously, i.e., a co-dissolution flow sheet. In the first series of tests, 0.15 and 0.20 molar (M) potassium fluoride (KF) solutions were used and the dissolution extended over several days. In the other series of tests, solutions with higher concentrations of fluoride (0.25 to 0.30 M) were used. Calcium fluoride (CaF_2) was used in those tests as the fluoride source.

2 Background

There are 38 unirradiated Mark 42 fuel tubes stored in the Receiving Basin for Offsite Fuel (RBOF). Those unirradiated fuel tubes failed to meet the PuO_2 density specifications after fabrication in the late 1970s and early 1980s.^{1,2,3} The Nuclear Materials Stabilization and Storage (NMSS) Division plans to dissolve the Mark 42 fuel tubes in F-Canyon and would like to use the resulting solutions to blend with solutions from the dissolution of Experimental Breeder Reactor II (EBR-II) spent nuclear fuel. The blended solution will be processed through the F-Canyon PUREX process flow sheet with the dissolved plutonium converted to metal in FB-Line.

Based on a literature review, the Chemical Technology (CT) Group concluded that the H-Canyon flow sheet for the dissolution of irradiated Mark 42 fuel tubes was not applicable to the dissolution of the unirradiated Mark 42 fuel tubes.⁴ The main issue was the solubility of the PuO_2 that is present in the Mark 42 fuel core. Unirradiated PuO_2 is more difficult to dissolve than irradiated PuO_2 . Uncomplexed fluoride ions are needed in the solution to facilitate the dissolution of the unirradiated PuO_2 . The simple inclusion of sufficient fluoride into the H-Canyon flow sheet is complicated by the presence of boron in the F-Canyon dissolver solution. The boron is required for nuclear criticality safety because the plutonium in the unirradiated Mark 42 fuel tubes is about 78% plutonium-239 and 2% plutonium-241. Boron complexes fluoride ions, thus reducing the amount of free fluoride available to assist with the PuO_2 dissolution. The amount of free fluoride ions is further reduced by the dissolved aluminum from the packaged Mark 42 fuel tubes (can, cladding, and core) because aluminum also complexes with fluoride ions. An experimental program was recommended to ascertain the requisite fluoride concentration for the successful dissolution of the PuO_2 in the unirradiated Mark 42 fuel tubes.

Experiments were done to determine the flow sheet requirements for the dissolution of the unirradiated Mark 42 fuel tubes. One series of tests focused on a dissolution flow sheet in which the aluminum and PuO_2 dissolve simultaneously. The fluoride requirements for the PuO_2 dissolution were examined. The results indicated that the required fluoride concentrations would be sufficiently high that there might be serious corrosion issues and the potential for the precipitation of the boron as potassium tetrafluoroborate (KBF_4) if KF were used as the fluoride source. The other series of tests considered a two-step acid dissolution in which the aluminum was dissolved in the first step and the PuO_2 was dissolved in the second step. The two-step flow sheet presented issues regarding the undissolved PuO_2 , specifically the transfer of those solids into the holding tank and criticality safety issues. The details of those experiments are reported in WSRC-TR-98-00457.⁵

¹ R. L. Frontroth, "Mark 42 Billet Fabrication" memorandum to G. F. Merz, Savannah River Plant, February 11, 1980.

² H. B. Peacock, "Inspection of Mark 42 Tubes" memorandum to W. G. Winn, Savannah River Plant, April 14, 1980.

³ W. G. Winn, Appraisal of High Density Spots in Mark 42 Fuel Tubes, Savannah River Plant Report DPST-80-398, June 13, 1980

⁴ A. M. Murray, Evaluation of Proposed Flow Sheet for the F-Canyon Dissolution of Unirradiated Mark 42 Fuel Tubes, Savannah River Site Report WSRC-TR-98-00304, September 4, 1998.

⁵ Alice M. Murray and William J. Crooks III; Flow Sheet Development for the Dissolution of Unirradiated Mark 42 Fuel Tubes in F-Canyon; Savannah River Site Report WSRC-TR-98-00457, April 30, 1999.

The NMSS Division approved additional tests on the dissolution of the Mark 42 fuel tubes. Those tests included longer dissolution times at lower fluoride concentrations for the dissolution flow sheet. Other dissolution tests involved the use of CaF_2 as the fluoride source so that higher fluoride concentrations could be tested without precipitation of boron-containing salts. The tests on extended dissolution and dissolution with CaF_2 are presented in this report.

3 Description of Mark 42 Fuel

A good description of the reject Mark 42 fuel tubes and packaging is critical to the development of the dissolution flow sheet. The Mark 42 fuel assembly contained three concentric fuel tubes: the inner, middle, and outer tubes. A cermet (ceramic/metal) of aluminum powder and PuO_2 was used for the fuel core. The initial distribution of plutonium isotopes in the Mark 42 fuel core is given in Table 1. More than half of the plutonium-241 has decayed over the past 18 years because the plutonium-241 half-life is about 14.4 years.

Table 1. Initial Distribution of Plutonium Isotopes in the Mark 42 Fuel⁶

Plutonium Isotope	Percent of Total Plutonium
Plutonium-238	0.15%
Plutonium-239	78.28%
Plutonium-240	18.58%
Plutonium-241	2.27%
Plutonium-242	0.71%

The aluminum/ PuO_2 composition of the Mark 42 fuel core that met specifications is given in Table 2. The composition of the reject Mark 42 fuel core should be within 5% of the Mark 42 fuel core that met specifications based on information given in Frontroth's report.¹ For example, the plutonium density for the inner fuel tube that met specifications was 61.6 grams/foot. According to Frontroth's report, the reject inner fuel tube had an average plutonium density of 63.5 grams/foot. Thus, there will be less aluminum in the fuel core of the reject inner fuel tubes than predicted by the specifications.

The cladding (Aluminum 6063) was extruded with core material. An estimate of the cladding can be made from information in a report by M. J. Beckum in which the amount of aluminum associated with a particular package (can + cladding + core) is given.⁷ The estimated amounts of aluminum cladding for the inner, middle, and outer fuel tubes are 3.40 kilograms, 3.23 kilograms, and 3.29 kilograms, respectively. Details of the estimate are given in Appendix A. The unirradiated Mark 42 fuel tubes are in storage in the RBOF. They will be packaged in aluminum General Purpose Cans (GPCs). Each GPC weighs 6.67 kilograms.

Table 2. Initial Composition of Mark 42 Fuel Core that Met Specifications (by weight)

Fuel Tube	Percent Plutonium	Percent PuO_2	Percent Aluminum
Inner Tube Core	18.7%	21.2%	78.8%
Middle Tube Core	21.8%	24.7%	75.3%
Outer Tube Core	15.4%	17.5%	82.5%

⁶ L. Traver, Internal Communication: Mark 42 Facts, August 10, 1998.

⁷ M. J. Beckum, Mk-42 Packaging Report, Savannah River Report NMP-SRB-92-0048, January 29, 1992.

4 Experimental Program

Two co-dissolution flow sheets were investigated: an extended dissolution flow sheet with KF as the fluoride source and a dissolution flow sheet that used CaF_2 as the fluoride source. Actual material from the unirradiated Mark 42 fuel tubes was not available for the experiments. Instead, crushed reject compact material from the Mark 42 program was used. As part of the formation of the Mark 42 fuel cores, aluminum powder and PuO_2 were compacted. Some of that compact material was rejected. That reject compact material has been stored in F-Area (initially the F-Area 410 vault and then in the FB-Line facility). The reject compacts were crushed prior to storage. One can of the reject compact material was sent to the CT Group for use in the Mark 42 flow sheet development. That material is nominally 12.24 weight% plutonium based on the Material Control and Accountability (MC&A) records. X-ray diffraction analyses of the Mark 42 reject compact material confirmed the presence of PuO_2 and aluminum. The distribution of plutonium isotopes in the Mark 42 reject compact material was determined by inductively-coupled plasma (ICP)/mass spectrometry (MS). Those results are given in Table 3.

Table 3. Distribution of Plutonium Isotopes in Mark 42 Reject Compact Material

Plutonium Isotope	Percent of Total Plutonium
Plutonium-238	0.14%
Plutonium-239	77%
Plutonium-240	19%
Plutonium-241/ Americium241	3%
Plutonium-242	0.71%

The amount of plutonium-238 alpha activity in the material relative to the total plutonium alpha activity in the material was determined experimentally and is given in Table 4. A thenoyltrifluoroacetone extraction was used to separate the plutonium from the americium to eliminate the americium alpha activity from the solution. Analyses were done on samples reported in WSRC-TR-98-00457.⁵

Table 4. Relative Plutonium-238 Alpha Activity

Experiment from WSRC-TR-98-00457	AMM05c ⁵	AMM06g ⁵	AMM06h ⁵
Alpha Activity Ratios			
Pu-238 / (Pu-239 and Pu-240)	0.166	0.165	0.168
Pu-238 / Total Pu Alpha Activity	0.142	0.142	0.144

The dissolution rate for the crushed compact material is expected to be different from that of actual Mark 42 fuel tubes and is only applicable to the Mark 42 fuel core. Even that applicability has limitations. The large surface area of the crushed compact material enhances that material's dissolution rate compared to intact compact material, i.e., the physical form of the Mark 42 fuel core. The crushed material has a relative large surface area compared to the bulk fuel core, and thus, dissolution of the crushed material is expected to occur more readily. Typically, mercuric nitrate ($\text{Hg}(\text{NO}_3)_2$) is added to the dissolver solutions to facilitate the dissolution of bulk aluminum. However, in these experiments with the crushed Mark 42 reject compact material, the dissolution proceeded readily without the addition of mercury.

4.1 Extended Dissolution Flow Sheet Development

The goal of this series of tests was to determine if the dissolution flow sheet could be successful at 0.15 or 0.20 molar fluoride if the dissolution was allowed to proceed over several days. Tests were done using the Mark 42 reject compact material.

The amount of Mark 42 reject compact material used in the extended dissolution experiments was based on the worst-case charging scenario that was described in WSRC-TR-98-00457. According to that scenario, the unirradiated Mark 42 fuel tubes will be repackaged in RBOF so that only two fuel tubes are in each GPC that is sent to F-Canyon for dissolution. A worst case scenario for dissolution was developed in which an outer fuel tube and a middle fuel tube are packaged together. This scenario has the highest amount of plutonium and aluminum for a combination of two unirradiated Mark 42 fuel tubes (Table A1, Appendix A). The first dissolution batch would involve four packages, each with an outer and a middle fuel tube. The second dissolution batch would be similarly composed. Table 5 contains the details for that worst case scenario.

Table 5. Composition of Worst Case Scenario for Dissolution of Two Batches of Mark 42 Fuel Tubes

Batch	Plutonium	Aluminum in Cermet	Aluminum from Cladding	Aluminum from Can
1	10.27 kilograms	43.55 kilograms	26.08 kilograms	26.68 kilograms
2	10.26 kilograms	43.53 kilograms	26.08 kilograms	26.68 kilograms

For the extended dissolution experiments, sufficient Mark 42 reject compact material was added to 250 milliliters of dissolver solution to duplicate the plutonium concentrations of the addition of the first batch in the worst-case scenario to 6,500 liters of dissolver solutions, i.e., 1.6 grams plutonium/liter and 0.55 M aluminum. There were four extended dissolution tests done. In two tests (AMM08a and AMM08b), the material was allowed to dissolve 48 hours before the aluminum-laden solutions were decanted and fresh solutions were added to complete the dissolution of the PuO_2 (AMM08c and AMM08d). The other two tests (AMM09a and AMM09b) had dissolution times of 196 hours. Not all of the PuO_2 had dissolved in those solutions. The aluminum-laden solutions were decanted and fresh solutions were added to complete the dissolution of the PuO_2 (AMM09c and AMM09d).

Aluminum nitrate nonahydrate (ANN) was added to the solutions to provide the aluminum expected from the dissolution of the cladding and the GPC. From Table 5, 52.76 kilograms of aluminum are expected from the dissolution of the cladding and the can in the first batch. In 6,500 liters, that amount of dissolved aluminum would have a concentration of 0.30 M.

Fluoride concentrations of 0.15 M and 0.20 M were tested. Potassium fluoride was the fluoride source. The aluminum:fluoride molar ratios were 3.7 and 2.7, respectively.

The detailed description of the test solutions is given in Table 6. All tests were done in 8 M HNO_3 and 2.2 grams boron/liter solutions (2.2 grams boron/liter is equivalent to 0.20 M boron).

4.1.1 Experimental Details

The experiments on the Mark 42 reject compacts were done in a glovebox with leaded-glass windows because of radiation exposure concerns. The dissolver solutions were prepared outside of the glovebox. Typically, the experiments were done with 250 milliliters of dissolver solution. The Mark 42 reject compact material was weighed in the glovebox and was added to a 600-milliliter Teflon beaker. Next, the dissolver solution was poured into the beaker. The solution was stirred and heated to 85°C. The solution was kept at 85°C during the day shift and allowed to cool overnight. Samples were taken the next day and

Table 6. Experimental Conditions for the Extended Dissolution Flow Sheet Tests

Test	Mark 42 Reject Compact	Fluoride	Fluoride Source	Dissolution Time at 85°C	Comments
AMM08a	3.38 grams	0.15 Molar	KF	48 hours	Solution decanted
AMM08b	3.39 grams	0.20 Molar	KF	48 hours	Solution decanted
AMM08c*	Residual solids from AMM08a	0.15 Molar	KF	8 hours	Solids completely dissolved
AMM08d*	Residual solids from AMM08b	0.15 Molar	KF	8 hours	Solids completely dissolved
AMM09a	3.40 grams	0.15 Molar	KF	215 hours	Solution decanted
AMM09b	3.39 grams	0.20 Molar	KF	215 hours	Solution decanted
AMM09c	Residual solids from AMM09a	0.15 Molar	KF	7 hours	Solids completely dissolved
AMM09d	Residual solids from AMM09b	0.15 Molar	KF	7 hours	Solids completely dissolved

* No boric acid added to those solutions.

the volume of the solution was measured. The heating/cooling/sampling cycle was repeated until the experiment was stopped. At that point, the aluminum-laden solution was decanted and fresh solution was added to complete the dissolution of the PuO_2 .

No mercury was needed for the dissolution of the aluminum in Mark 42 reject compact material. The aluminum dissolution proceeded quite readily as the solution was heated to 85°C. The aluminum dissolution was accompanied by the evolution of NO_x fumes. The aluminum dissolution was essentially completed in about 30 minutes, as noted by the decrease in NO_x fumes. The solutions were stirred (~300 rpm) until the heating was stopped. The undissolved solids were allowed to settle overnight as the solution cooled.

Samples were taken from the cooled solutions at periodic intervals. Typical analyses of the dissolver solutions included rad screen⁸ and gamma scan so that the progress of the plutonium dissolution could be monitored. Less frequently, samples were taken to monitor other constituents in the solution such as fluoride, aluminum, boron, and acid concentrations. Fluoride concentration was determined with ion-selective electrodes, total- and free-acid concentrations were determined by titration, and aluminum and boron concentrations were obtained from the ICP/atomic emission spectroscopy (AES) analysis. Results of the fluoride concentration analyses, acid concentration analyses, and ICP/AES analyses are discussed in Appendix B. Some undissolved solids were sampled for x-ray diffraction.

