

## **K Basin Sludge Conditioning Testing**

### **Nitric Acid Dissolution Testing of K East Canister Sludge**

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## Summary and Conclusions

This report describes tests performed by Pacific Northwest National Laboratory (PNNL) for Numatec Hanford Corporation (NHC) as part of the overall activities for the development of the K Basin Sludge Treatment System. These tests were conducted to examine the dissolution behavior of a K East Basin canister sludge composite in nitric acid at the following concentrations: 2 M, 4 M, 6 M, 7.8 M and 10 M and temperatures of 25°C and boiling. Assuming that the sludge was 100% uranium metal, a 4X stoichiometric excess of nitric acid was used for all testing, except that conducted at 4 M. In the 4 M nitric acid dissolution test, 50% excess nitric acid was used resulting in a dissolver solution with a significantly higher solids loading. The boiling tests were conducted for 11 hr; the 25°C dissolution tests were conducted from 24 hr to 2 weeks. For the 25°C dissolution testing, the weight percent residual solids was determined; however, chemical and radiochemical analyses were not performed.

Key observations, findings, and conclusions from this testing are summarized below:

Under boiling conditions, very little residual solids remained after 11 hr of dissolution (between 0.38% and 1.5%). In each of these tests, greater than 99% of the uranium compounds and radionuclides dissolved. For the dissolution testing conducted at 25°C, the residual solids ranged from 1.4% to 3.6%.

Although very small quantities of solids remained after dissolution under boiling conditions, the residual solids contained concentrations of some radionuclides above the Environmental Restoration Disposal Facility (ERDF) Waste Acceptance Criteria (WAC). For uranium, the ERDF criterion was exceeded by 9 to 21 times; for <sup>241</sup>Am, the ERDF criterion was exceeded by 23 to 99 times; and for <sup>239/240</sup>Pu, the ERDF criterion was exceeded by 280 to 930 times. Except for the high solids loading test (4 M), the <sup>137</sup>Cs concentration in the residual solids was below the ERDF limit for all tests.

The concentrations of uranium and radionuclides in the residual solids do not appear to be highly correlated with the acid concentrations used for the dissolution tests. The concentrations of these analytes in the residual solids generated in the 2 M, 6 M, and 7.8 M tests were similar.

The results from the analyses of the residual solids from this testing are similar to those obtained from the K Basin Sludge Scoping Studies (Schmidt et al. 1999), in which K East canister sludge sample 96-08 was dissolved in 10 M nitric acid at 95°C for 6 hr.

Chemical analyses show that the residual solids are primarily composed of silicon (~90% by weight SiO<sub>2</sub>) and iron compounds. In the 2 M dissolution test, the residual solids were approximately 45% silicon and 45% iron, most likely as oxides. X-ray diffraction analysis (XRD) were performed on the residual solids from the dissolution conducted at 4 M (the quantities of residual solids generated from the other tests were insufficient for XRD analysis). The XRD analysis indicated that the silicon is most likely an amorphous silicate and confirmed the presence of goethite [FeO(OH)].

Based on chemical analysis of the dissolver solutions, dissolutions for all tests (except the 2 M dissolution test) were greater than 95% complete within 2 hr, and 100% complete by 3 hr. In the 2 M dissolution test, dissolution was about 90% complete after 2 hr, and 100% complete after 8 hr.

During the dissolution testing conducted at boiling conditions, no obvious indications of gel formation were observed. Furthermore, filtration of the residual solids proceeded rapidly (an indication of little or no gel). Filtration of the residual solids from the dissolution testing conducted at 25°C was difficult and slow. Some of the filters were blinded, requiring use of a second filter. Some of the solutions from the 25°C testing sat unfiltered for about 2 weeks. These aged solutions were readily filtered.

During the dissolution testing, brown offgas (NO<sub>2</sub> fumes) were observed. The coloration was most intense during heating, prior to achieving boiling temperatures. The quantity and composition of the offgas was such that the offgas did not penetrate through the sodium hydroxide scrubber at any time during the run.

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## 1.0 Introduction

This report describes work performed by Pacific Northwest National Laboratory (PNNL) for Numatec Hanford Corporation (NHC) to assist in the development of the K Basin Sludge Treatment System. The work was performed under Letter of Instruction STP-003. The testing was performed in accordance with the report, "Testing Strategy to Support the Development of K Basin Sludge Treatment Process" (Flament 1998).

Two water-filled concrete pools in the 100K Area of the Hanford Site contain over 2,100 metric tons of N Reactor fuel elements stored in aluminum and stainless steel canisters. During the time the fuel has been stored, approximately 52 m<sup>3</sup> of heterogeneous solid material (sludge) have accumulated in the K Basins. The sludge is located in the fuel canisters, as well as on the floor and in the associated pits. This sludge is a mixture of spent fuel element corrosion products, ion exchange materials (organic and inorganic), graphite-based gasket materials, iron and aluminum metal corrosion products, sand, and debris (Makenas et al. 1996, 1997). Ultimately, it is planned to transfer the K Basin sludge to the Hanford double shell tanks (DSTs). Chemical pretreatment is required to address criticality issues and the destruction or removal of polychlorinated biphenyls (PCBs), found in some samples, before the K Basin sludge can be transferred to the DSTs.

The baseline chemical treatment process is nitric acid dissolution of all particulate material less than ¼ in. In this process, the acid insoluble fraction will be washed and leached as necessary and then transferred to the Environmental Restoration Disposal Facility (ERDF). The dissolver solution will be mixed with iron nitrate for plutonium criticality safety, and neutralized and made alkaline with sodium hydroxide. The neutralized liquid fraction and associated precipitates will be stored in the Tank Waste Remediation Systems (TWRS) pending vitrification.

The purpose of the work described in this report was to examine the dissolution behavior of actual K East canister sludge in nitric acid at various concentrations (i.e., 2 M, 4 M, 6 M, 7.8 M, and 10 M) and at two temperatures (25°C and boiling). The effectiveness of the dissolutions was evaluated by measuring the concentrations of key analytes in the dissolution solutions as a function of reaction (dissolution) time, and by analyzing the final acid-insoluble residual solids at the end of the dissolutions. The analytical results from the insoluble solids were compared to the ERDF Waste Acceptance Criteria (WAC) (ERDF 1997) to determine whether further processing (i.e., washing/leaching) of these solids may be necessary.

## 2.0 Experimental

### 2.1 Test Material: K East Canister Sludge Composite

The sludge composite used in this testing was prepared as described in the test instruction. Table 1 shows the samples that were used to prepare the K East canister sludge composite.

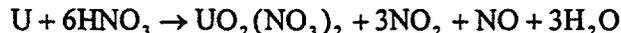
The final composite, a thick, brown slurry that flowed very slowly, was determined to be 38.4% moisture.

Table 1. K East Canister Sludge Composite

Sample	Dry Mass	Wet Mass	Wt% Solids	Mass Water	Dry in Comp	Wet in Comp
96-01	61.92	84.37	73.39	22.45	61.92	84.37
96-05	62.92	87.03	72.30	24.1	62.92	87.03
96-06 L	74.05	96.04	77.10	21.99	74.05	96.04
96-06 M/L	57.37	74.83	76.67	17.46	57.37	74.83
96-08	45.45	88.62	51.28	43.17	39.03	76.11
96-13	124.54	158.14	78.75	33.61	124.54	158.14
96-15	57.37	93.47	61.39	36.09	57.37	93.47
Total	483.62	682.51		198.89	477.21	670.00

## 2.2 Test Approach

The K East canister sludge composite was treated with nitric acid at two temperatures, boiling and 25°C. The test at 25°C was performed using the same acid concentrations as the boiling test, but served as a shakedown of the equipment and only provided information on percent of sludge dissolved. During the boiling tests, the samples were reacted for 11 hours in nitric acid. Six tests (including one blank) were performed simultaneously using acid concentrations of 2 M, 4 M, 6 M, 7.8 M, and 10 M. The initial plan was to perform all of the tests using ~5 grams of composite material and a 4X stoichiometric excess of nitric acid, assuming the sample was all uranium metal and 6 moles of acid were required to dissolve each mole of uranium (as shown in the equation below).