4.1.2 AMM08 Experiments

The first extended dissolution tests were done for 48 hours. Two fluoride concentrations were tested: 0.15 M and 0.20 M. Those two experiments were AMM08a and AMM08b, respectively. Potassium fluoride was the source of fluoride. After the solutions had been heated for 48 hours, the aluminum-laden solutions were decanted. About 250 milliliters of an 8 M HNO_3 /0.15 M KF solution was added to dissolve the remaining residues from experiments AMM08a and AMM08b. The new experiments were AMM08c and AMM08d, respectively. The remaining residues were dissolved after seven hours.

⁸ Rad screen refers to the liquid scintillation analysis in which pulse-shaped discrimination is used to differentiate the alpha events from the beta events.

It is important to note that a significant fraction of the AMM08a and AMM08b solutions had evaporated during the 48-hour dissolution. Solution AMM08a went from 250 milliliters to 130 milliliters (a 48% loss of volume) and solution AMM08b lost 36% of its volume: from 250 milliliters to 160 milliliters. Solids were noted on the walls of the beakers and of the sample vials after about 32 hours of heating. Thus, the evaporation caused some species in the solution to precipitate.

4.1.2.1 Analytical Results for AMM08 Experiments

Periodic samples for rad screen and gamma scan analyses were taken to establish the plutonium and americium dissolution profile in the dissolver solutions. Total alpha activity (plutonium-238, plutonium-239, plutonium-240, and americium-241) and total beta activity (plutonium-241) were determined by rad screen. To determine the americium-241 contribution to the total alpha activity, gamma scans were done. The results for the rad screen and gamma scan analyses are given in Table 7. A correction factor was applied to the alpha activity because the rad screen protocol uses a conservative alpha efficiency of 90%. The actual alpha efficiency of the liquid scintillation counter was measured as 97.2%. Therefore, a correction factor of (0.9/0.972) was applied to the reported values. The corrected values are given in Table 7.

Table 7. Rad Screen and Gamma Scan Results for AMM08 Solutions

Experiment	Volume of Solution Before Sampling	Time in Dissolution Sample Taken	Beta Activity dpm/ml - assumed to be Pu-241	Alpha Activity dpm/ml	Corrected Alpha Activity dpm/ml	Americium-241 Alpha Activity dpm/ml
AMM08a -1	245 ml	1.2 hours	8.80×10^8	2.07×10^8	1.92×10^8	5.22×10^7
AMM08a-2	215 ml	Not Taken	-	-	-	-
AMM08a-3	195 ml	16.3 hours	1.67×10^9	3.85×10^8	3.57×10^8	1.02×10^8
AMM08a-4	185 ml	24.1 hours	1.92×10^9	4.39×10^8	4.07×10^8	1.14×10^8
AMM08a-5	170 ml	31.6 hours	1.81×10^9	4.54×10^8	4.20×10^8	1.44×10^8
AMM08a-6	160 ml	39.8 hours	2.52×10^9	5.97×10^8	5.53×10^8	1.68×10^8
AMM08a-7	130 ml	48.0 hours	3.25×10^9	7.39×10^8	6.84×10^8	2.08×10^8
AMM08c	235ml	7.0 hours	4.90×10^8	1.12×10^8	1.04×10^8	2.81×10^7
AMM08b -1	245 ml	1.2 hours	1.59×10^9	3.65×10^8	3.38×10^8	9.73×10^7
AMM08b-2	225 ml	Not Taken	-	-	-	-
AMM08b-3	200 ml	16.3 hours	1.84×10^9	4.24×10^8	3.93×10^8	1.12×10^8
AMM08b-4	190 ml	24.1 hours	2.26×10^9	4.85×10^8	4.49×10^8	1.25×10^8
AMM08b-5	180 ml	31.6 hours	1.77×10^9	4.49×10^8	4.16×10^8	1.45×10^8
AMM08b-6	170 ml	39.8 hours	2.35×10^9	5.69×10^8	5.27×10^8	1.72×10^8
AMM08b-7	160 ml	48.0 hours	2.93×10^9	7.02×10^8	6.50×10^8	1.99×10^8
						1.98×10^8
AMM08d	160 ml	7.0 hours	2.64×10^8	6.08×10^7	5.63×10^7	1.49×10^7

White solids were observed in some of the sample vials taken from AMM08a and AMM08b for rad screen analyses for the 5, 6, and 7 sets. The samples with solids were filtered through a disk using a syringe. The solids were submitted from x-ray diffraction analyses. Those results are discussed in Appendix B. The x-ray diffraction analyses identified ANN and H_3BO_3 .

As mentioned previously, the results of the fluoride concentration analyses, acid analyses, and ICP/AES analyses are discussed in Appendix B.

4.1.2.2 Discussion of Results for AMM08 Experiments

The dissolution of the plutonium and americium in the Mark 42 reject compact material was monitored during the 48 hours at 85°C. The amount of dissolved plutonium and americium was calculated using the information in Table 3, Table 4, and Table 7. The grams of plutonium-241/milliliter were calculated assuming that the beta activity was due to the plutonium-241. The grams of americium-241/milliliter were calculated using the results of the gamma scan. Subtracting the americium alpha activity from the total alpha activity gave the plutonium activity. The contribution of plutonium-238 to the plutonium alpha activity was calculated based on the information from the thenoyltrifluoroacetone extraction and was subtracted from the plutonium alpha activity. The remaining plutonium alpha activity was from plutonium-239 and plutonium-240. The isotopic ratios from the ICP/MS analysis allowed the relative amounts of those isotopes to be determined. The results of the calculations are given in Table 8. The thenoyltrifluoroacetone extraction and the ICP/MS tests were done to support the first phase of the flow sheet work for the unirradiated Mark 42 fuel tubes.⁵

Table 8. Plutonium and Americium in AMM08 Solutions as a Function of Dissolution Time

Experiment	Dissolution Time	Plutonium-241 g/ml	Americium-241 g/ml	Plutonium-238 g/ml	Plutonium-239 g/ml	Plutonium-240 g/ml
AMM08a-1	1.2 hours	3.84×10^{-6}	6.86×10^{-6}	5.20×10^{-7}	4.53×10^{-4}	1.14×10^{-4}
AMM08a-3	16.3 hours	7.29×10^{-6}	1.34×10^{-5}	9.49×10^{-7}	8.27×10^{-4}	2.07×10^{-4}
AMM08a-4	24.1 hours	8.38×10^{-6}	1.50×10^{-5}	1.09×10^{-6}	9.50×10^{-4}	2.38×10^{-4}
AMM08a-5	31.6 hours	7.90×10^{-6}	1.89×10^{-5}	1.03×10^{-6}	8.98×10^{-4}	2.25×10^{-4}
AMM08a-6	39.8 hours	1.10×10^{-5}	2.21×10^{-5}	1.43×10^{-6}	1.25×10^{-3}	3.14×10^{-4}
AMM08a-7	48.0 hours	1.42×10^{-5}	2.73×10^{-5}	1.78×10^{-6}	1.55×10^{-3}	3.88×10^{-4}
AMM08c	7.0 hours	2.14×10^{-6}	3.70×10^{-6}	2.82×10^{-7}	2.46×10^{-4}	6.16×10^{-5}
AMM08b-1	1.2 hours	6.94×10^{-6}	1.28×10^{-5}	8.97×10^{-7}	7.82×10^{-4}	1.96×10^{-4}
AMM08b-3	16.3 hours	8.03×10^{-6}	1.47×10^{-5}	1.05×10^{-6}	9.11×10^{-4}	2.29×10^{-4}
AMM08b-4	24.1 hours	9.87×10^{-6}	1.64×10^{-5}	1.21×10^{-6}	1.05×10^{-3}	2.64×10^{-4}
AMM08b-5	31.6 hours	7.73×10^{-6}	1.91×10^{-5}	1.01×10^{-6}	8.79×10^{-4}	2.21×10^{-4}
AMM08b-6	39.8 hours	1.03×10^{-5}	2.26×10^{-5}	1.32×10^{-6}	1.15×10^{-3}	2.89×10^{-4}
AMM08b-7*	48.0 hours	1.28×10^{-5}	2.61×10^{-5}	1.68×10^{-6}	1.46×10^{-3}	3.68×10^{-4}
AMM08d	7.0 hours	1.15×10^{-5}	1.96×10^{-6}	1.54×10^{-7}	1.34×10^{-4}	3.37×10^{-5}

*Based on the average of the americium-241dpm/ml measurements given in Table 7.

The progress of the dissolution of the plutonium and americium was calculated using the information in Table 8 and the volumes in Table 7. The amounts of plutonium and americium that had dissolved at specific times during the dissolution are given in Table 9. Both the absolute amount and the fraction of the total plutonium and americium are given. The fraction of plutonium and americium was determined using the plutonium and americium values from the AMM08a-7 and AMM08c solutions and from the AMM08b-7 and AMM08d solutions. The loss of plutonium and americium from the periodic sampling was incorporated into the calculation. A plot of the progress of the plutonium and americium dissolution in AMM08a is given in Figure 1.

Table 9. Progress of Plutonium and Americium Dissolution in AMM08 Experiments

Experiment	Dissolution Time	Plutonium and Americium-241 in Solution (grams)	Fraction of Plutonium and Americium-241 in Solution
AMM08a-1	1.2 hours	0.14	0.42
AMM08a-3	16.3 hours	0.21	0.61
AMM08a-4	24.1 hours	0.23	0.67
AMM08a-5	31.6 hours	0.20	0.59
AMM08a-6	39.8 hours	0.26	0.78
AMM08a-7	48.0 hours	0.26	0.78
AMM08c	7.0 hours	0.074	0.22
AMM08b-1	1.2 hours	0.25	0.71
AMM08b-3	16.3 hours	0.23	0.68
AMM08b-4	24.1 hours	0.26	0.74
AMM08b-5	31.6 hours	0.21	0.60
AMM08b-6	39.8 hours	0.26	0.76
AMM08b-7*	48.0 hours	0.31	0.88
AMM08d	7.0 hours	0.040	0.12

The 0.20 M KF solution (AMM08b) was more effective dissolving the plutonium and americium than the 0.15 M KF solution (AMM08a). Neither set of fluoride conditions was able to dissolve all of the plutonium and americium in the Mark 42 reject compact material. The fractions of plutonium and americium that were dissolved in AMM08a and AMM08b are 78% and 88%, respectively.

Based on the amount of the plutonium and americium that was dissolved in AMM08a-7 and AMM08c and in AMM08b-7 and AMM08d, the percent of plutonium and americium in the Mark 42 reject compact material was calculated. Both sets of solutions gave 10% as the plutonium and americium content. That value is in agreement with the MC&A value (12.24 weight%) and with previous experiments.⁵

The x-ray diffraction analyses of the solids showed that both ANN and H_3BO_3 were present. As expected, no PuO_2 was shown in the x-ray diffraction analysis. The solids had precipitated from the sample solutions. None of the undissolved PuO_2 solids from the beaker were included in the x-ray diffraction sample.

4.1.3 AMM09 Experiments

The second set of extended dissolution tests was done for approximately 215 hours. Two fluoride concentrations were tested: 0.15 M and 0.20 M. Those two experiments were AMM09a and AMM09b, respectively. Potassium fluoride was the source of fluoride. During this extended dissolution, the AMM09a and AMM09b solutions were replenished to 250 milliliters with 5 M HNO_3 solution if the AMM09a and AMM09b solutions reduced to 200 milliliters. The 5 M HNO_3 solution was added to prevent the ANN and H_3BO_3 precipitation that was observed during the AMM08 experiments. The solutions were replenished after about 74 hours and 159 hours at 85°C. After 195 hours at 85°C, CaF_2 was added to the solutions to see if the PuO_2 dissolution could be enhanced. Sufficient CaF_2 was added to AMM09a and AMM09b to increase the fluoride content in each solution by 0.0257 moles. The resulting solutions would be 0.25 M (AMM09a) and 0.30 M (AMM09b) based on 250 milliliters of solution and if all of the original fluoride were still present.

Figure 1. 48-Hour Dissolution with 0.15 M KF

After the solutions had been heated for 215 hours, the aluminum-laden solutions were decanted. About 250 milliliters of an 8 M HNO_3 /0.20 M H_3BO_3 /0.15 M KF solution were added to dissolve the remaining residues from experiments AMM09a and AMM09b. The new experiments were AMM09c and AMM09d, respectively. The remaining residues were dissolved after 6.3 hours at 85°C.

4.1.3.1 Analytical Results for AMM09 Experiments

Just as with the AMM08 experiments, periodic samples for rad screen and gamma scan were obtained from the AMM09 solutions. Total alpha activity (plutonium-238, plutonium-239, plutonium-240, and americium-241) and total beta activity (plutonium-241) were determined by rad screen. To determine the americium-241 contribution to the total alpha activity, gamma scans were done. The results for the rad screen and gamma scan analyses are given in Table 10 and Table 11. As mentioned in Section 4.1.2.1, a correction factor was applied to the alpha activity because the rad screen protocol uses a conservative alpha efficiency of 90%. The measured alpha-emitter counting efficiency was 97.2%. Therefore, a correction factor of (0.9/0.972) was applied to the reported values. The corrected values also are given Table 10 and Table 11. The samples taken for AMM09a-19 and AMM09b-19 are duplicates of AMM09a-20 and AMM09b-20, respectively. The samples for AMM09a-23 and AMM09b-23 were taken immediately after the 5 M HNO_3 solution was added to replenish solutions AMM09a and AMM09b to 250 milliliters. Thus, a dilution factor should relate the results of those two samples to the results from samples AMM09a-22 and AMM09b-22, respectively.

A sample of the remaining solids was taken after 54 hours at 85°C. That sample was submitted for x-ray diffraction analysis.

Samples were taken less frequently for the ICP/AES analyses for aluminum and boron, ion-selective electrode analysis for fluoride concentration, and the analysis for total- and free-acid concentrations. Those results are discussed in Appendix B.

4.1.3.2 Discussion of Results for AMM09 Experiments

The dissolution of the plutonium and americium in the Mark 42 reject compact material was monitored during the 215 hours at 85°C. The amount of dissolved plutonium and americium was calculated using the information in Table 3, Table 4, Table 10, and Table 11. The grams of plutonium-241/milliliter were calculated assuming that the beta activity was due to the plutonium-241. The grams of americium-241/milliliter were calculated using the results of the gamma scan. Subtracting the americium alpha activity from the total alpha activity gave the plutonium alpha activity. The contribution of plutonium-238 to the plutonium alpha activity was calculated based on the information from the thenoyltrifluoroacetone extraction and was subtracted from the plutonium alpha activity. The remaining plutonium alpha activity was from plutonium-239 and plutonium-240. The isotopic ratios from the ICP/MS analysis allowed the relative amounts of those isotopes to be determined. The results of the calculations are given in Table 12 and Table 13. The thenoyltrifluoroacetone extraction and the ICP/MS tests were done to support the first phase of the flow sheet work for the unirradiated Mark 42 fuel tubes.⁵

The total amount of plutonium and americium dissolved was corrected to account for the amount of plutonium and americium that was removed in the periodic samples. Although each sample only depleted the plutonium and americium by a small amount, the cumulative effect over the thirty-one days of tests was substantial – about 21% of the plutonium and americium was in the samples.