This approach (i.e., constant stoichiometric excess) led to the use of different solution volumes and solids loadings for each test. Differences in solids loadings for the solutions can result in different dissolution characteristics if a solubility limit for a component were reached. However, given the composition of the starting material, it was not expected that any solubility limits would be exceeded.

For the testing, the 4 M test was designated as a process test (with a higher solids loading) and 15 grams of sample were used with a 50% excess of nitric acid (uranium metal basis). The remaining tests were performed as planned. Table 2 shows the parameters used for the dissolution testing at boiling temperatures. Similar parameters were used for the 25°C dissolution testing, except a process test at 4 M nitric acid was not conducted at 25°C.

Table 2. Testing Parameters

Test Number	HNO <sub>3</sub> Concentration (M)	HNO <sub>3</sub> Volume (mL)	Sample Mass, Dry Weight (g)	Solids Loading (g/L)
1	4	67	14.5568	217
2	10	69.8	4.8704	70
3	7.8	89.7	5.2192	58
4	6	119.2	5.3203	45
5	6	120	Blank	--
6	2	347.8	4.9664	14

## 2.3 Test Apparatus

The apparatus used for the experiments consisted of a set of three-necked round-bottom flasks (dissolver vessels), Graham condensers, thermometer wells, inlet valves, and ground glass plugs. Each flask was placed into a heating mantle inside a hot cell, and the condenser was placed in the middle neck of the flask. The thermometer well was filled with sand and placed into another neck, and a glass plug was put in the last neck for sample introduction and collection of liquid samples. At the top of the condenser was the inlet valve, which led to an air-filled trap and then a trap filled with sodium hydroxide solution to react with any  $\text{NO}_2$  generated during the dissolution test. Water at cell temperature ( $30^\circ\text{C}$ ) was recirculated through the condenser to keep as much liquid and  $\text{NO}_x$  as possible in the reaction vessel. The temperature of the cooling water increased during the test since no capability for cooling the water existed.

## 3.0 Results

Unless specifically identified otherwise, all results and discussions pertain to the dissolution testing conducted at boiling temperatures.

### 3.1 Description of Testing and Observations

Nitric acid was added to the vessels, and glass vials of sludge sample (one to three glass vials per test) were then dropped into the vessels through one of the necks. The acid/sludge solutions were heated to boiling. The 2 M  $\text{HNO}_3$  test (Test 6, Table 2), which contained a significantly larger volume of solution, required about 45 minutes to reach the boiling temperature while the remaining test solutions required between 15 and 25 minutes. No evidence of gel formation was observed in any of the dissolution vessels during the tests.

The temperature profile for each of the tests can be seen in Figure 1. After about 6 hours, the temperature profiles became somewhat erratic as a result of the cooling water connections coming undone and leaking water into the thermometer wells.

During the heating, the most intense coloration of the offgases was observed. This gas evolution occurred before the solutions reached boiling. At no time during the experiment did gas bubble through the NaOH trap, indicating that all of the gases generated condensed or reacted with the sodium hydroxide in the trap. The color of the gases was brown, as expected for  $\text{NO}_2$  fumes.

The majority of the solids in the 10 M, 7.8 M and 6 M tests were dissolved by the time the first solution samples were taken at one hour. For the remaining two tests, the solids were mostly dissolved by the third sample (4 hours). The gases were observed throughout most of the reaction, with some blue solution collecting in the condensers. The blue was most likely nitrous acid forming as the  $\text{NO}_x$  came in contact with condensed water.

Solution samples were collected at 1, 2, 4, 8, and 11 hours (measured from the addition of the sludge sample). The final solution samples (11 hours) were collected immediately after the heat was turned off

(before the dissolution solutions cooled). These samples were first collected with a transfer pipette, allowed to cool, and then a 0.5-mL aliquot was filtered (0.2- $\mu$ m filter) for analysis. Due to the high dose of the samples, a 100- $\mu$ L sample of each solution was diluted to 10 mL prior to removal from the hot cell. These samples were then analyzed by ICP-AES and gamma energy analysis.

The tests were concluded after 11 hours, since the amount of solids in the vessels appeared to be remaining constant, and the cooling water was continuing to leak. The vessels were allowed to come to room temperature and the final dissolver solutions were filtered after 4 days. The solutions were filtered through 0.45- $\mu$ m acetate/cellulose filters, then the residual solids were washed with two 2-mL aliquots of 2% HNO<sub>3</sub> and one 2-mL aliquot of distilled deionized water. Since the amount of solids collected was small, the total amount of residual solids was used for analysis (the fusion reactions were performed on the sample with the filter). Filtration of the residual solids proceeded rapidly (an indication of little or no gel associated with the residual solids).

### 3.2 Test Results

Significant differences exist in the concentrations of radionuclides in duplicate aliquots used to characterize the K East canister sludge composite. These differences indicate that the composition of the sludge composite, even after extensive mixing, is not homogeneous. Thus, it cannot be assumed that the individual aliquots used for the dissolution tests contained radionuclides at the same concentration as the aliquots used to characterize the composite sludge. Therefore, (except for <sup>239/240</sup>Pu) rather than use the composite characterization data for the evaluation of the dissolution test results, for each test, the quantities of the radionuclides in the starting material were calculated by summing the quantities of radionuclides measured in the individual dissolution fractions (i.e., quantities of radionuclides in the residual solids plus the quantities of radionuclides in the solutions). For <sup>239/240</sup>Pu, the composite characterization data was used for evaluation of dissolution test results since the <sup>239/240</sup>Pu concentrations were not determined for the solution samples.

Figures 2 through 6 (discussed below) show the percent of each analyte dissolved for each of the five tests [mass of analyte in solution divided by the calculated mass of the analyte in the starting material (K East canister sludge composite) times 100]. Figure 7 shows the percent of each analyte remaining in the solid residuals (mass of analyte in residual solids divided by the calculated mass of the analyte in the starting materials times 100). In Figure 7, the silicon data were not included to provide a clear picture of the remaining analytes.

Figure 2 indicates that the dissolution for the 4 M process test was about 80% complete by the time the first solution sample was collected and complete by the second solution sampling (2 hours). Chemical analyses (ICP-AES) showed the majority of the residual solids were silicon and iron compounds. The XRD analysis indicated the silicon is most likely present as an amorphous silicate and also showed the presence of goethite (FeO(OH)). Table 3 lists the initial and final concentrations of selected analytes, the decontamination factor (DF), percent of the total remaining undissolved, and the ERDF limits where applicable. DFs were calculated by dividing the calculated concentrations of the analytes in the initial samples by the concentrations of analytes in the final residual solids.