After about 98 hours, the plutonium and americium dissolution in AMM09a reached a plateau. The average amount of plutonium and americium dissolved was calculated using the sample results from 98 hours through 195 hours. The amount of plutonium and americium dissolved in AMM09a after 195 hours was calculated as 0.33 grams $\pm$ 0.01 grams or 90% of the plutonium and americium. After the CaF_2 was added to AMM09a to increase the fluoride concentration, the amount of plutonium and americium dissolved increased to 0.36 grams $\pm$ 0.1 grams or 98% of the amount of plutonium and americium. After decanting the aluminum-laden solution and adding 250 milliliters of a 8 M HNO_3 /0.20 M H_3BO_3 /

Table 10. Rad Screen and Gamma Scan Results for AMM09a and AMM09c Solutions

Experiment	Volume of Solution Before Sampling	Time Sample Taken	Beta Activity dpm/ml - assumed to be Pu-241	Alpha Activity dpm/ml	Corrected Alpha Activity dpm/ml	Americium-241 Alpha Activity dpm/ml
AMM09a-1	230ml	4.5 hours	1.15×10^9	2.76×10^8	2.56×10^8	8.13×10^7
AMM09a-2	230ml	12.2 hours	1.46×10^9	3.47×10^8	3.21×10^8	9.68×10^7
AMM09a-3	225ml	20.15 hours	1.62×10^9	3.79×10^8	3.51×10^8	1.06×10^8
AMM09a-4	215ml	28.35 hours	1.77×10^9	4.15×10^8	3.84×10^8	1.15×10^8
AMM09a-5	210ml	37.65 hours	1.94×10^9	4.55×10^8	4.21×10^8	1.23×10^8
AMM09a-6	210 ml	45.65 hours	2.08×10^9	4.81×10^8	4.45×10^8	1.30×10^8
AMM09a-7	200 ml	53.65 hours	2.16×10^9	5.06×10^8	4.69×10^8	1.36×10^8
AMM09a-8	185 ml	59.65 hours	2.23×10^9	5.17×10^8	4.79×10^8	1.37×10^8
AMM09a-9	200 ml	66.45 hours	2.41×10^9	5.61×10^8	5.19×10^8	1.46×10^8
			2.20×10^9	5.30×10^8	4.91×10^8	
			2.52×10^9	5.86×10^8	5.43×10^8	
AMM09a-10	185 ml	74.2 hours	2.29×10^9	5.56×10^8	5.15×10^8	1.51×10^8
AMM09a-11*	240 ml	81 hours	1.81×10^9	4.26×10^8	3.94×10^8	1.13×10^8
AMM09a-12	230 ml	90.6 hours	1.92×10^9	4.45×10^8	4.12×10^8	1.16×10^8
AMM09a-13	230 ml	98.3 hours	1.96×10^9	4.54×10^8	4.20×10^8	1.20×10^8
AMM09a-14	225 ml	105.55 hours	2.06×10^9	4.78×10^8	4.43×10^8	1.26×10^8
AMM09a-15	220 ml	111.15 hours	1.96×10^9	5.32×10^8	4.93×10^8	1.40×10^8
			2.28×10^9	5.07×10^8	4.69×10^8	
AMM09a-16	215 ml	118.55 hours	2.14×10^9	4.97×10^8	4.60×10^8	1.28×10^8
AMM09a-17	210 ml	126.65 hours	2.20×10^9	5.08×10^8	4.70×10^8	1.34×10^8
AMM09a-18	205 ml	134.75 hours	2.25×10^9	5.21×10^8	4.82×10^8	1.35×10^8
AMM09a-19	200 ml	142.25 hours	2.32×10^9	5.36×10^8	4.96×10^8	1.42×10^8
AMM09a-20	200 ml	142.25 hours	$1.58 \times 10^{9***}$	$4.66 \times 10^{8***}$	$4.32 \times 10^{8***}$	1.31×10^8
			2.12×10^9	5.07×10^8	4.69×10^8	
AMM09a-21	200 ml	151.05 hours	$1.78 \times 10^{9***}$	$4.80 \times 10^{8***}$	$4.44 \times 10^{8***}$	1.43×10^8
			2.22×10^9	5.40×10^8	5.00×10^8	
AMM09a-22	195 ml	159.05 hours	2.24×10^9	5.35×10^8	4.95×10^8	1.40×10^8
AMM09a-23*	250 ml	159.05 hours	1.65×10^9	3.83×10^8	3.55×10^8	0.97×10^8
			1.55×10^9	3.83×10^8	3.55×10^8	1.01×10^8
AMM09a-24	240 ml	165.75 hours	1.66×10^9	4.08×10^8	3.78×10^8	1.04×10^8
						1.22×10^8
AMM09a-25	235 ml	173.55 hours	1.78×10^9	4.22×10^8	3.91×10^8	2.48×10^8
						1.12×10^8
AMM09a-26	230 ml	181.35 hours	1.72×10^9	4.36×10^8	4.04×10^8	1.16×10^8
			1.78×10^9	4.40×10^8	4.07×10^8	
AMM09a-27	230 ml	189.15 hours	1.69×10^9	4.34×10^8	4.02×10^8	1.17×10^8
AMM09a-28	230 ml	194.95 hours	1.56×10^9	4.31×10^8	3.99×10^8	1.20×10^8
AMM09a-29**	220 ml	200.55 hours	2.22×10^9	5.11×10^8	4.73×10^8	1.33×10^8
			2.07×10^9	4.91×10^8	4.55×10^8	1.36×10^8
AMM09a-30	215 ml	207.55 hours	2.01×10^9	4.64×10^8	4.30×10^8	1.31×10^8
AMM09a-31	215 ml	214.8 hours	2.23×10^9	5.15×10^8	4.77×10^8	1.37×10^8
			2.08×10^9	4.85×10^8	4.49×10^8	1.32×10^8
AMM09c	245 ml	6.3 hours	4.31×10^7	9.92×10^6	9.19×10^6	2.54×10^6

* 5 Molar HNO₃ added to reach 250 milliliters. ** CaF₂ added to solution. *** Not used.

Table 11. Rad Screen and Gamma Scan Results for AMM09b and AMM09d Solutions

Experiment	Volume of Solution Before Sampling	Time Sample Taken	Beta Activity dpm/ml - assumed to be Pu-241	Alpha Activity dpm/ml	Corrected Alpha Activity dpm/ml	Americium-241 Alpha Activity dpm/ml
AMM09b -1	230ml	4.5 hours	1.40×10^9	3.32×10^8	3.07×10^8	9.29×10^7
AMM09b-2	230ml	12.2 hours	1.66×10^9	3.82×10^8	3.54×10^8	1.04×10^8
AMM09b-3	230ml	20.15 hours	1.73×10^9	4.10×10^8	3.80×10^8	1.11×10^8
AMM09b-4	215ml	28.35 hours	1.98×10^9	4.61×10^8	4.27×10^8	1.17×10^8
AMM09b-5	210ml	37.65 hours	1.93×10^9	4.62×10^8	4.28×10^8	1.27×10^8
AMM09b-6	210 ml	45.65 hours	2.12×10^9	4.93×10^8	4.57×10^8	1.35×10^8
AMM09b-7	200 ml	53.65 hours	2.20×10^9	5.11×10^8	4.73×10^8	1.38×10^8
AMM09b-8	190 ml	59.65 hours	2.22×10^9	5.14×10^8	4.76×10^8	1.38×10^8
AMM09b-9	200 ml	66.45 hours	2.32×10^9	5.36×10^8	4.96×10^8	1.40×10^8
AMM09b-10	195 ml	74.2 hours	2.41×10^9	5.57×10^8	5.16×10^8	1.48×10^8
AMM09b-11*	240 ml	81 hours	1.90×10^9	4.39×10^8	4.07×10^8	1.12×10^8
AMM09b-12	235 ml	90.6 hours	1.95×10^9	4.51×10^8	4.18×10^8	1.19×10^8
AMM09b-13	225 ml	98.3 hours	2.07×10^9	4.79×10^8	4.44×10^8	1.20×10^8
AMM09b-14	230ml	105.55 hours	2.08×10^9	4.76×10^8	4.41×10^8	1.22×10^8
AMM09b-15	225 ml	111.15 hours	2.07×10^9	4.80×10^8	4.44×10^8	1.24×10^8
AMM09b-16	220 ml	118.55 hours	2.10×10^9	4.84×10^8	4.48×10^8	1.27×10^8
AMM09b-17	220 ml	126.65 hours	2.13×10^9	4.92×10^8	4.56×10^8	1.27×10^8
AMM09b-18	215 ml	134.75 hours	2.13×10^9	4.92×10^8	4.56×10^8	1.33×10^8
AMM09b-19	210 ml	142.25 hours	2.22×10^9	5.09×10^8	4.71×10^8	1.35×10^8
AMM09b-20	215 ml	142.25 hours	1.83×10^9	4.89×10^8	4.53×10^8	1.28×10^8
			2.08×10^9	4.90×10^8	4.54×10^8	
AMM09b-21	210 ml	151.05 hours	1.98×10^9	5.13×10^8	4.75×10^8	1.36×10^8
AMM09b-22	205 ml	159.05 hours	2.09×10^9	4.17×10^8	4.79×10^8	1.30×10^8
AMM09b-23*	250 ml	159.05 hours	1.64×10^9	3.89×10^8	3.60×10^8	0.99×10^8
						1.05×10^8
AMM09b-24	245 ml	165.75 hours	1.57×10^9	4.08×10^8	3.78×10^8	1.05×10^8
						1.09×10^8
AMM09b-25	240 ml	173.55 hours	Not Valid	Not Valid	Not Valid	Not Valid
AMM09b-26	235 ml	181.35 hours	1.67×10^9	4.21×10^8	3.90×10^8	1.12×10^8
AMM09b-27	235 ml	189.15 hours	1.50×10^9	4.14×10^8	3.83×10^8	1.14×10^8
			1.76×10^9	4.29×10^8	3.97×10^8	
AMM09b-28	235ml	194.95 hours	1.86×10^9	4.32×10^8	4.00×10^8	1.16×10^8
AMM09b-29**	220 ml	200.55 hours	2.04×10^9	4.69×10^8	4.34×10^8	1.24×10^8
AMM09b-30	220 ml	207.55 hours	2.06×10^9	4.75×10^8	4.40×10^8	1.24×10^8
			1.94×10^9	4.57×10^8	4.23×10^8	1.25×10^8
AMM09b-31	215 ml	214.8 hours	2.05×10^9	4.73×10^8	4.38×10^8	1.24×10^8
AMM09d	245 ml	6.3 hours	4.87×10^7	1.11×10^7	1.03×10^7	1.24×10^8

*Solution replenished with 5 Molar HNO₃ to reach 250 milliliters. ** CaF₂ added to solution.

Table 12. Plutonium and Americium in AMM09a and AMM09c Solutions as a Function of Dissolution Time

Experiment	Time Sample Taken	Plutonium-241 g/ml	Americium-241 g/ml	Plutonium-238 g/ml	Plutonium-239 g/ml	Plutonium-240 g/ml
AMM09a-1	4.5 hours	5.02×10^{-6}	1.07×10^{-5}	6.50×10^{-7}	5.66×10^{-4}	1.42×10^{-4}
AMM09a-2	12.2 hours	6.38×10^{-6}	1.27×10^{-5}	8.37×10^{-7}	7.29×10^{-4}	1.83×10^{-4}
AMM09a-3	20.15 hours	7.07×10^{-6}	1.39×10^{-5}	9.13×10^{-7}	7.96×10^{-4}	2.00×10^{-4}
AMM09a-4	28.35 hours	7.73×10^{-6}	1.51×10^{-5}	1.00×10^{-6}	8.75×10^{-4}	2.20×10^{-4}
AMM09a-5	37.65 hours	8.47×10^{-6}	1.62×10^{-5}	1.11×10^{-6}	9.69×10^{-4}	2.43×10^{-4}
AMM09a-6	45.65 hours	9.08×10^{-6}	1.71×10^{-5}	1.18×10^{-6}	1.05×10^{-3}	2.57×10^{-4}
AMM09a-7	53.65 hours	9.43×10^{-6}	1.79×10^{-5}	1.24×10^{-6}	1.08×10^{-3}	2.71×10^{-4}
AMM09a-8	59.65 hours	9.74×10^{-6}	1.80×10^{-5}	1.27×10^{-6}	1.11×10^{-3}	2.79×10^{-4}
AMM09a-9	66.45 hours	1.01×10^{-5}	1.92×10^{-5}	1.34×10^{-6}	1.17×10^{-3}	2.93×10^{-4}
AMM09a-10	74.2 hours	1.05×10^{-5}	1.98×10^{-5}	1.41×10^{-6}	1.24×10^{-3}	3.08×10^{-4}
AMM09a-11*	81 hours	7.90×10^{-6}	1.48×10^{-5}	1.05×10^{-6}	9.14×10^{-4}	2.29×10^{-4}
AMM09a-12	90.6 hours	8.38×10^{-6}	1.52×10^{-5}	1.10×10^{-6}	9.62×10^{-4}	2.41×10^{-4}
AMM09a-13	98.3 hours	8.56×10^{-6}	1.58×10^{-5}	1.12×10^{-6}	9.76×10^{-4}	2.45×10^{-4}
AMM09a-14	105.55 hours	9.00×10^{-6}	1.66×10^{-5}	1.18×10^{-6}	1.03×10^{-3}	2.58×10^{-4}
AMM09a-15	111.15 hours	9.57×10^{-6}	1.84×10^{-5}	1.27×10^{-6}	1.11×10^{-3}	2.78×10^{-4}
AMM09a-16	118.55 hours	9.34×10^{-6}	1.68×10^{-5}	1.24×10^{-6}	1.08×10^{-3}	2.71×10^{-4}
AMM09a-17	126.65 hours	9.61×10^{-6}	1.76×10^{-5}	1.25×10^{-6}	1.09×10^{-3}	2.74×10^{-4}
AMM09a-18	134.75 hours	9.83×10^{-6}	1.77×10^{-5}	1.29×10^{-6}	1.13×10^{-3}	2.83×10^{-4}
AMM09a-19	142.25 hours	1.01×10^{-5}	1.87×10^{-5}	1.32×10^{-6}	1.15×10^{-3}	2.89×10^{-4}
AMM09a-20	142.25 hours	9.26×10^{-6}	1.72×10^{-5}	1.22×10^{-6}	1.04×10^{-3}	2.61×10^{-4}
AMM09a-21	151.05 hours	9.69×10^{-6}	1.88×10^{-5}	1.23×10^{-6}	1.07×10^{-3}	2.69×10^{-4}
AMM09a-22	159.05 hours	9.78×10^{-6}	1.84×10^{-5}	1.32×10^{-6}	1.15×10^{-3}	2.90×10^{-4}
AMM09a-23*	159.05 hours	6.99×10^{-6}	1.30×10^{-5}	9.53×10^{-7}	8.30×10^{-4}	2.08×10^{-4}
AMM09a-24	165.75 hours	7.25×10^{-6}	1.49×10^{-5}	9.87×10^{-7}	8.60×10^{-4}	2.16×10^{-4}
AMM09a-25	173.55 hours	7.77×10^{-6}	1.47×10^{-5}	1.04×10^{-6}	9.05×10^{-4}	2.27×10^{-4}
AMM09a-26	181.35 hours	7.64×10^{-6}	1.52×10^{-5}	1.08×10^{-6}	9.41×10^{-4}	2.37×10^{-4}
AMM09a-27	189.15 hours	7.38×10^{-6}	1.54×10^{-5}	1.06×10^{-6}	9.25×10^{-4}	2.32×10^{-4}
AMM09a-28	194.95 hours	6.81×10^{-6}	1.58×10^{-5}	1.04×10^{-6}	9.06×10^{-4}	2.28×10^{-4}
AMM09a-29**	200.55 hours	9.38×10^{-6}	1.77×10^{-5}	1.23×10^{-6}	1.07×10^{-3}	2.69×10^{-4}
AMM09a-30	207.55 hours	8.78×10^{-6}	1.72×10^{-5}	1.11×10^{-6}	9.70×10^{-4}	2.43×10^{-4}
AMM09a-31	214.8 hours	9.41×10^{-6}	1.77×10^{-5}	1.22×10^{-6}	1.07×10^{-4}	2.68×10^{-4}
AMM09c	6.3 hours	1.88×10^{-7}	3.34×10^{-7}	2.48×10^{-8}	2.16×10^{-5}	5.42×10^{-6}

*Solution replenished with 5 Molar HNO_3 to reach 250 milliliters. ** CaF_2 added to solution.