Figure 3 shows that the dissolution for the 10 M test was essentially complete at the first solution sampling (1 hour). The amount of the analytes dissolved was greater than 100%. This could be due to a slight loss of residual solids or an error in the analysis of the final solution. In this test, the majority of the

**Table 3. Analyte Removal for the 4 M Process Test**

Analyte	Calculated Sludge Concentration <sup>(a)</sup>	Final Dry Residual Concentration	DF	% Residual <sup>(b)</sup>	ERDF Criterion
U	639 mg/g	50.8 mg/g	12.6	0.12	2.6 mg/mL
Fe	11.1 mg/g	105 mg/g	0.11	1.42	--
Al	17.1 mg/g	15.0 mg/g	1.14	1.32	--
Si	51.2 mg/g	195 mg/g	0.26	50.5	--
Ca	11.6 mg/g	5.48 mg/g	2.12		--
<sup>137</sup> Cs	521 µCi/g	82.7 µCi/g	6.30	0.45	32 µCi/mL
<sup>241</sup> Am	76.2 µCi/g	4.93 µCi/g	15.4	0.18	0.05 µCi/g <sup>(c)</sup>
<sup>239/240</sup> Pu	121 µCi/g <sup>(d)</sup>	26.9 µCi/g	4.50	0.33	0.029 µCi/g <sup>(e)</sup>

(a) Total mass of the analyte recovered (solution plus residual solids) divided by the mass of starting material.  
 (b) Mass of analyte in the residual solids divided by the mass of the analyte in the starting material times 100.  
 (c) The limit for the total TRU elements is 0.1 µCi/g.  
 (d) For <sup>239/240</sup>Pu, data from characterization of the K East canister sludge composite was used for the initial concentration.  
 (e) The limit for each isotope (<sup>239</sup>Pu and <sup>240</sup>Pu).

sample remaining was silicon (90% of the total as SiO<sub>2</sub>). Because of the small amount of residual solids (see Figure 7) no XRD was performed. Table 4 lists the initial and final concentrations of selected analytes, the DF, percent of the total remaining undissolved, and the ERDF limits where applicable.

**Table 4. Analyte Removal for the 10 M Test**

Analyte	Calculated Sludge Concentration <sup>(a)</sup>	Final Dry Residual Concentration	DF	% Residual <sup>(b)</sup>	ERDF Criterion
U	703 mg/g	53.6 mg/g	13.1	0.076	2.6 mg/mL
Fe	12.7 mg/g	12.3 mg/g	1.03	0.963	--
Al	17.7 mg/g	16.5 mg/g	1.07	0.928	--
Si	10.7 mg/g	332 mg/g	0.03	31.1	--
Ca	1.18 mg/g	11.9 mg/g	0.10	10.1	--
<sup>137</sup> Cs	627 µCi/g	23.4 µCi/g	26.8	0.03	32 µCi/mL
<sup>241</sup> Am	81.2 µCi/g	2.45 µCi/g	33.1	0.03	0.05 µCi/g <sup>(c)</sup>
<sup>239/240</sup> Pu	121 µCi/g <sup>(d)</sup>	21.7 µCi/g	5.6	0.18	0.029 µCi/g <sup>(e)</sup>

(a) Total mass of the analyte recovered (solution plus residual solids) divided by the mass of starting material.  
 (b) Mass of analyte in the residual solids divided by the mass of the analyte in the starting material times 100.  
 (c) The limit for the total TRU elements is 0.1 µCi/g.  
 (d) For <sup>239/240</sup>Pu, data from characterization of the K East canister sludge composite was used for the initial concentration.  
 (e) The limit for each isotope (<sup>239</sup>Pu and <sup>240</sup>Pu).

The results from the 10 M test conducted with the K East canister composite are comparable to those obtained during dissolution of K East canister sludge sample 96-08 in 10 M nitric acid in the K Basin Sludge Scoping Studies (Schmidt et al. 1999). Within the Scoping Studies, sample 96-08 was dissolved in 10 M nitric acid at 95°C for 6 hours (Table 5). From this testing 12.1% of the mass of 96-08 remained as residual solids (compared to 0.998% for the 10 M dissolution of K East canister composite after 11 hours at boiling). With the exception uranium and <sup>239/240</sup>Pu, the concentrations of the key analytes in the residual solids from the K East canister sludge composite were somewhat lower than those in the residual solids from 96-08. The differences in results between the two tests can likely be attributed to the differences in the compositions between the two starting sludge materials.

**Table 5.** Analyte Removal for the 10 M Scoping Test (Schmidt et al. 1999)

Analyte	Initial Dry Sludge Con. in KE Can Sample 96-08	Final Dry Residual Concentration	DF	% Residual <sup>(a)</sup>	ERDF Criterion
U	400 mg/g	21.0 mg/g	19.0	0.625	2.6 mg/mL
Fe	73 mg/g	31.4 mg/g	2.32	5.20	--
Al	79 mg/g	44.4 mg/g	1.78	6.80	--
<sup>137</sup> Cs	1180 µCi/g	72.5 µCi/g	16.3	0.743	32 µCi/mL
<sup>241</sup> Am	77.3 µCi/g	5.05 µCi/g	15.3	0.791	0.05 µCi/g <sup>(b)</sup>
<sup>239/240</sup> Pu	93.5 µCi/g	5.86 µCi/g	16.0	0.758	0.029 µCi/g <sup>(c)</sup>

(a) Mass of analyte in the residual solids divided by the mass of the analyte in the starting material times 100.  
 (b) The limit for the total TRU elements is 0.1 µCi/g.  
 (c) The limit for each isotope (<sup>239</sup>Pu and <sup>240</sup>Pu).

Figure 4 shows that the dissolution for the 7.8 M test was approximately 80% complete after the first solution sample was taken and nearly complete after the sampling at 2 hours. Again, the majority of the sample remaining was silicon (90% of the total as SiO<sub>2</sub>), and because of the small amount of residual solids (see Figure 7) no XRD was performed. Table 6 lists the initial and final concentrations of selected analytes, the DF, percent of the total remaining undissolved, and the ERDF limits where applicable.

Figure 5 shows that the dissolution for the 6 M test was approximately 80-90% complete after the first solution sample was taken and nearly complete after the sampling at 4 hours. The cesium showed a lower solubility than would be expected, but the amount of cesium in the residuals is very low, see Figure 7.

Silicon is the major component of the solids at approximately 90% of the total residual. Again, the majority of the sample remaining was silicon (90% of the total as SiO<sub>2</sub>). Because of the small amount of residual solids (see Figure 7) no XRD was performed. Table 7 lists the initial and final concentrations of selected analytes, the DF, percent of the total remaining undissolved, and the ERDF limits where applicable.

Table 6. Analyte Removal for the 7.8 M Test

Analyte	Calculated Sludge Concentration <sup>(a)</sup>	Final Dry Residual Concentration	DF	% Residual <sup>(b)</sup>	ERDF Criterion
U	709 mg/g	37.0 mg/g	19.1	0.048	2.6 mg/mL
Fe	15.0 mg/g	10.4 mg/g	1.44	0.632	--
Al	20.0 mg/g	16.1 mg/g	1.24	0.734	--
Si	13.0 mg/g	356 mg/g	0.04	25.0	--
Ca	1.18 mg/g	7.91 mg/g	0.15	6.14	--
<sup>137</sup> Cs	597 µCi/g	14.9 µCi/g	40.1	0.070	32 µCi/mL
<sup>241</sup> Am	86.3 µCi/g	1.57 µCi/g	55.0	0.051	0.05 µCi/g <sup>(c)</sup>
<sup>239/240</sup> Pu	121 µCi/g <sup>(d)</sup>	11.0 µCi/g	11	0.08	0.029 µCi/g <sup>(e)</sup>

(a) Total mass of the analyte recovered (solution plus residual solids) divided by the mass of starting material.  
 (b) Mass of analyte in the residual solids divided by the mass of the analyte in the starting material times 100.  
 (c) The limit for the total TRU elements is 0.1 µCi/g.  
 (d) For <sup>239/240</sup>Pu, data from characterization of the K East canister sludge composite was used for the initial concentration.  
 (e) The limit for each isotope (<sup>239</sup>Pu and <sup>240</sup>Pu).