Table 13. Plutonium and Americium in AMM09b and AMM09d Solutions as a Function of Dissolution Time

Experiment	Time Sample Taken	Plutonium-241 g/ml	Americium-241 g/ml	Plutonium-238 g/ml	Plutonium-239 g/ml	Plutonium-240 g/ml
AMM09b -1	4.5 hours	6.11×10^{-6}	1.22×10^{-5}	8.00×10^{-7}	6.97×10^{-4}	1.75×10^{-4}
AMM09b-2	12.2 hours	7.25×10^{-6}	1.37×10^{-5}	9.31×10^{-7}	8.11×10^{-4}	2.04×10^{-4}
AMM09b-3	20.15 hours	7.55×10^{-6}	1.46×10^{-5}	1.00×10^{-6}	8.73×10^{-4}	2.19×10^{-4}
AMM09b-4	28.35 hours	8.65×10^{-6}	1.54×10^{-5}	1.00×10^{-6}	1.01×10^{-3}	2.53×10^{-4}
AMM09b-5	37.65 hours	8.43×10^{-6}	1.67×10^{-5}	1.12×10^{-6}	9.77×10^{-4}	2.45×10^{-4}
AMM09b-6	45.65 hours	9.26×10^{-6}	1.77×10^{-5}	1.20×10^{-6}	1.04×10^{-3}	2.62×10^{-4}
AMM09b-7	53.65 hours	9.61×10^{-6}	1.81×10^{-5}	1.25×10^{-6}	1.09×10^{-3}	2.73×10^{-4}
AMM09b-8	59.65 hours	9.69×10^{-6}	1.81×10^{-5}	1.26×10^{-6}	1.10×10^{-3}	2.76×10^{-4}
AMM09b-9	66.45 hours	1.01×10^{-5}	1.84×10^{-5}	1.33×10^{-6}	1.16×10^{-3}	2.90×10^{-4}
AMM09b-10	74.2 hours	1.05×10^{-5}	1.94×10^{-5}	1.37×10^{-6}	1.19×10^{-3}	3.00×10^{-4}
AMM09b-11*	81 hours	8.30×10^{-6}	1.47×10^{-5}	1.10×10^{-6}	9.57×10^{-4}	2.40×10^{-4}
AMM09b-12	90.6 hours	8.52×10^{-6}	1.56×10^{-5}	1.11×10^{-6}	9.70×10^{-4}	2.43×10^{-4}
AMM09b-13	98.3 hours	9.04×10^{-6}	1.58×10^{-5}	1.21×10^{-6}	1.05×10^{-3}	2.64×10^{-4}
AMM09b-14	105.55 hours	9.08×10^{-6}	1.60×10^{-5}	1.19×10^{-6}	1.04×10^{-3}	2.60×10^{-4}
AMM09b-15	111.15 hours	9.04×10^{-6}	1.63×10^{-5}	1.19×10^{-6}	1.04×10^{-3}	2.61×10^{-4}
AMM09b-16	118.55 hours	9.17×10^{-6}	1.67×10^{-5}	1.20×10^{-6}	1.04×10^{-3}	2.62×10^{-4}
AMM09b-17	126.65 hours	9.30×10^{-6}	1.67×10^{-5}	1.22×10^{-6}	1.07×10^{-3}	2.68×10^{-4}
AMM09b-18	134.75 hours	9.30×10^{-6}	1.75×10^{-5}	1.20×10^{-6}	1.05×10^{-3}	2.63×10^{-4}
AMM09b-19	142.25 hours	9.69×10^{-6}	1.77×10^{-5}	1.25×10^{-6}	1.09×10^{-3}	2.74×10^{-4}
AMM09b-20	142.25 hours	8.53×10^{-6}	1.68×10^{-5}	1.21×10^{-6}	1.06×10^{-3}	2.66×10^{-4}
AMM09b-21	151.05 hours	8.65×10^{-6}	1.79×10^{-5}	1.26×10^{-6}	1.10×10^{-3}	2.76×10^{-4}
AMM09b-22	159.05 hours	9.13×10^{-6}	1.71×10^{-5}	1.30×10^{-6}	1.13×10^{-3}	2.84×10^{-4}
AMM09b-23*	159.05 hours	7.15×10^{-6}	1.34×10^{-5}	9.63×10^{-7}	8.39×10^{-4}	2.11×10^{-4}
AMM09b-24	165.75 hours	6.86×10^{-6}	1.41×10^{-5}	1.01×10^{-6}	8.80×10^{-4}	2.21×10^{-4}
AMM09b-25	173.55 hours	-	-	-	-	-
AMM09b-26	181.35 hours	7.29×10^{-6}	1.47×10^{-5}	1.04×10^{-6}	9.02×10^{-4}	2.26×10^{-4}
AMM09b-27	189.15 hours	7.12×10^{-6}	1.50×10^{-5}	1.03×10^{-6}	8.98×10^{-4}	2.26×10^{-4}
AMM09b-28	194.95 hours	8.12×10^{-6}	1.52×10^{-5}	1.06×10^{-6}	9.22×10^{-4}	2.32×10^{-4}
AMM09b-29**	200.55 hours	8.91×10^{-6}	1.63×10^{-5}	1.16×10^{-6}	1.01×10^{-3}	2.53×10^{-4}
AMM09b-30	207.55 hours	8.74×10^{-6}	1.63×10^{-5}	1.14×10^{-6}	1.00×10^{-3}	2.51×10^{-4}
AMM09b-31	214.8 hours	8.95×10^{-6}	1.64×10^{-5}	1.17×10^{-6}	1.02×10^{-3}	2.55×10^{-4}
AMM09d	6.3 hours	2.13×10^{-7}	4.02×10^{-7}	2.69×10^{-8}	2.34×10^{-5}	5.88×10^{-6}

*Solution replenished with 5 Molar HNO_3 to reach 250 milliliters. ** CaF_2 added to solution.

0.15 M KF solution, the remaining plutonium and americium dissolved. A total of 0.37 grams of plutonium and americium dissolved. The amount of plutonium and americium in the initial Mark 42 reject compact material was calculated as 11 weight% (3.4007 grams of Mark 42 reject compact material was dissolved.)

After about 91 hours, the plutonium and americium dissolution in AMM09b reached a plateau. The average amount of plutonium and americium dissolved was calculated using the sample results from 91 hours through 195 hours. The amount of plutonium and americium dissolved in AMM09b after 195 hours was calculated as 0.34 grams $\pm$ 0.01 grams or 92% of the plutonium and americium. After the CaF_2 was added to AMM09b to increase the fluoride concentration, the amount of plutonium and americium dissolved increased to 0.36 grams $\pm$ 0.1 grams or 98% of the amount of plutonium and americium. After decanting the aluminum-laden solution and adding 250 milliliters of a 8 M HNO_3 /0.20 M H_3BO_3 / 0.15 M KF solution, the remaining plutonium and americium dissolved. A total of 0.36 grams of plutonium and americium dissolved. The amount of plutonium and americium in the initial Mark 42 reject compact material was calculated as 11 weight% (3.3868 grams of Mark 42 reject compact material was dissolved.)

The progress of the dissolution of the plutonium and americium was calculated using the information in Table 12 and Table 13 with the volumes in Table 10 and Table 11, respectively. The amounts of plutonium and americium that had dissolved at specific times during the dissolution are given in Table 14 and Table 15. Both the absolute amount and the fraction of the total plutonium and americium are given. The fraction of plutonium and americium was determined using the total plutonium and americium values from the AMM09a-31 and AMM09c solutions and from the AMM09b-31 and AMM09d solutions. As mentioned previously, the loss of plutonium and americium from the periodic sampling was incorporated into the calculation. A plot of the progress of the plutonium and americium dissolution in AMM09a is given in Figure 2 and for AMM09b in Figure 3.

The x-ray diffraction analysis of the sample taken 54 hours at 85°C showed PuO_2 . A minor amount of vermiculite also was identified.

4.1.4 Extended Dissolution Conclusions

The extended dissolution tests indicate that neither 0.15 M nor 0.20 M fluoride solutions are sufficient to dissolve the PuO_2 in the unirradiated Mark 42 fuel tubes. The aluminum:fluoride molar ratios for those two fluoride tests were 4.6 and 3.5, so it is not unexpected that PuO_2 did not completely dissolve. Addition of CaF_2 to the solutions to increase the fluoride concentrations to 0.25 M and 0.30 M did result in an increase in the dissolved PuO_2 - up to 98%. The corresponding aluminum:fluoride molar ratios would be 2.8 and 2.3.

The promising results of the addition of CaF_2 led to the next series of tests in which higher concentrations of fluoride were studied. Simultaneously, the proposed batching of the unirradiated Mark 42 fuel tubes was changed to a set of conditions that was more favorable for dissolution - fewer fuel tubes per batch. Use of CaF_2 as the fluoride source has the advantage that higher fluoride concentrations can be used without the concern about boron salts precipitating, as is the case for KF. A previous study reported the precipitation of a solids from a 0.75 M fluoride (0.375 M CaF_2)/9.3 M HNO_3 /0.23 M boron solution.⁹ The next series of tests for the Mark 42 flow sheet development examined much lower concentrations of CaF_2 : 0.125 to 0.15 M (with corresponding to fluoride concentrations of 0.25 to 0.30 M).

⁹ David 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.

Table 14. Progress of Plutonium and Americium Dissolution in AMM09a Experiment

Experiment	Time Sample Taken	Plutonium and Americium-241 in Solution (grams)	Fraction of Plutonium and Americium -241 in Solution
AMM09a -1	4.5 hours	0.17	0.45
AMM09a-2	12.2 hours	0.22	0.58
AMM09a-3	20.15 hours	0.23	0.63
AMM09a-4	28.35 hours	0.24	0.66
AMM09a-5	37.65 hours	0.26	0.72
AMM09a-6	45.65 hours	0.28	0.76
AMM09a-7	53.65 hours	0.29	0.78
AMM09a-8	59.65 hours	0.28	0.75
AMM09a-9	66.45 hours	0.31	0.85
AMM09a-10	74.2 hours	0.31	0.83
AMM09a-11*	81 hours	0.31	0.83
AMM09a-12	90.6 hours	0.32	0.85
AMM09a-13	98.3 hours	0.32	0.87
AMM09a-14	105.55 hours	0.33	0.90
AMM09a-15	111.15 hours	0.35	0.94
AMM09a-16	118.55 hours	0.33	0.90
AMM09a-17	126.65 hours	0.33	0.90
AMM09a-18	134.75 hours	0.34	0.91
AMM09a-19	142.25 hours	0.34	0.91
AMM09a-20	142.25 hours	0.32	0.88
AMM09a-21	151.05 hours	0.34	0.92
AMM09a-22	159.05 hours	0.33	0.90
AMM09a-23*	159.05 hours	0.32	0.87
AMM09a-24	165.75 hours	0.33	0.88
AMM09a-25	173.55 hours	0.33	0.91
AMM09a-26	181.35 hours	0.34	0.92
AMM09a-27	189.15 hours	0.34	0.91
AMM09a-28	194.95 hours	0.33	0.90
AMM09a-29**	200.55 hours	0.37	1.0
AMM09a-30	207.55 hours	0.34	0.93
AMM09a-31	214.8 hours	0.37	1.0
AMM09c	6.3 hours	0.007	1.0

*Solution replenished with 5 Molar HNO_3 to reach 250 milliliters. ** CaF_2 added to solution.

Table 15. Progress of Plutonium and Americium Dissolution in AMM09b Experiment

Experiment	Time Sample Taken	Plutonium and Americium-241 in Solution (grams)	Fraction of Plutonium and Americium-241 in Solution
AMM09b-1	4.5 hours	0.21	0.57
AMM09b-2	12.2 hours	0.24	0.66
AMM09b-3	20.15 hours	0.26	0.71
AMM09b-4	28.35 hours	0.28	0.77
AMM09b-5	37.65 hours	0.27	0.74
AMM09b-6	45.65 hours	0.29	0.79
AMM09b-7	53.65 hours	0.29	0.80
AMM09b-8	59.65 hours	0.28	0.77
AMM09b-9	66.45 hours	0.31	0.86
AMM09b-10	74.2 hours	0.31	0.87
AMM09b-11*	81 hours	0.32	0.88
AMM09b-12	90.6 hours	0.32	0.90
AMM09b-13	98.3 hours	0.34	0.93
AMM09b-14	105.55 hours	0.34	0.94
AMM09b-15	111.15 hours	0.34	0.93
AMM09b-16	118.55 hours	0.33	0.92
AMM09b-17	126.65 hours	0.34	0.94
AMM09b-18	134.75 hours	0.33	0.91
AMM09b-19	142.25 hours	0.34	0.93
AMM09b-20	142.25 hours	0.33	0.92
AMM09b-21	151.05 hours	0.34	0.94
AMM09b-22	159.05 hours	0.34	0.95
AMM09b-23*	159.05 hours	0.33	0.91
AMM09b-24	165.75 hours	0.34	0.93
AMM09b-25	173.55 hours	-	-
AMM09b-26	181.35 hours	0.33	0.92
AMM09b-27	189.15 hours	0.33	0.90
AMM09b-28	194.95 hours	0.34	0.95
AMM09b-29**	200.55 hours	0.36	0.98
AMM09b-30	207.55 hours	0.36	0.98
AMM09b-31	214.8 hours	0.36	0.98
AMM09d	6.3 hours	0.007	1.0

*Solution replenished with 5 Molar HNO_3 to reach 250 milliliters. ** CaF_2 added to solution.

Figure 2. 215-Hour Dissolution with 0.15 M KF

Figure 3. 215-Hour Dissolution with 0.20 M KF

4.2 CaF₂ Dissolution Flow Sheet Development

This series of tests examined the effect of higher fluoride concentrations on the dissolution of the Mark 42 reject compact material. Calcium fluoride was used as the fluoride source. Fluoride concentrations of 0.25 M, 0.275 M, and 0.30 M were tested (corresponding to CaF₂ concentrations of 0.125 M, 0.1375 M, and 0.15 M respectively). At these CaF₂ concentrations, no boron salts are expected to precipitate.