Table 7. Analyte Removal for the 6 M Test

Analyte	Calculated Sludge Concentration <sup>(a)</sup>	Final Dry Residual Concentration	DF	% Residual <sup>(b)</sup>	ERDF Criterion
U	749 mg/g	24.0 mg/g	31.2	0.032	2.6 mg/mL
Fe	14.6 mg/g	12.1 mg/g	1.21	0.838	--
Al	20.1 mg/g	16 mg/g	1.26	0.809	--
Si	19.0 mg/g	313 mg/g	0.061	16.7	--
Ca	1.18 mg/g	8.86 mg/g	0.13	7.64	--
<sup>137</sup> Cs	712 µCi/g	15.6 µCi/g	45.6	0.0601	32 µCi/mL
<sup>241</sup> Am	91.1 µCi/g	1.45 µCi/g	62.8	0.0437	0.05 µCi/g <sup>(c)</sup>
<sup>239/240</sup> Pu	121 µCi/g <sup>(d)</sup>	8.17 µCi/g	15	0.07	0.029 µCi/g <sup>(e)</sup>

(a) Total mass of the analyte recovered (solution plus residual solids) divided by the mass of starting material.  
 (b) Mass of analyte in the residual solids divided by the mass of the analyte in the starting material times 100.  
 (c) The limit for the total TRU elements is 0.1 µCi/g.  
 (d) For <sup>239/240</sup>Pu, data from characterization of the K East canister sludge composite was used for the initial concentration.  
 (e) The limit for each isotope (<sup>239</sup>Pu and <sup>240</sup>Pu).

The 2 M test took the longest to reach equilibrium due to the greater volume of nitric acid, almost three times the volume of the largest of the other tests. The results for the analytes in solution were not normalized, and the curves represent what was in solution as compared to the total in the starting solids. As can be seen in Figure 6, approximately 80% of the uranium was dissolved within the first hour, but it appears that the dissolution was not complete until the 8-hour sample was collected. The residual solids were about 45% silicon and 45% iron, most likely as the oxides. An interesting aspect of this test was that it had the lowest percentage of residual solids. There were no obvious solids remaining in the flask following filtration. It is possible that the low amount of residual solid was due to an inhomogeneity of the sample. Because of the small amount of residual solids (see Figure 8) no XRD was performed. Table 8 lists the initial and final concentrations of selected analytes, the DF, percent of the total remaining undissolved, and the ERDF limits where applicable.

Table 8. Analyte Removal for the 2 M Test

Analyte	Calculated Sludge Concentration <sup>(a)</sup>	Final Dry Residual Concentration	DF	% Residual <sup>(b)</sup>	EDRF Criterion
U	874 mg/g	29.0 mg/g	30.1	0.0126	2.6 mg/mL
Fe	14.1 mg/g	18.1 mg/g	0.779	0.486	--
Al	22.1 mg/g	24.9 mg/g	0.888	0.427	--
Si	52.6 mg/g	172 mg/g	0.306	1.24	--
Ca	1.18 mg/g	12 mg/g	0.098	3.86	--
<sup>137</sup> Cs	812 µCi/g	15.4 µCi/g	53	0.0441	32 µCi/mL
<sup>241</sup> Am	103 µCi/g	1.16 µCi/g	88.8	0.0262	0.05 µCi/g <sup>(c)</sup>
<sup>239/240</sup> Pu	121 µCi/g	21.9 µCi/g	5.5	0.07	0.029 µCi/g <sup>(d)</sup>

(a) Total mass of the analyte recovered (solution plus residual solids) divided by the mass of starting material.  
 (b) Mass of analyte in the residual solids divided by the mass of the analyte in the starting material times 100.  
 (c) The limit for the total TRU elements is 0.1 µCi/g.  
 (d) The limit for each isotope (<sup>239</sup>Pu and <sup>240</sup>Pu).

Figure 8 and Table 9 show the residual solids data for both the initial shakedown test at 25°C and the boiling test. In all cases, the percentage of residual solids was larger for the lower temperature test, as

Table 9. Residual Solids Following Dissolution

Acid Concentration	25°C Test		Boiling Test	
	Residual Solids, g	Percent Residual	Residual Solids, g	Percent Residual
4 M Process Test	--	--	0.2185	1.50
10 M	0.1059	2.20	0.0486	0.998
7.8 M <sup>(a)</sup>	0.1566	3.56	0.0477	0.914
6 M	0.0637	1.37	0.0540	1.01
2 M <sup>(a)</sup>	0.0815	1.45	0.0188	0.378

(a) Solutions from the 7.8 M and 2 M dissolution tests conducted at 25°C sat unfiltered for about 2 weeks before being filtered.

was expected. The 25°C test samples proved to be more difficult to filter. The filtering was slow and some of the filters clogged, requiring a second filtration. Some of the samples from the low temperature test sat unfiltered for about 2 weeks prior to filtering. The samples filtered later showed none of the clogging problems observed earlier. The first sample filter showed the most difficulty and required a second filter to complete the process. The samples that sat the longest in solution filtered the fastest. It appears that the solids age in solution the easier the filtering becomes. During the next set of tests, the samples will be filtered as soon as they cool down to room temperature.

## 4.0 Discussion

In general, it appears that, except for the 2 M HNO<sub>3</sub> test, all of the dissolution reactions were greater than 95% complete by the second sampling (2 hours into the reaction) and had completely leveled off (no additional dissolution) by the third sampling at 4 hours. The 2 M test appeared to be about 90% complete by the second sampling and did not level off until the 8-hour sample. For all of the reactions, a large percentage of the sample was dissolved by the time the first solution sample was taken with the remaining solids going into solution in an asymptotic manner. While the dissolution increased with the amount of time in the solution, the effective reduction in solids volume per unit time decreased rapidly.

Acid concentration does not appear to have a large effect on the concentrations of uranium and radionuclides in the residual solids. The concentrations of these analytes in the residual solids were similar for the 2 M, 6 M, and 7.8 M tests.

The acid concentration has some effect on the dissolution rates. Since the bulk of the composite is uranium (68.5% U and 77.7% as UO<sub>2</sub>) and the appearance of the other analytes in the solutions parallels the uranium concentration, the effect of acid concentration on the dissolution of uranium will be discussed. Figure 9 shows the uranium dissolution for the four tests with a 4X stoichiometric excess of nitric acid. As the acid concentration increases, the time it takes for the uranium to reach its maximum concentration decreases. This difference between the 10 M and 6 M cases is only about 2 hours. The added benefit of using the lower acid concentration should make up for the slightly longer time required for the dissolution to reach its maximum. The 2 M nitric acid test does not reach its equilibrium value until around 8 hours, so this concentration appears to be too low.

Another variable that was tested was the solids loading. For four of the tests (10 M, 7.8 M, 6 M, and 2 M), the molar quantity of acid was held constant, so the loading was different for all of the samples. Since this was not independent, a reasonable comparison cannot be made. For the 4 M process tests, the solids loading was increased greatly. This can be compared to a test with a similar acid concentration, namely the 6 M test. Figure 10 shows the percent uranium dissolved as a function of reaction time for the 4 M process test and 6 M test. The percent dissolved for uranium in the first sample in both tests is similar, but the amount of uranium going into the solutions as the reaction progresses increases rapidly for the low solids loading sample and becomes level for the high solids loading sample. This indicates that a continuous feed system with an initial excess of acid would provide the most efficient method for dissolving this type of sludge.

In Tables 3 through 7, the DF for various analytes is shown. If the DF is greater than 1, the solution (nitric acid) is selectively removing the analyte. As expected, the DF is greater than 1 for uranium,

cesium, americium, and plutonium. The species with the lowest DF is silicon, with values below 0.05. The analytical results for silicon in the solutions was not very conclusive, because all of the solution samples were diluted to get a dose low enough to handle as well as to make the solution concentrations be within the calibration ranges. The actual silicon results for each of the analyzed samples were close to the same, so when the dilution factors were included, large variations were observed. It is apparent that the silicon is at its solubility limit in the diluted samples, and the silicon was probably precipitating during the dilutions.

In addition to the DF values, the residual solids data are important for determining the effectiveness of the dissolution. As shown in Figure 8, most of the solids have dissolved, with the percent residual being directly related to the solids loading. It should be noted that in the 4 M process test, three glass vials were used to add the samples to the dissolver vessel, while all of the remaining tests were conducted using only a single glass vial for sample addition. If the boiling were not vigorous enough to overturn the thimbles, it is possible that the contact of the acid with the sludge was insufficient for complete reaction. These results suggest a solubility phenomenon may be occurring that affects the amount of solids going into solution. If this is the case, this also suggests that a continuous feed system may increase the rate and extent of the dissolution.

While the dissolution of uranium in all of these systems proceeded to greater than 99%, there was still a measurable amount of uranium in the residual solids. A possible explanation would be that during the final isolation of the residual solids, some entrained supernatant liquid remained. As noted in Section 3.1, the solids were washed with two small aliquots of 2% nitric acid and one small aliquot of deionized water. However, the washing occurred while the residual solids remained on the filter, and it is conceivable that some of the original dissolver solution remained. The volumes of solution required to remain to account for the uranium found in the residual solids for each of the tests are 79.9  $\mu\text{L}$ , 53.5  $\mu\text{L}$ , 42.7  $\mu\text{L}$ , 38.7  $\mu\text{L}$  and 43.6  $\mu\text{L}$  for the 4 M, 10 M, 7.8 M, 6 M, and 2 M tests, respectively. Since the mass of the other analytes in these quantities of solutions would not be greater than the mass found in the residual solids, this possibility cannot be ruled out.

Overall, the dissolution of the canister sludge was successful, leaving less than 2% of the original solids. However, the residual solids that remained had  $^{239/240}\text{Pu}$ ,  $^{241}\text{Am}$ , and uranium at levels above the ERDF criteria. Further leaching of the solids to remove the TRU species may be necessary before the residual solids can be placed in a waste form for disposal.

## 5.0 References

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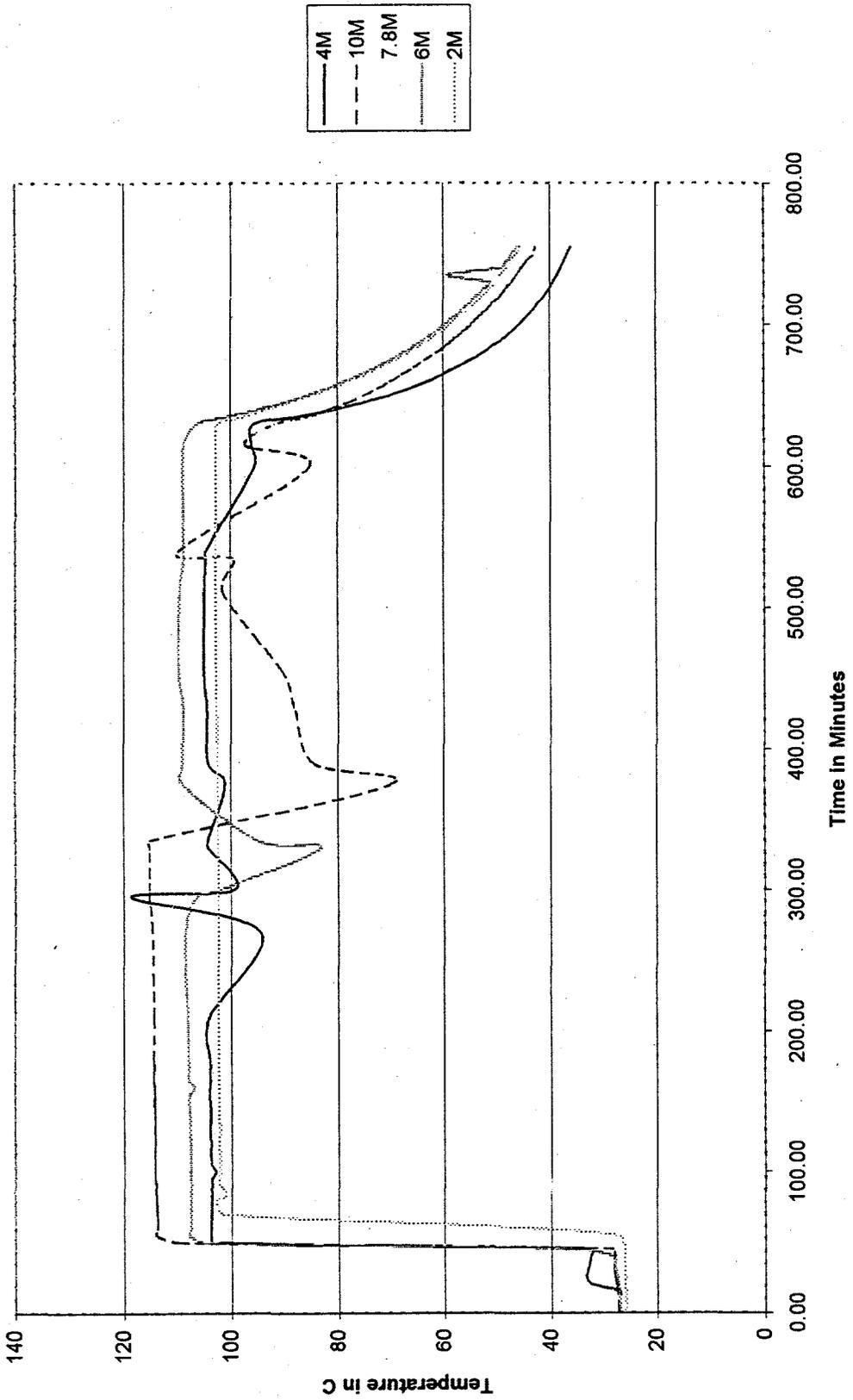