The amount of Mark 42 reject compact material used in the CaF₂ experiments was based on a different charging plan than the plan used for the extended dissolution tests. The new charging plan had been developed in response to nuclear criticality safety concerns. In the new charging plan only one outer fuel tube or one middle fuel tube could be packaged per GPC. Two inner fuel tubes could be packaged together in a GPC. A worst case scenario for dissolution was developed in which two inner fuel tubes are packaged together. This scenario has the highest amount of plutonium and aluminum for the three possible packaging configurations. Four GPC would be dissolved in one batch. Based on that scenario, there would be about 6.2 kilograms of plutonium and 80.2 kilograms of aluminum.

For the CaF₂ experiments, sufficient Mark 42 reject compact material and ANN were added to 250 milliliters of dissolver solution to duplicate the selected dissolution conditions. There were five CaF₂ tests done. In two tests (AMM010a and AMM10b), 0.30 M fluoride was tested with the concentrations of aluminum and PuO₂ set for a dissolver solution with 6,500 liters and 10,000 liters. The AMM11a and AMM11b tests examined 0.25 M and 0.275 M fluoride, respectively. Both AMM11a and AMM11b tests were based on a 6,500-liter dissolver solution. Aluminum nitrate nonahydrate was added to the AMM10 and AMM11 solutions to provide the aluminum expected from the dissolution of the cladding and the GPC.

The final test, AMM12, used a coupon of a GPC to provide the aluminum from the cladding and can. Once the coupon dissolved, the Mark 42 reject compact material was added. The fluoride concentration was 0.275 M in the AMM12 solution.

The detailed description of the CaF₂ test solutions is given in Table 16. All tests were done in 8 M HNO₃ and 2.2 grams boron/liter solutions. The experiments were done in Teflon beakers. As a result, the progress of the dissolution only could be checked periodically as opposed to when glass beakers are used and the solutions and solids can be viewed continuously. The dissolution times in Table 16 are the times between the check when solids were last observed and the final check when no solids were observed.

Table 16. Experimental Conditions for the CaF₂ Dissolution Flow Sheet Tests

Test	Mark 42 Reject Compact	Fluoride	Basis for Dissolver Solution	Dissolution Time at 85°C	Comments
AMM10a	2.33 grams	0.30Molar	6,500 liters	7 - 14 hours	Solids dissolved
AMM10b	1.51 grams	0.30 Molar	10,000 liters	1 - 6 hours	Solids dissolved
AMM11a	2.33 grams	0.275 Molar	6,500 liters	13 - 20 hours	Solids dissolved
AMM11b	2.33 grams	0.25Molar	6,500 liters	18 - 25 hours	Solids dissolved
AMM12a	2.34 grams	0.275 Molar	6,500 liters	16 - 24 hours	Solids dissolved

4.2.1 AMM10 Tests

The AMM10 tests used 0.30 M fluoride with CaF₂ as the fluoride source. Two tests were done based on different F-Canyon dissolver volumes. Tests AMM10a and AMM10b were based on 6,500 liters and 10,000 liters in the dissolver, respectively.

After the first hour at 85°C, no solids were observed in AMM10b. There were still solids present in AMM10a. Although there were no solids observed in AMM10b, that solution was heated for another 6.5 hours along with AMM10a to assure that indeed all of the solids had dissolved. Solution AMM10b was heated for an additional 6.5 hours after which no solids were observed.

4.2.1.1 Analytical Results for AMM10 Experiments

Samples were pulled for rad screen and gamma scan analyses periodically during the dissolution. The results of those analyses are given in Table 17. Total alpha activity (plutonium-238, plutonium-239, plutonium-240, and americium-241) and total beta activity (plutonium-241) were determined by rad screen. To determine the americium-241 contribution to the total alpha activity, gamma scans were done. The alpha activity results were corrected for the alpha-emitter counting efficiency as described in Sections 4.1.2.1 and 4.1.3.1.

Table 17. Rad Screen and Gamma Scan Results for AMM10 Solutions

Experiment	Volume of Solution Before Sampling	Time Sample Taken	Beta Activity dpm/ml assumed to be Pu-241	Alpha Activity dpm/ml	Corrected Alpha Activity dpm/ml	Americium-241 Alpha Activity dpm/ml
AMM10a-2	245ml	0.75 hours	Sample lost	Sample lost	-	Sample lost
AMM10a-3	245ml	7.15 hours	1.29×10^9	2.99×10^8	2.77×10^8	8.51×10^7 8.86×10^7
AMM10a-4	245 ml	13.65 hours	1.25×10^9	2.92×10^8	2.70×10^8	7.53×10^7 8.76×10^7
AMM10b-2	245ml	0.75 hours	1.07×10^9	2.50×10^8	2.32×10^8	6.34×10^7
AMM10b-3	275ml	7.15 hours	1.04×10^9	2.42×10^8	2.24×10^8	6.32×10^7

Samples were taken less frequently for the ICP/AES analyses for aluminum and boron, ion-selective electrode analysis for fluoride, and the analysis for total- and free-acid concentrations. Those results are discussed in Appendix B.

4.2.1.2 Discussion of Results for AMM10 Experiments

The grams of plutonium and of americium per liter were calculated using the information in Table 17 and those values are given in Table 18. The total amounts of plutonium and americium that had dissolved in the experiment were calculated as described in Sections 4.1.2.2 and 4.1.3.2. The total amounts dissolved in the solution were corrected for any plutonium and americium that was removed from the solution in samples. Those corrections were small. The corrected amounts are given in Table 19.

Table 18. Plutonium and Americium in AMM10 Solutions as a Function of Dissolution Time

Experiment	Time Sample Taken	Plutonium-241 g/ml	Americium-241 g/ml	Plutonium-238 g/ml	Plutonium-239 g/ml	Plutonium-240 g/ml
AMM10a-3	7.15 hours	5.63×10^{-6}	1.14×10^{-5}	7.09×10^{-7}	6.17×10^{-4}	1.55×10^{-4}
AMM10a-4	13.65 hours	5.46×10^{-6}	1.07×10^{-6}	7.27×10^{-7}	6.34×10^{-4}	1.59×10^{-4}
AMM10b-2	0.75 hours	4.67×10^{-6}	8.33×10^{-6}	6.27×10^{-7}	5.46×10^{-4}	1.37×10^{-4}
AMM10b-3	7.15 hours	4.54×10^{-6}	8.30×10^{-6}	6.00×10^{-7}	5.23×10^{-4}	1.31×10^{-4}

Table 19. Plutonium and Americium Dissolved in AMM10 Experiments

Experiment	Time Sample Taken	Plutonium and Americium-241 in Solution (grams)
AMM10a-3	7.15 hours	0.19
AMM10a-4	13.65 hours	0.20
AMM10b-2	0.75 hours	0.17
AMM10b-3	7.15 hours	0.18

Using the information in Table 16 and Table 19, the amount of plutonium and americium in the Mark 42 reject compact material can be calculated. The AMM10a results indicate that the Mark 42 reject compact material is only 8.6 weight% plutonium and americium whereas based on AMM10b, the Mark 42 reject compact material is 12 weight%. The AMM10b result agrees with the MC&A value (12.24 weight%). The 8.6 weight% value from the AMM10a experiment is lower than expected.

After dissolution was complete, it was observed that the volume of the AMM10b solution was about 275 milliliters. As the solution had been 245 milliliters the previous day, it was concluded that water (about 30 milliliters) from the condenser had splashed into the solution during sampling. Later tests (AMM11b) indicated that there was an actual leak in the condenser and that during the dissolution water was dripping into the solution. That dilution would result in the plutonium concentration being closer to an 11,000-liter dissolver case as opposed to the 10,000-liter dissolver case. The fluoride would be diluted to 0.26 M. As most of the PuO_2 had dissolved during the first hour at 85°C, this dilution during the next 6.4 hours at 85°C probably did not have a significant effect on the dissolution of the remaining PuO_2 .

4.2.2 AMM11 Tests

The AMM11 tests examined the dissolution of the Mark 42 reject compact material with 0.25 M and 0.275 M fluoride in the dissolver solution with CaF_2 as the fluoride source. The two tests were done based on an F-Canyon dissolver solution volume of 6,500 liters.

No solids were observed in AMM11a and AM11b after 20 hours and 25 hours, respectively, at 85°C. The solutions were checked for solids after 5.2 hours, 13 hours, 17.8 hours, and 25 hours. Initial observations of the AMM11a solution after 13 hours at 85°C indicated that there were no solids. However, further examination revealed that there were solids and that solution was heated for an additional seven hours.

4.2.2.1 Analytical Results for AMM11 Experiments

Samples were pulled for rad screen and gamma scan analyses periodically during the dissolution. The results of those analyses are given in Table 20. Total alpha activity (plutonium-238, plutonium-239, plutonium-240, and americium-241) and total beta activity (plutonium-241) were determined by rad screen. To determine the americium-241 contribution to the total alpha activity, gamma scans were done. The alpha activity results were corrected for the alpha-emitter counting efficiency as described in Sections 4.1.2.1 and 4.1.3.1.

Table 20. Rad Screen and Gamma Scan Results for AMM11 Solutions

Experiment	Volume of Solution Before Sampling	Time Sample Taken	Beta Activity dpm/ml assumed to be Pu-241	Alpha Activity dpm/ml	Corrected Alpha Activity dpm/ml	Americium-241 Alpha Activity dpm/ml
AMM11a-2	245 ml	5.2 hours	1.86×10^9	4.36×10^8	4.04×10^8	1.09×10^8
			1.75×10^9	4.16×10^8	3.85×10^8	
AMM11a-3	240 ml	13 hours	1.66×10^9	4.09×10^8	3.79×10^8	1.11×10^8
			1.78×10^9	4.18×10^8	3.87×10^8	
AMM11a-4	245 ml	13 hours	1.83×10^9	4.28×10^8	3.96×10^8	1.08×10^8
			1.77×10^9	4.20×10^8	3.89×10^8	
AMM11a-5	230 ml	20 hours	1.65×10^9	3.83×10^8	3.55×10^8	1.12×10^8
			$3.09 \times 10^{9*}$	$7.20 \times 10^{8*}$	$6.67 \times 10^{8*}$	
AMM11b-2	235 ml	5.2 hours	1.72×10^9	4.04×10^8	4.03×10^8	8.99×10^7
			1.61×10^9	3.78×10^8	3.84×10^8	
AMM11b-3	Not taken, > 250 ml	13 hours	1.47×10^9	3.40×10^8	3.15×10^8	8.60×10^7
			1.48×10^9	3.51×10^8	3.25×10^8	
AMM11b-4	Not taken, > 250 ml	17.8 hours	1.39×10^9	3.24×10^8	3.00×10^8	8.89×10^7
			1.47×10^9	3.46×10^8	3.20×10^8	
AMM11b-5	280 ml	24.8 hours	1.28×10^9	3.00×10^8	2.78×10^8	8.08×10^7
			1.51×10^9	3.58×10^8	3.32×10^8	

* Values not used in further calculations.

Samples were taken less frequently for the ICP/AES analyses for aluminum and boron, ion-selective electrode analysis for fluoride, and the analysis for total- and free-acid concentrations. Those results are discussed in Appendix B.

4.2.2.2 Discussion of Results for AMM11 Experiments

The grams of plutonium and of americium per liter were calculated using the information in Table 20 and those values are given in Table 21. The values for AMM11b-3 and AMM11b-4 were combined because they were duplicate samples. The amounts of plutonium and americium that had dissolved in the experiments were calculated as described in Sections 4.1.2.2 and 4.1.3.2. The total amounts dissolved in the solution were corrected for any plutonium and americium that was removed from the solution as samples. Those corrections were small. The corrected amounts are given in Table 22. No values for the total amount of plutonium and americium in AMM11b-3 and AMM11b-4 were obtained because the volumes of the solutions were not measured.

During the dissolution, it was observed that the volume of AMM11b was greater than 250 milliliters. The previous volume (after about 5 hours of heating) was 235 milliliters. This same phenomenon had been observed for AMM10b. At the time of the AMM10b observation, the increased volume was attributed to spillage from the condenser during the sampling. However, it is more likely that the condenser leaked. As a result, water was slowly added to the solution. After the Mark 42 reject compact material had dissolved and the solution had cooled, the volume of the solution was measured. The final volume was 280 milliliters, including the six milliliters that had been removed from samples. The new volume would correspond to about 11,000 liters in the F-Canyon dissolver with a fluoride concentration of 0.22 M. Although the volume change may have affected the equilibria among the various fluoride-complexing

Table 21. Plutonium and Americium in AMM11 Solutions as a Function of Dissolution Time

Experiment	Time Sample Taken	Plutonium-241 g/ml	Americium-241 g/ml	Plutonium-238 g/ml	Plutonium-239 g/ml	Plutonium-240 g/ml
AMM11a-2	5.2 hours	7.88×10^{-6}	1.43×10^{-5}	1.06×10^{-6}	9.27×10^{-4}	2.33×10^{-4}
AMM11a-3	13 hours	7.51×10^{-6}	1.46×10^{-5}	1.01×10^{-6}	8.84×10^{-4}	2.22×10^{-4}
AMM11a-4	13 hours	7.86×10^{-6}	1.42×10^{-5}	1.06×10^{-6}	9.24×10^{-4}	2.32×10^{-4}
AMM11a-5	20 hours	7.21×10^{-6}	1.48×10^{-5}	9.03×10^{-7}	7.87×10^{-4}	1.98×10^{-4}
AMM11b-2	5.2 hours	7.27×10^{-6}	1.18×10^{-5}	9.98×10^{-7}	8.92×10^{-4}	2.24×10^{-4}
AMM11b-3/4	13 hours	6.35×10^{-6}	1.15×10^{-5}	8.48×10^{-7}	7.39×10^{-4}	1.86×10^{-4}
AMM11b-5	24.8 hours	5.59×10^{-6}	1.06×10^{-5}	7.34×10^{-7}	6.40×10^{-4}	1.61×10^{-4}

species, it is expected that essentially the same amount of free fluoride was available to assist with the dissolution of the PuO_2 . Therefore, this volume change probably did not significantly change the dissolution time of the Mark 42 reject compact material.

Using the information in Table 16 and Table 22, the amount of plutonium and americium in the Mark 42 reject compact material can be calculated. The value of plutonium and americium in AMM11a-5 seems too low compared to the values obtained for AMM11a-2, AMM11a-3, and AMM11a-4. There is no obvious explanation for the AMM11a-5 value. The volume of the final solution was rechecked and was 230 milliliters. Before sampling the volume would have been 235 milliliters, the value used in the calculations. Using the AMM11a-5 value, the plutonium and americium content of the Mark 42 reject compact material is about 10 weight%. If the higher AMM11a-4 value is used, the plutonium and americium content of the Mark 42 reject compact material is 12 weight%. The value for plutonium and americium content in Mark 42 reject compact material from AMM11b-5 is 11 weight%. All three values are in agreement with the MC&A value of 12.24 weight% and the values obtained in previous work.⁵

Table 22. Plutonium and Americium Dissolved in AMM11 Experiments

Experiment	Time Sample Taken	Plutonium and Americium-241 in Solution (grams)
AMM11a-2	5.2 hours	0.28
AMM11a-3	13 hours	0.27
AMM11a-4	13 hours	0.29
AMM11a-5	20 hours	0.24
AMM11b-2	5.2 hours	0.27
AMM11b-5	24.8 hours	0.26

4.2.3 AMM12 Tests

In previous tests, ANN was added as a surrogate for the dissolved aluminum from the GPC and cladding of the unirradiated Mark 42 fuel tubes. As a result, the acid concentrations of the previous tests were higher than expected for the actual dissolution of the unirradiated Mark 42 fuel tubes because as the bulk aluminum (from the GPC and cladding) dissolves, it consumes acid. The only acid depletion in those

previous tests was from the dissolution of the aluminum in the Mark 42 reject compact material (i.e., the fuel core). In the AMM12 test, an aluminum coupon from a GPC was added to the dissolver solution to test the dissolution of the Mark 42 reject compact material in the lower acid solution. Once the aluminum coupon had dissolved, the Mark 42 reject compact material was added. The fluoride concentration was 0.275 M with CaF_2 as the fluoride source. The test was done based on an F-Canyon dissolver solution volume of 6,500 liters.