Figure 1. Vessel Temperature Profiles for Dissolution Tests

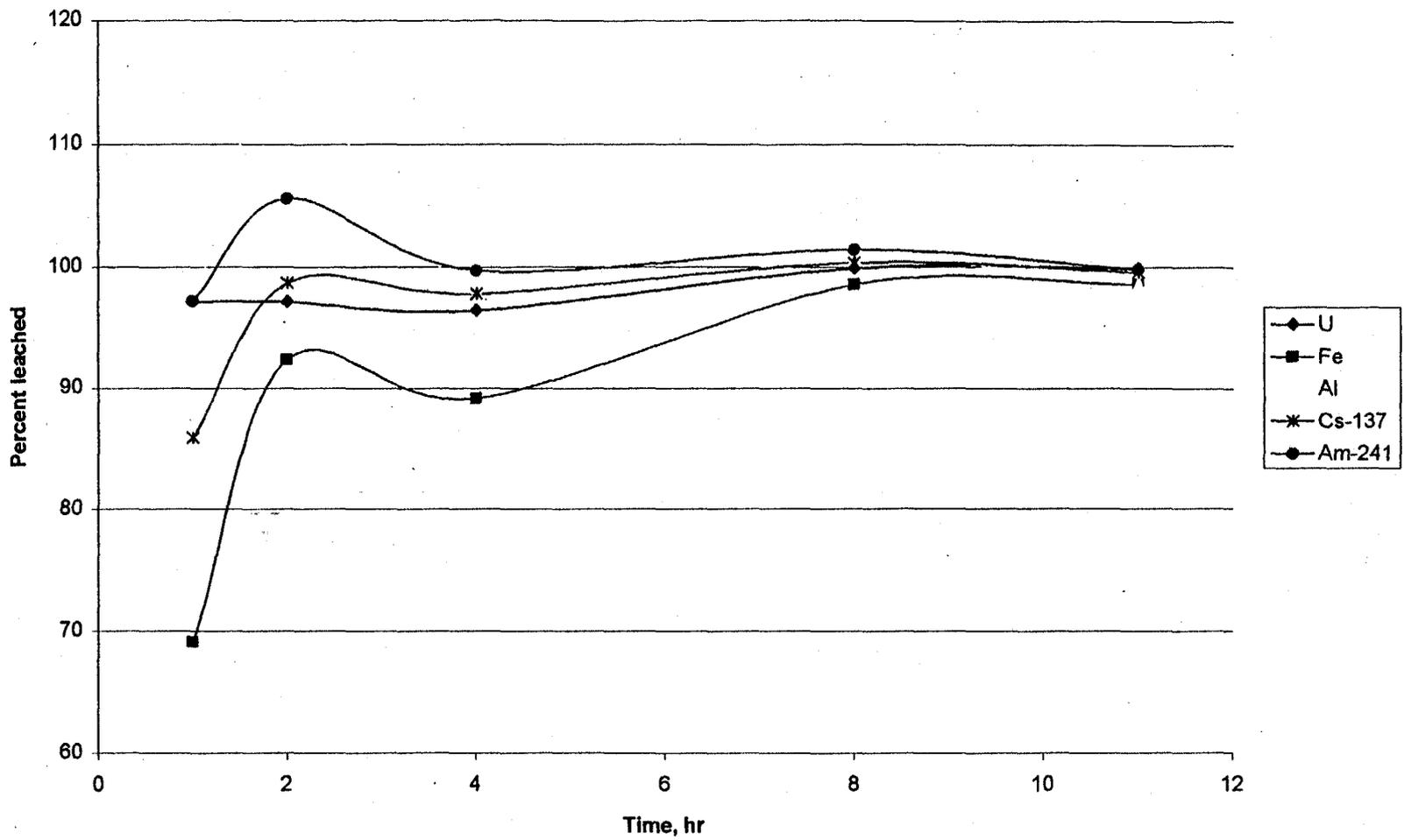


Figure 2. Percent Analyte in Solution, 4 M Process Test

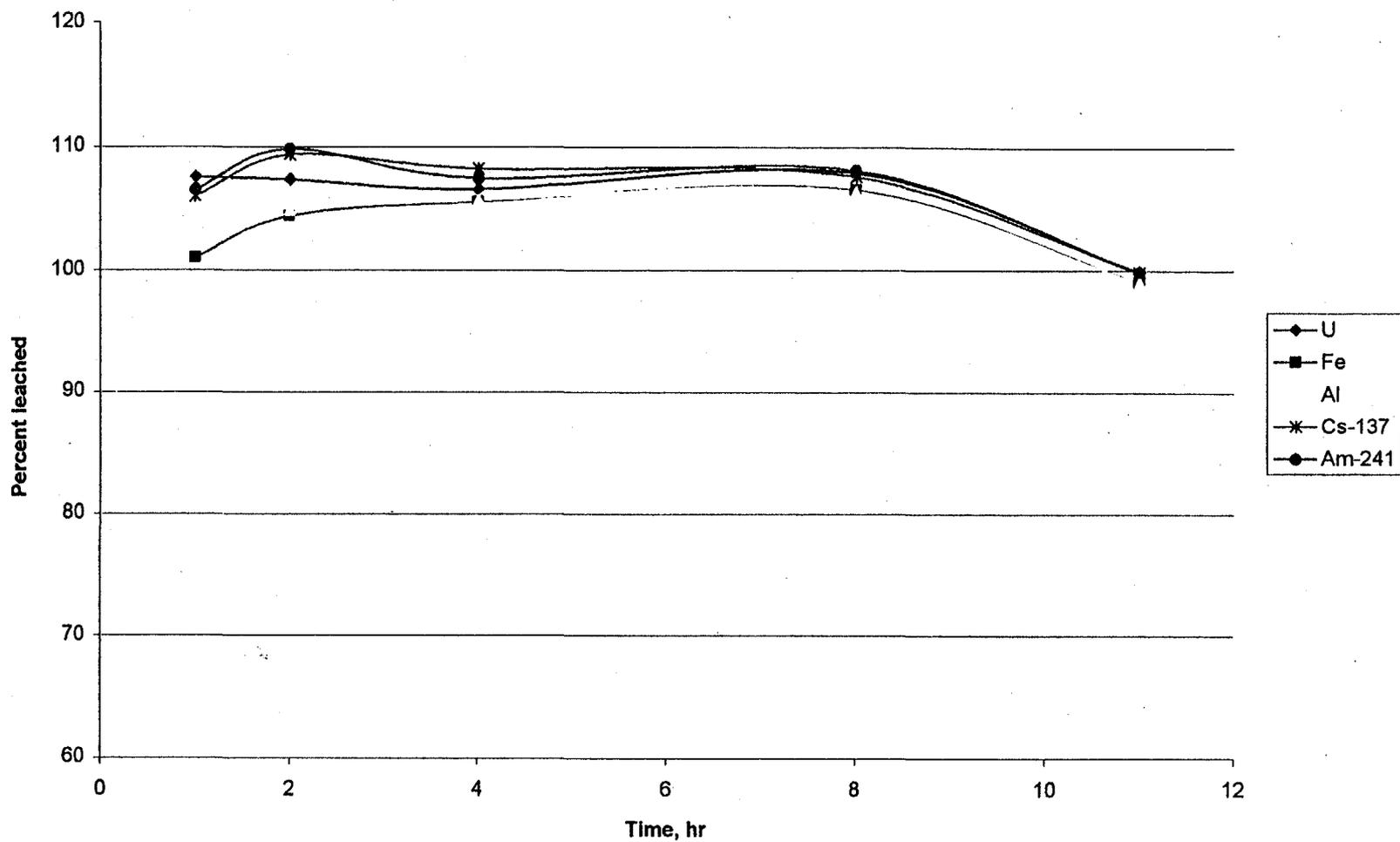