The aluminum coupon (1.21 grams) dissolved after 5.5 hours at 85°C. The Mark 42 reject compact material was added to the cooled solution. Solids were observed after 7.6 hours and 16.3 hours at 85°C. No solids were observed after 24.3 hours at 85°C.

The only difference between AMM11a and AMM12 was the way that aluminum was provided to the dissolver solution as a surrogate for the GPC and cladding. An aluminum coupon was used in AMM12 and ANN was used in AMM11a. The dissolution of the Mark 42 reject compact material was similar for the two experiments. In AMM11a, the material dissolved between 13 and 20 hours at 85°C and in AMM12 the material dissolved between 16 and 24 hours at 85°C. Thus, the dissolution of the Mark 42 reject compact material did not appear to be affected whether ANN or an aluminum coupon was used as surrogate for the GPC and cladding.

4.2.3.1 Analytical Results for AMM12 Experiments

Samples were pulled for rad screen and gamma scan analyses periodically during the dissolution. The results of those analyses are given in Table 23. Total alpha activity (plutonium-238, plutonium-239, plutonium-240, and americium-241) and total beta activity (plutonium-241) were determined by rad screen. To determine the americium-241 contribution to the total alpha activity, gamma scans were done. The alpha activity results were corrected for the alpha-emitter counting efficiency as described in Sections 4.1.2.1 and 4.1.3.1.

Table 23. Rad Screen and Gamma Scan Results for AMM12 Solution

Experiment	Volume of Solution Before Sampling	Time Sample Taken	Beta Activity dpm/ml assumed to be Pu-241	Alpha Activity dpm/ml	Corrected Alpha Activity dpm/ml	Americium-241 Alpha Activity dpm/ml
AMM12-3	220 ml	7.6 hours	1.61×10^9	3.78×10^8	3.50×10^8	1.00×10^8
AMM12-4	220 ml	16.3 hours	1.46×10^9	3.38×10^8	3.13×10^8	1.05×10^8
AMM12-5	220 ml	24.3 hours	1.71×10^9	3.95×10^8	3.66×10^8	1.02×10^8

Samples were taken less frequently for the ICP/AES analyses for aluminum and boron, ion-selective electrode analysis for fluoride, and the analysis for total- and free-acid concentrations. Those results are discussed in Appendix B.

4.2.3.2 Discussion of Results for AMM12 Experiment

The grams of plutonium and of americium per liter were calculated using the information in Table 23 and those values are given in Table 24. The total amounts of plutonium and americium that had dissolved in the experiment were calculated as described in Sections 4.1.2.2 and 4.1.3.2. The total amounts dissolved in the solution were corrected for any plutonium and americium that was removed from the solution as samples. Those corrections were small. The corrected amounts are given in Table 25. The values for AMM12-3 and AMM12-4 are not in agreement with the progress of the dissolution. Either the value for AMM12-3 is too high or the value for AMM12-4 is too low.

Table 24. Plutonium and Americium in AMM12 Solution as a Function of Dissolution Time

Experiment	Time Sample Taken	Plutonium-241 g/ml	Americium-241 g/ml	Plutonium-238 g/ml	Plutonium-239 g/ml	Plutonium-240 g/ml
AMM12-3	7.6 hours	7.03×10^{-6}	1.31×10^{-5}	9.32×10^{-7}	8.12×10^{-4}	2.04×10^{-4}
AMM12-4	16.3 hours	6.38×10^{-6}	1.37×10^{-5}	7.77×10^{-7}	6.77×10^{-4}	1.70×10^{-4}
AMM12-5	24.3 hours	7.47×10^{-6}	1.34×10^{-5}	9.83×10^{-7}	8.57×10^{-4}	2.15×10^{-4}

Table 25. Plutonium and Americium Dissolved in AMM12 Experiments

Experiment	Time Sample Taken	Plutonium and Americium-241 in Solution (grams)
AMM12-3	0.75 hours	0.23
AMM12-4	7.15 hours	0.19
AMM12-5	13.65 hours	0.24

Using the information in Table 16 and Table 25, the amount of plutonium and americium in the Mark 42 reject compact material can be calculated. The calculated amount of plutonium and americium in the Mark 42 reject compact material was 10 weight%. That value agrees with the MC&A (12.24 weight%) value, other values obtained in this set of experiments, and values obtained in previous work.⁵

4.2.4 CaF₂ Dissolution Conclusions

The CaF₂ dissolution experiments demonstrated that fluoride concentrations between 0.25 M and 0.30 M can be used to dissolve the Mark 42 reject compact material with the new batching scenario. The most effective of the tested fluoride concentrations for dissolution was 0.30 M (AMM10a and AMM10b). That result is not surprising because the aluminum:fluoride mole ratios were 1.5 and 1, respectively. Previous tests⁵ had shown aluminum:fluoride ratios of less than 1.3 were successful in dissolving Mark 42 reject compact material in about 4 hours. Those tests also included an aluminum:fluoride mole ratio of 1.5. That material was not dissolved within six hours and for AMM10a almost 14 hours were required for dissolution of the solids. As the fluoride concentration was decreased, the dissolution time increased (AMM11a and AMM11b). The use of ANN or an aluminum coupon (AMM12) as a source of GPC and cladding aluminum did not seem to affect the dissolution of the Mark 42 reject compact material.

4.3 Dissolution of 6063-Aluminum Coupons

As mentioned previously, no mercury was added to the crushed Mark 42 reject compact material to assist with the dissolution of aluminum. Initially, the enhanced dissolution rate was observed in this study was attributed to the larger surface area of the crushed material compared to bulk aluminum. Larger surface areas usually promote dissolution. However, recent work at Idaho National Engineering and Environmental Laboratory has identified another reason that the aluminum dissolution proceeded so readily. Anderson and Christian reported that HBF₄ behaves similarly to the Hg(NO₃)₂ catalyst for dissolving aluminum.¹⁰ It is reasonable to expect HBF₄ in the dissolution solutions in equilibria with H₃BO₃, HNO₃, and KF or CaF₂.

¹⁰ Philip A. Anderson and Jerry D. Christian, Journal of Materials Research, 13(1), 68 (1998).

The aim of this study was to compare the dissolution of aluminum coupons in representative solutions. In one solution, HBF_4 was added to an HNO_3 solution. A second solution had a composition similar to the solutions used for the dissolution of Mark 42 reject compact material (8 M HNO_3 /0.20 M H_3BO_3 /0.1375 CaF_2). The third solution was simply an HNO_3 solution without any boron. If the HBF_4 species was present in the dissolver solution, then the dissolution of aluminum coupon in the 8 M HNO_3 /0.20 M H_3BO_3 /0.1375 CaF_2 solution should be better than the dissolution in the 8 M HNO_3 solution. Of particular interest was the comparison of the dissolution in the two solutions containing boron.

Three solutions were made up as described below:

Solution A:	0.2036 M HBF_4 /8 M HNO_3
Solution B:	0.2036 M H_3BO_3 /0.1375 M CaF_2 /8 M HNO_3
Solution C:	8 M HNO_3 .

Aluminum coupons (~3.1 grams) from a GPC were added to the solutions. Once the aluminum dissolved, the aluminum concentration would be 0.46 M, the aluminum concentration for AMM11a (6,500 liter case). The solutions were heated to 85°C with a maximum of 95°C being reached during the aluminum dissolution because of the exothermicity of that reaction. Evaporation from the solutions was minimized by use of an ice-cooled condenser watch glass.

The aluminum dissolution in Solutions A and B proceeded more vigorously than the dissolution in Solution C. Dark orange NO_x fumes evolved from Solutions A and B, evidence of the oxidation of the aluminum by HNO_3 . Only a trace of NO_x fumes was observed from Solution C. As expected, the aluminum coupon in Solution A dissolved most rapidly, after 1.5 hours at 85°C. The aluminum coupon in Solution B needed four hours for dissolution. After 10 hours, the aluminum coupon in Solution C had not dissolved. Furthermore, a visual inspection of the coupon in Solution C indicated that very little of the aluminum coupon had dissolved.

These results are promising for developing a flow sheet that does not require mercury to catalyze the dissolution of bulk aluminum. The actual function of the HBF_4 on the aluminum is not known. The HBF_4 could be consumed as the aluminum is dissolved or it may be catalytic. It may be advantageous to explore the ability of HBF_4 to promote aluminum dissolution because if HBF_4 did promote the aluminum dissolution in a satisfactory manner, then mercury would not be needed. The disuse of mercury in the dissolution of bulk aluminum materials at SRS would be an important waste and hazard minimization step.

5 Summary

The extended dissolution tests (AMM08 and AMM09) were not successful. Solutions of crushed Mark 42 reject compact material were heated at 85°C for up to 195 hours without complete dissolution of the PuO_2 . Those tests used 0.15 M and 0.20 M fluoride and were premised on a flow sheet in which 10.3 kilograms of plutonium and 96.3 kilograms from the unirradiated Mark 42 fuel tubes were added to 6,500 liters of dissolver solution per batch.

The CaF_2 dissolution tests (AMM10, AMM11, and AMM12) were successful because all of the crushed Mark 42 reject compact material was dissolved within seven to 24 hours depending on the fluoride concentration. The most effective fluoride concentration was 0.30 M (AMM10a and AMM10b). The flow sheet for these tests was based on the addition of 6.2 kilograms of plutonium and 80.2 kilograms from the unirradiated Mark 42 fuel tubes to the dissolver solution per batch. Dissolver solution volumes of 6,500 and 10,000 liters were tested. The dissolution in the larger volume (AMM10b) was completed in the shortest amount of time because it had the smallest aluminum:fluoride molar ratio (1:1).

The corrosive effect of the higher-fluoride concentrations is important to the acceptance of those fluoride concentrations for F-Canyon processing solutions. A study is being done by the Materials Applications and Technology Group to determine the corrosion effects of fluoride concentrations in the range of 0.2 to 0.4 M using the Mark 42 dissolution flow sheet. Those results will be published in a separate report. As part of that study, the effective free-fluoride concentrations will be measured.

Scoping tests indicate that use of mercury to promote the dissolution of bulk aluminum may not be necessary in solutions in which boron and fluoride are present. The HBF_4 species may serve a similar catalytic role in the dissolution of aluminum as mercury serves. Further testing is recommended.

Appendix A

Estimate of Amount of Aluminum in Mark 42 Fuel Tube Cladding

The information in the NMP-SRB-92-0048 was used to estimate the quantity of aluminum in the cladding of the Mark 42 fuel tubes.⁷ These estimates are based on the specification for the Mark 42 fuel tube. It is important to note that the reject mark 42 fuel tubes did not meet the plutonium density specifications. Therefore, the aluminum content of the reject fuel tubes is different. Based on Frontroth's report,¹ the reject inner fuel tube may have about 5% less aluminum than required by the specification. Although the following calculations may over- or under estimate the amount of aluminum in the reject fuel core with a corresponding under- or over estimate of the aluminum in the cladding, the total aluminum that will be dissolved is known from Beckum's report.⁷

Inner Fuel Tube

According to that report, there are five bundles of Mark 42 fuel that each contains two inner tubes. The plutonium content is given as 0.78 kilograms per inner tube in the report. The inner tube core has a plutonium content of 18.7 weight%. Therefore, the amount of aluminum in each inner fuel tube core is 3.29 kilograms. The total aluminum content of the bundle (core + cladding + GPC) with two inner tubes is given as 20.04 kilograms in the report. There are 6.67 kilograms of aluminum in each GPC. Therefore, the amount of aluminum in the cladding of each inner fuel tube is 3.40 kilograms.

Middle Fuel Tube

One bundle is listed in the report as containing only one fuel tube, a middle fuel tube. The amount of plutonium in the fuel tube core is given as 1.51 kilograms. Using the middle tube core composition of 21.8 weight% plutonium, the amount of aluminum in the middle tube core is 5.20 kilograms. The total aluminum content of the bundle (core + cladding + GPC) is given as 15.09 kilograms in the report. There are 6.67 kilograms of aluminum in each GPC. Therefore, the amount of aluminum in the cladding of the middle fuel tube is 3.23 kilograms.

Outer Fuel Tube

The amount of aluminum in the outer tube's cladding had to be estimated indirectly because there was no information on individual outer tubes. According to the report, there are several bundles that contain the complete fuel tube assembly (i.e., outer, middle, and inner fuel tubes). The plutonium content in the outer fuel tube core is given as 1.06 kilograms. With a plutonium content of 15.4 weight%, the outer fuel tube core has 5.68 kilograms of aluminum. The total aluminum in the bundle is 30.75 kilograms. Subtracting the contributions by the GPC (6.67 kilograms), the fuel cores (5.68 kilograms – outer, 5.20 kilograms – middle, and 3.29 kilograms – inner), the inner fuel tube cladding (3.40 kilograms), and the middle fuel tube cladding (3.23 kilograms), the cladding on the outer fuel tube is estimated at 3.29 kilograms.

Table A1 summarizes the composition of the fuel tubes.

Table A1. Composition of Mark 42 Fuel Tubes (in kilograms)

Fuel tube	Plutonium	PuO ₂	Aluminum in Cermet (Core)	Aluminum in Cladding
Inner Tube	0.78	0.88	3.29	3.40
Middle Tube	1.51	1.71	5.20	3.23
Outer Tube	1.06	1.20	5.68	3.29

Appendix B

Results of Fluoride Concentration Analyses, Acid Concentration Analyses, and ICP/AES Analyses

AMM08 Tests

The aluminum and boron concentrations in the solutions were determined with ICP/AES. The results of those analyses are given in Table B1. Initial and final sets of samples were taken from the AMM08a and AMM08b solutions. The first set of samples was taken after the ANN had been added but before the Mark 42 reject compact material had been added. The second set of samples was taken after 48 hours of dissolution. One set of samples was from the AMM08c and AMM08d solutions. Those samples were taken after the solids had dissolved.

Table B1. ICP/AES Results for Aluminum and Boron for AMM08 Solutions

Experiment	Time into Dissolution Sample Taken	Aluminum mg/liter	% Aluminum as ANN Added	Boron mg/liter	% Boron Added
AMM08a-0	0 hours	7,800	97%	2,200	101%
AMM08b-0	0 hours	7,800	96%	2,220	102%
AMM08a-7	48 hours	31,500	-	3,340	81%
AMM08b-7	48 hours	28,200	-	3,160	94%
AMM08c	8 hours	9,200	-	420	None Added
AMM08d	8 hours	1,900	-	240	None Added

The ICP/AES data were expected to help with a material balance and to establish the amount of aluminum in the Mark 42 reject compact material. The boron results would confirm the amount of boron that was used in the experiments. The aluminum and boron results for AMM08a-0 and AMM08b-0 did correspond to the amount of aluminum in ANN and the amount of boron in the H_3BO_3 that were added to the AMM08a and AMM08b solutions.