Figure 3. Percent Analyte in Solution, 10 M Test

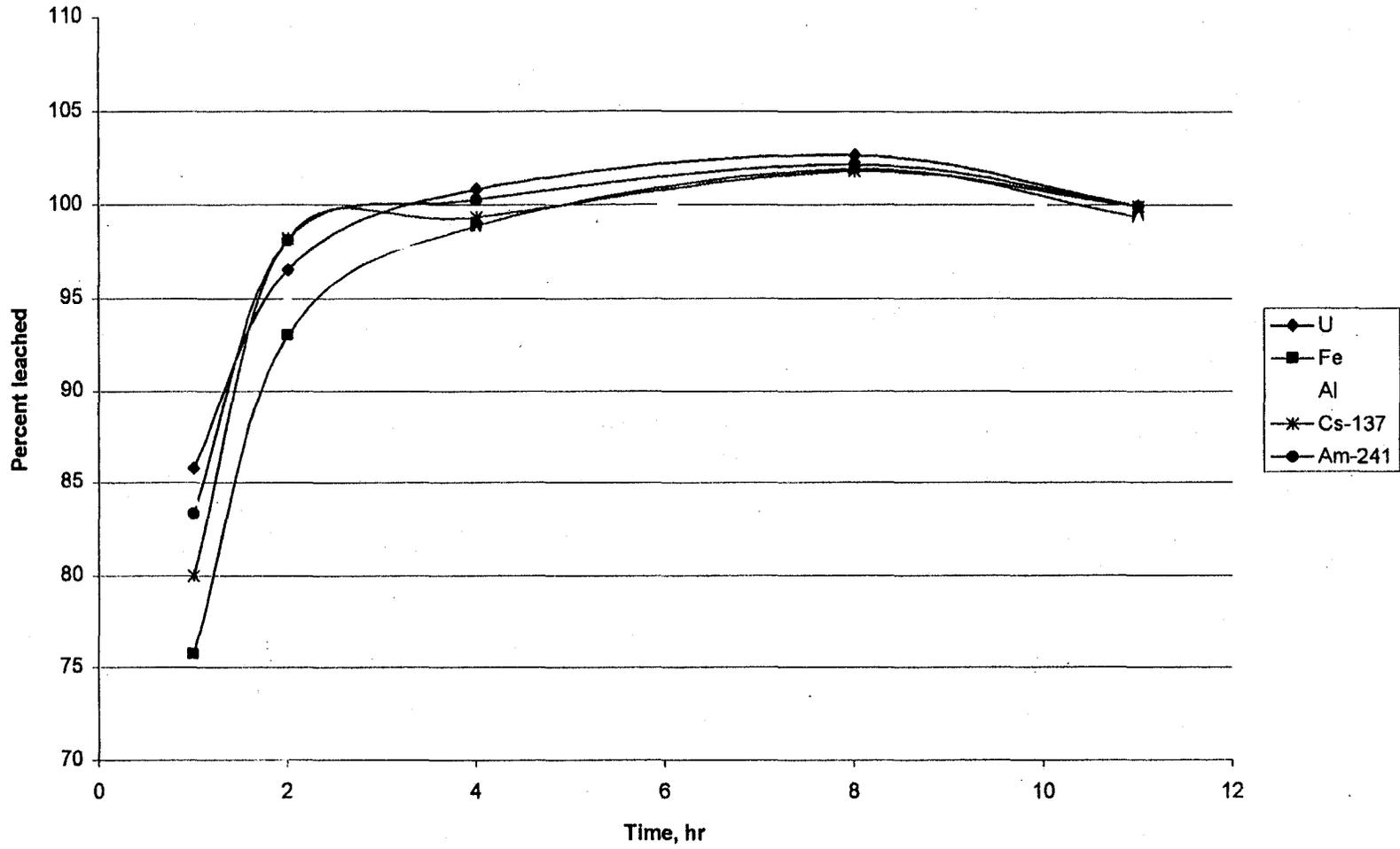


Figure 4. Percent Analyte in Solution, 7.8 M Test

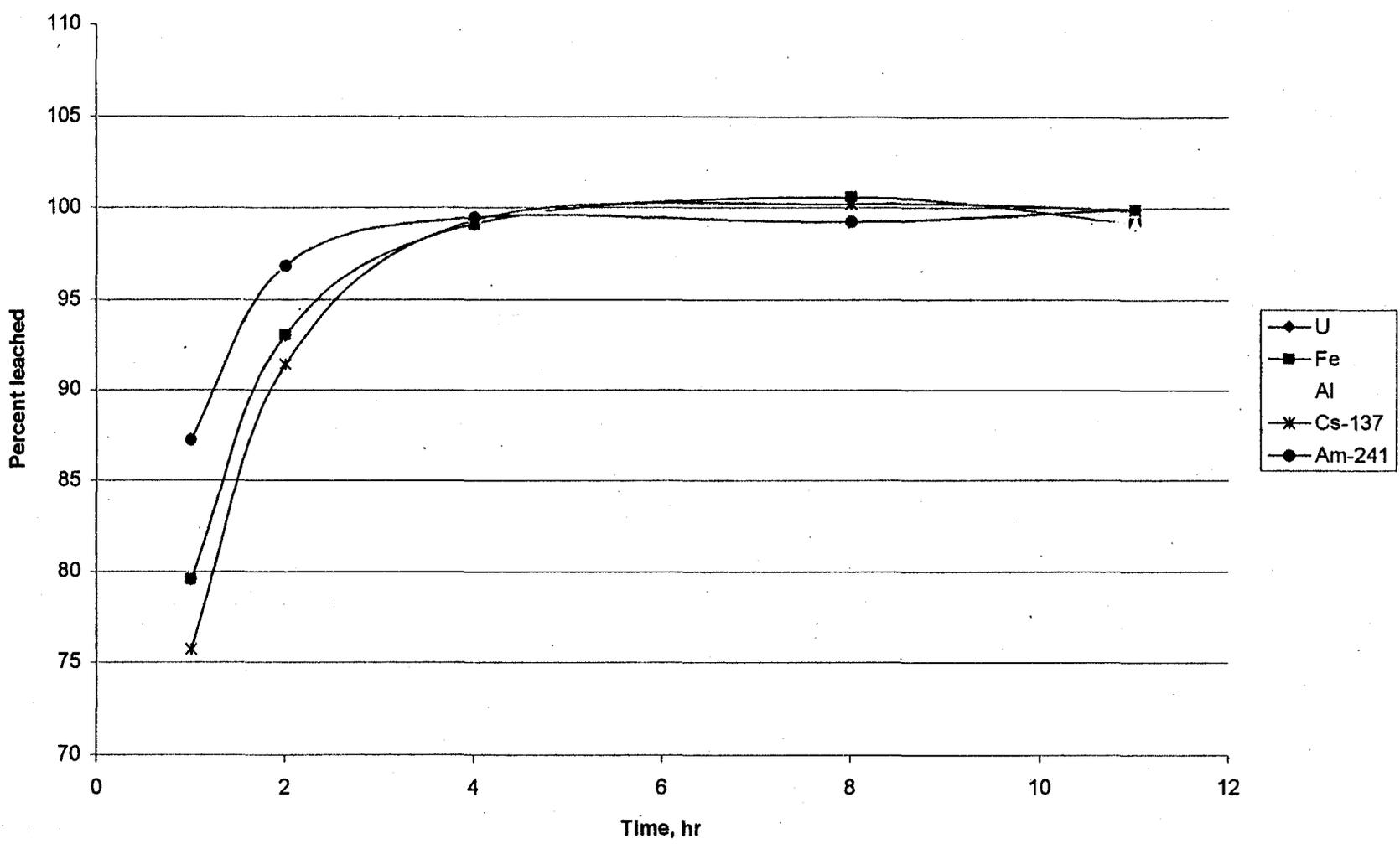


Figure 5. Percent Analyte in Solution, 6 M Test