The results for AMM08a-7 and AMM08b-7 cannot be used for a material balance of the Mark 42 reject compact material because of the precipitation of solids as the solutions evaporated during the 48 hours at temperature. The x-ray diffraction analyses of the solids showed that both ANN and H_3BO_3 were present. Thus, the total amount of aluminum dissolved from the Mark 42 reject compact material could not be determined.

According to the literature,¹¹ at 25°C the solubility of H_3BO_3 decreases in HNO_3 solutions as the HNO_3 concentration increases. For example the H_3BO_3 solubility in 4.698 M HNO_3 is given as 27 grams per liter and 18.31 grams per liter in 8.410 M HNO_3 . Solutions 8a and 8b were initially 8 M nitric acid/0.20 M boron (close to the solubility limit of H_3BO_3). After 48 hours at 85°C, sufficient solution had evaporated to increase the free-acid concentrations to about 9.7 M. The precipitation of H_3BO_3 from the solutions at higher acid concentrations is not surprising.

Milligan¹² reported the solubility of aluminum nitrate ($Al(NO_3)_3$) in HNO_3 solutions as a function of HNO_3 concentration and temperature. The solubility of $Al(NO_3)_3$ decreased in HNO_3 solutions as the HNO_3 concentration increased. Therefore, the precipitation of ANN from the evaporated solutions is not unexpected because the free-acid concentration had increased to 9.7 M.

The precipitation of ANN does explain why aluminum was found by the ICP/AES analyses of samples from the AMM08c and AMM08d solutions. Very little aluminum, if any, was expected in those two solutions because all of the aluminum in the Mark 42 reject compact material should have dissolved in the

¹¹ Atherton Seidel, "Solubilities of Inorganic and Metal Organic Compounds", D. Van Nostrand Company, New York, 1940.

¹² Lowell H. Milligan, Journal of the American Chemical Society, 44, (1922), 567.

first hours of the dissolution (i.e., the AMM008a and AMM08b solutions). However, any precipitated ANN present in the solids remaining after the AMM08a and AMM08b solutions were decanted would have been redissolved in AMM08c and AMM08d, respectively. Similarly, no boron was expected in the AMM08c and AMM08d solutions because no H_3BO_3 had been added to the solutions. The ICP/AES analyses of samples from AMM08c and AMM08d found 420 and 240 milligrams of boron per liter, respectively. That boron must have been from precipitated H_3BO_3 in the solid residue left after the AMM08a and AMM08b solutions had been decanted.

The total- and free-acid concentrations were measured for the solutions. Those results are given in Table B2. The interference from complexing metal ions (e.g., aluminum) is removed in the free-acid concentration analysis while the total-acid concentration analysis includes the metal ion effects. The total- and free-acid concentrations confirm that the evaporation of the solutions resulted in increased acid concentration. Typically, after the Mark 42 reject compact material dissolved, the acid concentration decreased from about 8 M to 6 M because of the aluminum dissolution.

Table B2. Total- and Free-Acid Concentrations and Fluoride Concentration for AMM008 Solutions

Experiment	Free Acid (Molar)	Total Acid (Molar)	Fluoride (ppm)
AMM08a-0	7.32	8.66	1,250
AMM08b-0	7.52	8.78	1,690
AMM08a-7	10.13	11.6	1,510
AMM08b-7	9.32	11.31	1,460
AMM08c	7.46	8.66	814
AMM08d	7.81	8.26	818

The dissolution of the PuO_2 is dependent on the availability of free-fluoride ions. If complexing ions are present in the solution, e.g., boron or aluminum, the amount of free fluoride ions is expected to be reduced. The fluoride-ion concentration was measured with an ion-selective electrode. In general, that analysis is a measure of total fluoride-ion concentration. However, the analysis does not provide the free-fluoride concentration for these samples because the analysis is not calibrated to provide the free-fluoride value in the presence of complexing agents (e.g., boron and aluminum). Thus, this analysis provides qualitative information on the free-fluoride ions in the solution. The results are presented in Table B2.

The AMM08a-0 and AMM08b-0 samples were taken of the dissolver solution after the addition of ANN but before the addition of the Mark 42 reject compact material. Based on the initial fluoride concentrations of the solutions, the expected results were 2,850 ppm and 3,800 ppm for AMM08a and AMM08b, respectively. The analytical results indicate that some of the fluoride is being complexed by the aluminum and boron.

The results from AMM08a-7 and AMM08b-7 cannot be interpreted easily. Typically, the fluoride concentration from the initial solution could be compared with the fluoride concentration from the final solution to see the effect of the aluminum dissolution from the Mark 42 reject compact material. However, because ANN and H_3BO_3 precipitated, the resulting fluoride complexing equilibria have shifted. It is not possible to draw any conclusions from the results regarding the effect of the aluminum from the dissolved Mark 42 reject compact material on the fluoride concentration.

The fluoride concentration results from the AMM08c and AMM08d samples are unexpected. Based on the ICP/AES results, those solutions had significantly less aluminum and boron available for complexation than the AMM08a-0 and AMM08b-0 solutions. However, for the same fluoride concentration (0.15 M), the fluoride concentration results indicate there are more complexing reagents available in AMM08c compared to AMM08a-0.

AMM09

Table B3 contains the ICP/AES results for aluminum, boron, and calcium for the AMM09 experiments. In addition to providing material balance information, it was expected that the ICP/AES analyses would help monitor the effect of the periodic additions of the 5 Molar nitric acid to the solutions. For example, the samples for AMM09a-23 and AMM09b-23 were taken immediately after the 5 M HNO_3 solution was added to replenish solutions AMM09a and AMM09b to 250 milliliters. Thus, a dilution factor should relate the results of those two samples to the results from samples AMM09a-22 and AMM09b-22, respectively.

Table B3. ICP/AES Results for Aluminum, Boron, and Calcium for AMM09 Solutions

Experiment	Time into Dissolution Sample Taken	Aluminum mg/liter	Boron mg/liter	Calcium mg/liter
AMM09a-0	0 hours	7,500	2,010	-
AMM09a-6	45.65 hours	19,400	2,110	-
AMM09a-11*	74.2 hours	15,800	1,770	-
AMM09a-22	159.05 hours	19,700	2,160	-
AMM09a-23*	159.05 hours	14,000	1,540	-
AMM09a-28	194.95 hours	16,700	1,830	-
AMM09a-31**	214.8 hours	18,500	1,980	2,570
AMM09c	6.3 hours	235	2,170	-
AMM09b-0	0 hours	7,330	1,960	-
AMM09b-6	45.65 hours	21,600	2,300	-
AMM09b-11*	74.2 hours	16,600	1,810	-
AMM09b-22	159.05 hours	19,900	2,130	-
AMM09b-23*	159.05 hours	14,700	1,580	-
AMM09b-28	194.95 hours	15,600	1,660	-
AMM09b-31**	214.8 hours	18,300	1,920	2,550
AMM09d	6.3 hours	370	2,190	-

Replenished dissolver solution to 250 milliliters with 5 M HNO_3

** CaF_2 added to the AMM09-29 solutions

Typically, the amount of aluminum in the Mark 42 reject compact material can be calculated as the difference between the amount of the aluminum from the ANN and the total amount of aluminum in solution based on the ICP/AES results. The ICP/AES results for boron are used as a check because the boron quantity is not expected to change during the dissolution. To use the ICP/AES data for material balance, the effect of the cumulative removal of the rad screen/gamma scan samples needed to be included. Each one-milliliter sample for the rad screen/gamma scan analyses removed some of the aluminum and boron from the solution, as well as plutonium and americium. The amounts of aluminum and boron in the solutions based on the ICP/AES data are given in Table B4. Both the amounts based on the raw data and the corrected amounts are given in Table B4.

Table B4. Total Aluminum and Boron in AMM09 Solutions Based on ICP/AES Data

Experiment	Time into Dissolution Sample Taken	Aluminum grams		% Aluminum Added	Boron grams		% Boron Added	Calcium grams	% Calcium Added
		raw	corr		raw	corr			
AMM09a-0	0 hours	2.03	N/A	100	0.54	N/A	100	-	-
AMM09a-6	45.65 hours	4.08	4.14	-	0.44	0.45	85	-	-
AMM09a-11*	74.2 hours	3.79	4.07	-	0.42	.48	91	-	-
AMM09a-22	159.05 hours	3.84	4.39	-	0.42	0.49	92	-	-
AMM09b-23a*	159.05 hours	3.49	4.10	-	0.39	0.47	89	-	-
AMM09a-28	194.95 hours	3.84	4.68	-	0.42	0.51	96	-	-
AMM09a-31**	214.8 hours	3.88	4.92	-	0.43	0.54	102	0.54	108
AMM09c	6.3 hours	0.06	N/A	-	0.55	N/A	101	-	-
AMM09b-0	0 hours	1.98	N/A	97	0.53	N/A	98	-	-
AMM09b-6	45.65 hours	4.53	4.61	-	0.48	0.49	92	-	-
AMM09b-11*	74.2 hours	3.98	4.28	-	0.43	0.47	89	-	-
AMM09b-22	159.05 hours	4.09	4.69	-	0.44	0.51	96	-	-
AMM09b-23b*	159.05 hours	3.68	4.34	-	0.40	0.48	91	-	-
AMM09b-28	194.95 hours	3.66	4.46	-	0.39	0.49	92	-	-
AMM09b-31**	214.8 hours	3.93	5.00	-	0.42	0.11	98	0.55	110
AMM09d	6.3 hours	0.09	N/A	-	0.54	N/A	97	-	-

Replenished dissolver solution to 250 milliliters with 5 M HNO₃

**CaF₂ added to the AMM09-29 solutions

As can be seen, the value for the percent of boron added is not constant. It varies from 85 to 102%. Initially that discrepancy was attributed to error in the ICP/AES sample preparation prior to the submission of the samples to the Analytical Development Section (ADS).¹³ For the ICP/AES sample, a one-milliliter aliquot of the solution was pulled and diluted into ten milliliters of 5 M HNO₃. If that dilution was not done accurately, then the ICP/AES results will be inaccurate. That assertion is supported by the results of the AMM09-22 and AMM09-23 analyses. Those samples were taken before and after the addition of 5 M HNO₃ to the dissolver solutions. The amount of boron should not be affected and yet for AMM09b-22 and AMM09b-23 the boron values are 0.51 and 0.48 grams, respectively.

One way to estimate the amount of aluminum in Mark 42 reject compact material is adjust the aluminum values by the factor that adjusts the boron values to their correct value. For example, in AMM06a the boron value needs to be multiplied by 1.17 to give the amount of boron added to the solution. If that factor is applied to the aluminum value (4.14 grams), the new aluminum value is 4.84 grams. Subtracting the amount of ANN aluminum, gives 2.85 grams as the amount of aluminum from the Mark 42 reject compact material. Based on the 2.85 grams, aluminum is 84% of the Mark 42 reject compact material. Considering the corrections for the samples and the adjustment for the boron value, that is a reasonable value for the aluminum content. Similar adjustments were made to the other aluminum values and the calculated aluminum contents of the Mark 42 reject compact material are given in Table B5 along with the calculated aluminum contents without the boron adjustment.

The average value for the aluminum content of the Mark 42 reject compact material was calculated using the adjusted values given in Table B4. It was assumed that all of the aluminum dissolved immediately and all of the ICP/AES values could be averaged. For AMM09a, the calculated aluminum content of the Mark 42 reject compact material was 80% $\pm$ 4% by weight. The calculated aluminum content of the Mark 42

¹³ Results from the AMM10, AMM11, and AMM12 ICP/AES samples (both diluted and undiluted) indicate that the error may be due to sample preparation errors in ADS or instrument drift.

Table B5. Calculated Aluminum Content of Mark 42 Reject Compact Material Based on ICP/AES Data

Experiment	Aluminum Based on Data Corrected for Sample Removal		Boron Adjustment	Aluminum with Adjustment	
	grams	%*		grams	%*
AMM09a-0	No Mark 42			No Mark 42	
AMM09a-6	4.14	63	1.17	4.84	85
AMM09a-11**	4.07	61	1.10	4.49	74
AMM09a-22	4.39	71	1.08	4.74	81
AMM09b-23a**	4.10	62	1.12	4.60	77
AMM09a-28	4.68	79	1.04	4.86	85
AMM09a-31***	4.92	86	0.98	4.82	83
			0.93 (from Ca)	4.58	76
AMM09b-0	No Mark 42			No Mark 42	
AMM09b-6	4.53	77	1.08	4.98	88
AMM09b-11**	4.28	68	1.12	4.81	83
AMM09b-22	4.69	80	1.04	4.88	85
AMM09b-23b**	4.34	70	1.10	4.77	82
AMM09b-28	4.46	73	1.09	4.86	85
AMM09b-31***	5.00	89	1.02	5.10	92
			0.91 (from Ca)	4.55	76

* The amount of aluminum from the ANN (2.03 grams) is subtracted before % is calculated.

**Replenished dissolver solution to 250 milliliters with 5 M HNO₃

***CaF₂ added to the AMM09-29 solutions

reject compact material was $84.5\% \pm 3\%$ by weight for AMM09b. The error is probably more on the order of 10% based on the number of corrections applied to the ICP/AES data. Both of those values are in agreement with the values determined in previous experiments.⁵

The total- and free-acid concentrations were measured for the solutions. Those results are given in Table B6. The interference from complexing metal ions (e.g., aluminum) is removed in the free-acid concentration analysis while the total-acid concentration analysis includes the metal ion effects. The change in free-acid concentration between the AMM09-0 and AMM09-6 samples shows that as the aluminum the Mark 42 reject compact material dissolved, HNO₃ was consumed.

Overall, the results of the analyses for total- and free-acid concentrations were as expected. As the solutions evaporated, the acid concentrations increased and after the replenishment to bring the solutions back to 250 milliliters, the acid concentrations decreased. The AMM09a-11 result for the free-acid concentration seems to be an anomalous result because the sample was obtained after the solution was replenished to 250 milliliters and the AMM09a-11 value should be less than the value for AMM09a-6. The AMM09a-6 sample was taken from the solution at 210 milliliters.

The dissolution of the PuO₂ is dependent on the availability of free-fluoride ions. If complexing ions are present in the solution, e.g., boron or aluminum, the amount of free-fluoride ions is expected to be reduced. The fluoride-ion concentration was measured with an ion-selective electrode. In general, that analysis is a measure of total fluoride-ion concentration. However, the analysis does not provide the free-fluoride concentration for these samples because the analysis is not calibrated to provide the free-fluoride value in the presence of complexing agents (e.g., boron and aluminum). Thus, this analysis provides qualitative information on the free-fluoride ions in the solution. The results are presented in Table B6.

Table B6. Total- and Free-Acid Concentrations and Fluoride Concentration for AMM09 Solutions

Experiment	Free Acid (Molar)	Total Acid (Molar)	Fluoride (ppm)
AMM09a-0	7.12	8.07	920
AMM09a-6	6.33	8.86	320
AMM09a-11*	6.78	8.32	650
AMM09a-22	6.84	9.23	780
AMM09a-23*	6.25	8.40	650
AMM09a-28	7.20	9.30	730
AMM09a-29**	Not Taken	Not Taken	1,260
AMM09a-30	Not Taken	Not Taken	1,310
AMM09a-31	7.41	9.31	1,190
AMM09c	8.12	8.02	2,120
AMM09b-0	7.11	7.17	1,100
AMM09b-6	6.06	8.52	220
AMM09b-11*	6.48	8.01	800
AMM09b-22	6.84	9.78	830
AMM09b-23*	5.96	8.17	830
AMM09b-28	6.52	8.69	900
AMM09b-29**	Not Taken	Not Taken	1,260
AMM09b-30	Not Taken	Not Taken	1,370
AMM09b-31	6.78	8.82	1,250
AMM09d	8.09	8.11	1,930

* Solutions replenished with 5 M HNO₃ to reach 250 milliliters. ** CaF₂ added to solutions.

The initial AMM09a and AMM09b solutions should have fluoride concentrations of 2850 ppm and 3800 ppm, respectively. The measured values were 920 ppm (AMM09a-0) and 1,100 ppm (AMM09b-0). The lower than expected values indicate that the aluminum and boron in the solutions are complexing with the fluoride ions. The fluoride-ion concentration decreased as the aluminum from the Mark 42 reject compact material dissolved. The increase in fluoride concentrations from the AMM09-6 to the AMM09-11 samples was not expected. The solution volumes when the AMM09-11 samples were taken were 250 milliliters while the solution volumes when the AMM09-6 samples were taken were less than 200 milliliters. The fluoride concentrations in the AMM09-29 solutions were larger than the concentrations in the AMM09-28 solutions because CaF₂ had been added. The fluoride concentrations in the AMM09c and AMM09d solutions were expected to be 2850 ppm based on the amount of KF added to the solutions. The lower measured fluoride concentration was due to the effect of the boron in the solutions because no ANN was added. The effect of the ANN can be seen by comparing the measured fluoride concentrations of solutions AMM09a, AMM09c, and AMM09d. Those three solutions were made to be 0.15 M KF. The AMM09c and AMM09d values are higher than the AMM09a-0 values because the aluminum from the ANN in AMM09a complexes with the fluoride ions and interferes with the analysis.

AMM10, AMM11, and AMM12

The results from the ICP/AES, total- and free-acid concentrations, and fluoride analyses for AMM10, AMM11, and AMM12 will be discussed together because those sets of experiments were conducted similarly. Table B7 contains the ICP/AES results for aluminum, boron, and calcium for those experiments. The ICP/AES results were expected to provide information regarding the amount of aluminum in the Mark 42 reject compact material.

Table B7. ICP/AES Results for Aluminum, Boron, and Calcium for AMM10, AMM11, and AMM12 Solutions

Experiment	Aluminum mg/liter	% Aluminum Added as ANN	Boron mg/liter	% Boron Added	Calcium mg/liter	% Calcium Added
AMM10a-1	4,600	100	2,100	100	5,800	100
AMM10a-3	11,300	-	1,900	87*	5,000	83
AMM10b-1	3,100	99	2,150	100	5,800	98
AMM10b-3	6,500	-	1,800	91*	4,600	86*
AMM11a-1	4,400	95	2,200	104	5,000	95
AMM11a-3	12,000	-	2,100	95*	5,000	90*
AMM11a-5	10,200	-	1,800	80*	4,400	77*
AMM11b-1	4,600	97	2,300	105	4,700	95
AMM11b-5	11,300	-	2,000	104	4,300	100
AMM12-1	1,000	None added	2,400	108	5,300	97
AMM12-2	4,900	95	2,250	98*	5,300	93*
AMM12-5	13,900	-	2,300	97*	5,400	93*

*Corrected for removal of samples.

Samples for the ICP/AES analyses were obtained from the initial solution before the addition of the Mark 42 reject compact material and after all of the solids had dissolved. An intermediate ICP/AES sample was taken from AMM11a-3 and AMM12-2. The sample results were corrected for the removal of the initial and any intermediate samples, e.g., rad screen/gamma scan samples.

The percent of added material was based on the amounts of ANN (for aluminum), H_3BO_3 (for boron), and CaF_2 (for fluoride) that were added to the initial solutions. The results for the initial solutions agree within ten percent of the amounts of ANN, H_3BO_3 , and CaF_2 that were added to the solutions. The values for the other AMM10 and AMM11a samples are low. Initially, the low values were attributed to dilution errors in the preparation of the samples prior to sending them to the ADS for analysis. Another set of ICP/AES samples were obtained from the AMM10a, AMM10b, AMM11a, AMM11b, and AMM12 final solutions and were sent to ADS without any dilution. The results of those new analyses are given in Table B8, Table B9, and Table B10 for aluminum, boron, and calcium, respectively. Those three tables also contain the results of recheck analyses on the original samples from AMM11a and AMM11b.

As can be seen in Table B8, the aluminum values from the rechecks for the original samples are slightly lower than the values from the first analyses. For both the AMM11a and AMM11b, the aluminum values from the rechecks are about 5% lower than the first values. The aluminum results of the additional samples agree with the results from the original sample with the exception of the aluminum results from the AMM11a additional sample. That agreement indicates that there was no dilution error in the preparation of the original sample from AMM10a, AMM10b, AMM11b, and AMM12. The results for the additional sample from AMM11a are about 20% higher than the results for the original sample, thus indicating that there might have been a dilution problem.

Using the aluminum values from the ICP/AES data, the percent of aluminum in the Mark 42 reject compact material was calculated. The values for AMM11b and AMM12 (81% and 82%, respectively) agree with results from the previous report.⁵ The other three values are about 15% lower at about 70 weight% aluminum. This discrepancy in the measured aluminum content cannot be explained. It is probably due to

Table B8. Additional ICP/AES Results for Aluminum for AMM10, AMM11, and AMM12 Solutions

Experiment	Aluminum mg/liter					Total Aluminum (grams)	Mark 42 Aluminum (grams)/%
	Original Sample	Original Recheck-1	Original Recheck Duplicate	Additional Sample	Additional Sample - Duplicate		
AMM10a-1	4,600	-	-	-	-	1.20*	-
AMM10a-3	11,300	-	-	11,200	11,700	2.83**	1.62/69%
AMM10b-1	3,100	-	-	-	-	0.78*	-
AMM10b-3	6,500	-	-	6,400	6,500	1.80**	1.01/67%
AMM11a-1	4,400	-	-	-	-	1.16*	-
AMM11a-3	12,000	11,600	11,700	-	-	2.85**	1.63/70%
AMM11a-5	10,200	9,700	9,800	12,300	12,600	2.62/2.98***	1.40/60% 1.76/76%
AMM11b-1	4,600	-	-	-	-	-	-
AMM11b-5	11,300	10,700	10,800	11,000	10,700	3.10**	1.88/81%
AMM12-1	1,000	-	-	-	-	-	-
AMM12-2	4,900	-	-	-	-	1.16*	-
AMM12-5	13,900	-	-	14,300	13,900	3.14**	1.92/82%

* Initial solution, only source of aluminum is the ANN (or GPC coupon for AMM12)

** Corrected for removal of samples

*** Corrected for removal of samples and second number is based only on the ICP/AES results for the additional sample

sample preparation errors or instrument drift. However, to determine if there was a systematic error, the boron and calcium ICP/AES values were examined because both of those elements can be considered as internal standards.

The boron and calcium values are given in Table B9 and Table B10 for the original analyses, recheck analyses, and additional sample analyses. The boron and calcium values seem to be low by a similar factor as the aluminum values. Using an average of the boron and calcium factors, an adjusted value for the aluminum can be calculated, and that adjusted value can be used to estimate the amount of aluminum in the Mark 42 reject compact material. The adjusted values for AMM10a-3, AMM10b-3, AMM11a-3, AMM11a-5, AMM11b-5, and AMM12-5 are given in Table B11. Based on the adjusted values, the average aluminum content for the Mark 42 reject compact material is 86 ± 3 weight%. That value agrees with the 86 weight% expected from the MC&A 12.24 weight% value for the plutonium. The 86 weight% is higher than the 80 weight% value obtained in earlier experiments.⁵ However, there was no attempt to use the boron in those earlier experiments as an internal standard to correct the aluminum ICP/AES values (CaF₂ was not used as a fluoride source in those experiments; KF was used as the fluoride source.).

Table B9. Additional ICP/AES Results for Boron for AMM10, AMM11, and AMM12 Solutions

Experiment	Boron mg/liter					Boron (grams/%)
	Original Sample	Original Recheck-1	Original Recheck Duplicate	Additional Sample	Additional Sample - Duplicate	
AMM10a-1	2,100	-	-	-	-	0.55/100%
AMM10a-3	1,900	-	-	1,900	2,000	0.48/87%*
AMM10b-1	2,150	-	-	-	-	0.55/100%
AMM10b-3	1,800	-	-	1,700	1,700	0.49/89%*
AMM11a-1	2,200	-	-	-	-	0.57/104%
AMM11a-3	2,100	2,000	2,000	-	-	0.51/92%*
AMM11a-5	1,800	1,700	1,700	2,100	2,200	0.46/84% 0.52/95%**
AMM11b-1	2,300	-	-	-	-	0.58/105%
AMM11b-5	2,000	1,850	1,900	1,900	1,800	0.54/98%*
AMM12-1	2,400	-	-	-	-	0.59/108%
AMM12-2	2,250	-	-	-	-	0.54/98%*
AMM12-5	2,300	-	-	2,300	2,300	0.53/97%*

* Corrected for removal of samples

** Corrected for removal of samples and the second number is based only on the ICP/AES results for the additional sample

The total- and free-acid concentrations were measured for the solutions. Those results are given in Table B12. The interference from complexing metal ions (e.g., aluminum) is removed in the free-acid concentration analysis while the total-acid concentration analysis includes the metal ion effects. The results for AMM12-5 indicate that the dissolution of the aluminum coupon resulted in a lower free-acid concentration compared to providing the aluminum as ANN (AMM11a-5) in a solution with similar fluoride, aluminum, and plutonium concentrations, 5.6 M and 6.8 M, respectively.

The dissolution of the PuO_2 is dependent on the availability of free-fluoride ions. If complexing ions are present in the solution, e.g., boron or aluminum, then the amount of free-fluoride ions is expected to be reduced. The fluoride-ion concentration was measured with an ion-selective electrode. In general, that analysis is a measure of total fluoride-ion concentration. However, the analysis does not provide the free-fluoride concentration for these samples because the analysis is not calibrated to provide the free-fluoride value in the presence of complexing agents (e.g., boron and aluminum). Thus, this analysis provides qualitative information on the free-fluoride ions in the solution. The results are presented in Table B12. The corrosion study being conducted by the Materials Applications and Technology Group includes the measurement of effective free-fluoride concentrations in the CaF_2 solutions that are proposed for the flow sheet for the dissolution of the unirradiated Mark 42 fuel tubes.¹⁴

¹⁴ The report on the corrosion studies being performed by John Mickalonis will include fluoride-ion concentrations that are more representative of the effective free-fluoride concentration in the dissolver solutions.

Table B10. Additional ICP/AES Results for Calcium for AMM10, AMM11, and AMM12 Solutions

Experiment	Calcium mg/liter					Calcium (grams/%)
	Original Sample	Original Recheck-1	Original Recheck Duplicate	Additional Sample	Additional Sample - Duplicate	
AMM10a-1	5,800	-	-	-	-	1.5/100%
AMM10a-3	5,000	-	-	4,950	5,100	1.3/84%*
AMM10b-1	5,800	-	-	-	-	1.5/98%
AMM10b-3	4,600	-	-	4,500	4,500	1.3/85%*
AMM11a-1	5,000	-	-	-	-	1.3/95%
AMM11a-3	5,000	4,800	4,800	-	-	1.2/87%*
AMM11a-5	4,400	4,000	4,100	5,150	5,300	1.1/81% 1.3/92%**
AMM11b-1	4,650	-	-	-	-	1.2/95%
AMM11b-5	4,300	4,050	4,100	4,200	4,100	1.2/95%
AMM12-1	5,300	-	-	-	-	1.3/97%
AMM12-2	5,300	-	-	-	-	1.3/93%
AMM12-5	5,400	-	-	5,500	5,450	1.3/93%

* Corrected for removal of samples

** Corrected for removal of samples and the second number is based only on the ICP/AES results for the additional sample

Table B11. Calculated Aluminum Content of Mark 42 Reject Compact Material Based on ICP/AES Data

Experiment	Aluminum**			Boron/ Calcium Adjustment	Aluminum with Adjustment**		
	Total grams	Mark 42 grams	Mark 42 %		Total grams	Mark 42 grams	Mark 42 %
AMM10a-3	2.83	1.62	69	1.17	3.31	2.10	90
AMM10b-3	1.80	0.79	67	1.15	2.08	1.29	86
AMM11a-3	2.85	1.63	70	1.12	3.19	1.97	84
AMM11a-5	2.62/2.98*	1.40/1.76	60/76	1.21/1.07	3.17/3.20*	1.95/1.98	84/85
AMM11b-5	3.10	1.88	81	1.03	3.21	1.99	85
AMM12-5	3.14	1.92	82	1.05	3.31	2.09	89

* Corrected for removal of samples and second number is based only on the ICP/AES results for the additional sample

** Corrected for removal of samples

Table B12. Total- and Free-Acid Concentrations and Fluoride Concentration for AMM10, AMM11 and AMM12 Solutions

Experiment	Free Acid (Molar)	Total Acid (Molar)	Fluoride (ppm)
AMM010a-1	6.54	7.8	-
AMM010a-3	6.10	7.56	1,360
AMM10b-1	6.58	7.5	-
AMM10b-3	5.84	6.50	1,220
AMM11a-1	7.01	7.9	-
AMM11a-3	6.72	7.98	1,360
AMM11a-5	6.76	8.14	1,350
AMM11b-1	6.96	8.40	-
AMM11b-3	5.95	7.01	1,240
AMM12-1	7.32	7.55	3,750
AMM12-2	7.09	7.67	1,270
AMM12-5	5.62	7.69	1,350

The fluoride concentrations for the initial samples of AMM10 and AMM11 were not measured. Based on the amounts of CaF_2 added to the solutions the fluoride concentrations were expected to be 5,700 ppm (AMM10a and AMM10b), 5,230 ppm (AMM11a) and 4,750 ppm (AMM11b). The measured fluoride concentrations are about one-fourth of the expected amount. Thus, the aluminum and boron are complexing with the fluoride ions. Another mechanism for the reduction of available fluoride is the CaF_2 equilibrium with fluoride ions and the CaF^{+1} species.⁹

The initial AMM12 solution only contains boron to complex with the fluoride. However, as mentioned previously, the dissolved CaF_2 exists in equilibrium with fluoride ions and the CaF^{+1} species.⁹ Based on the amount of CaF_2 added to the AMM12 solution, the fluoride concentrations should be 5,230 ppm. The measured value was 3,750 ppm (AMM12-1). After the aluminum coupon was added and allowed to dissolve, the fluoride concentration was measured again (AMM12-2). That value was 1,270 ppm. A value of 1,350 ppm was measured after the Mark 42 material was added and dissolved. It was expected that the measured fluoride concentration of AMM12-5 should be less than that of AMM12-2 because more aluminum was dissolved.