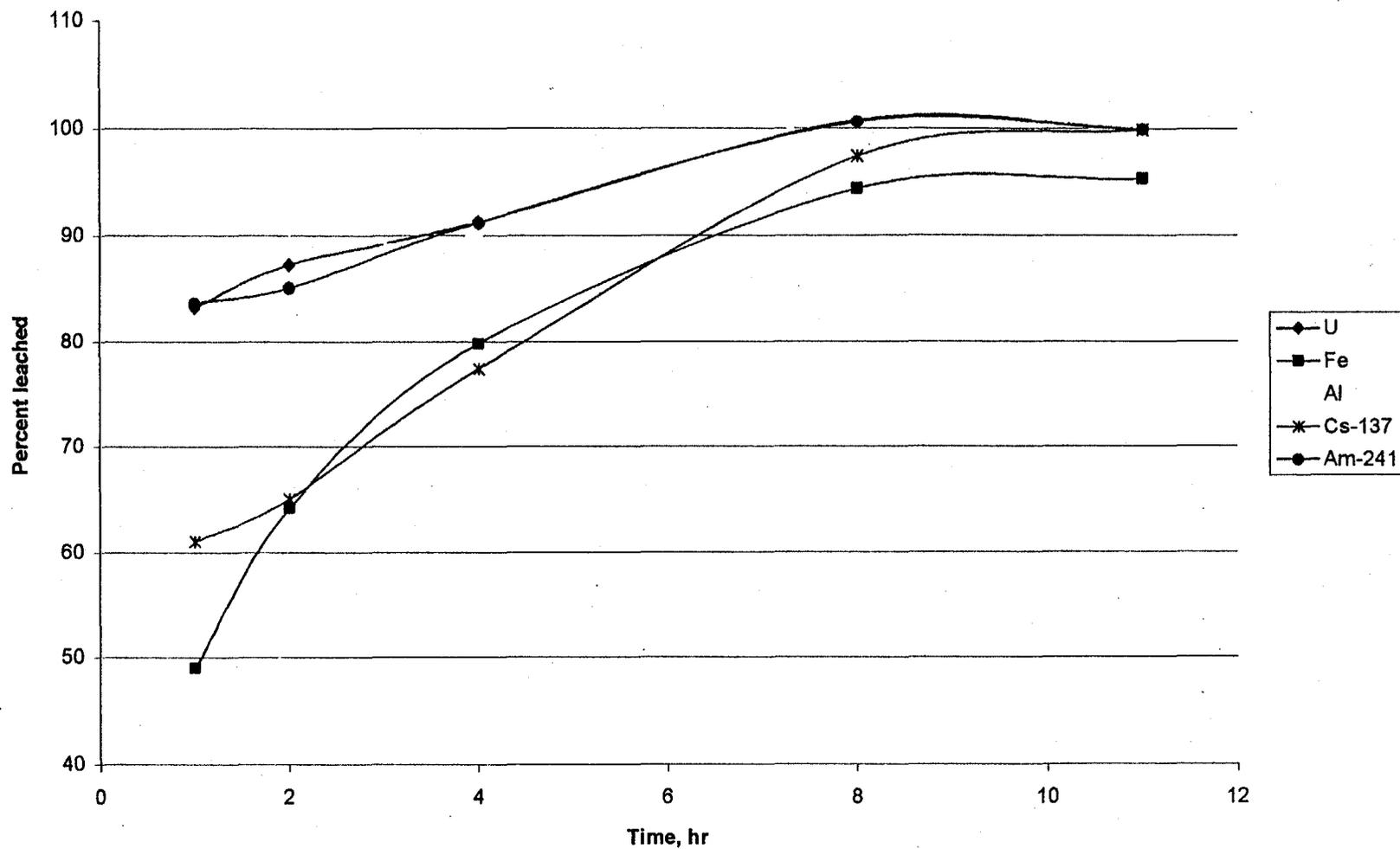


Figure 6. Percent Analyte in Solution, 2 M Test

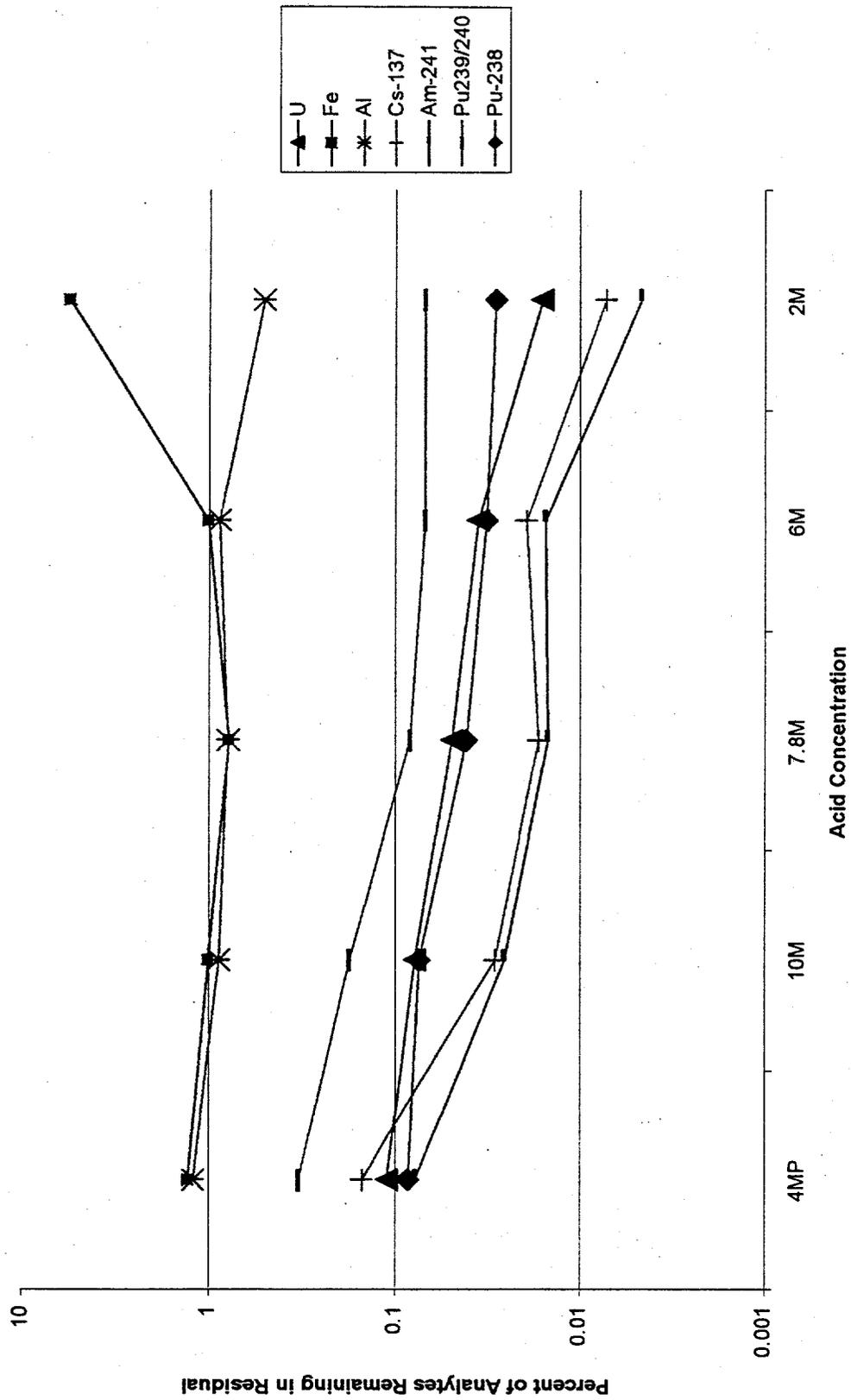


Figure 7. Analytes in Residual Solids



Figure 8. Percent Residual Solids as a Function of Acid Concentration

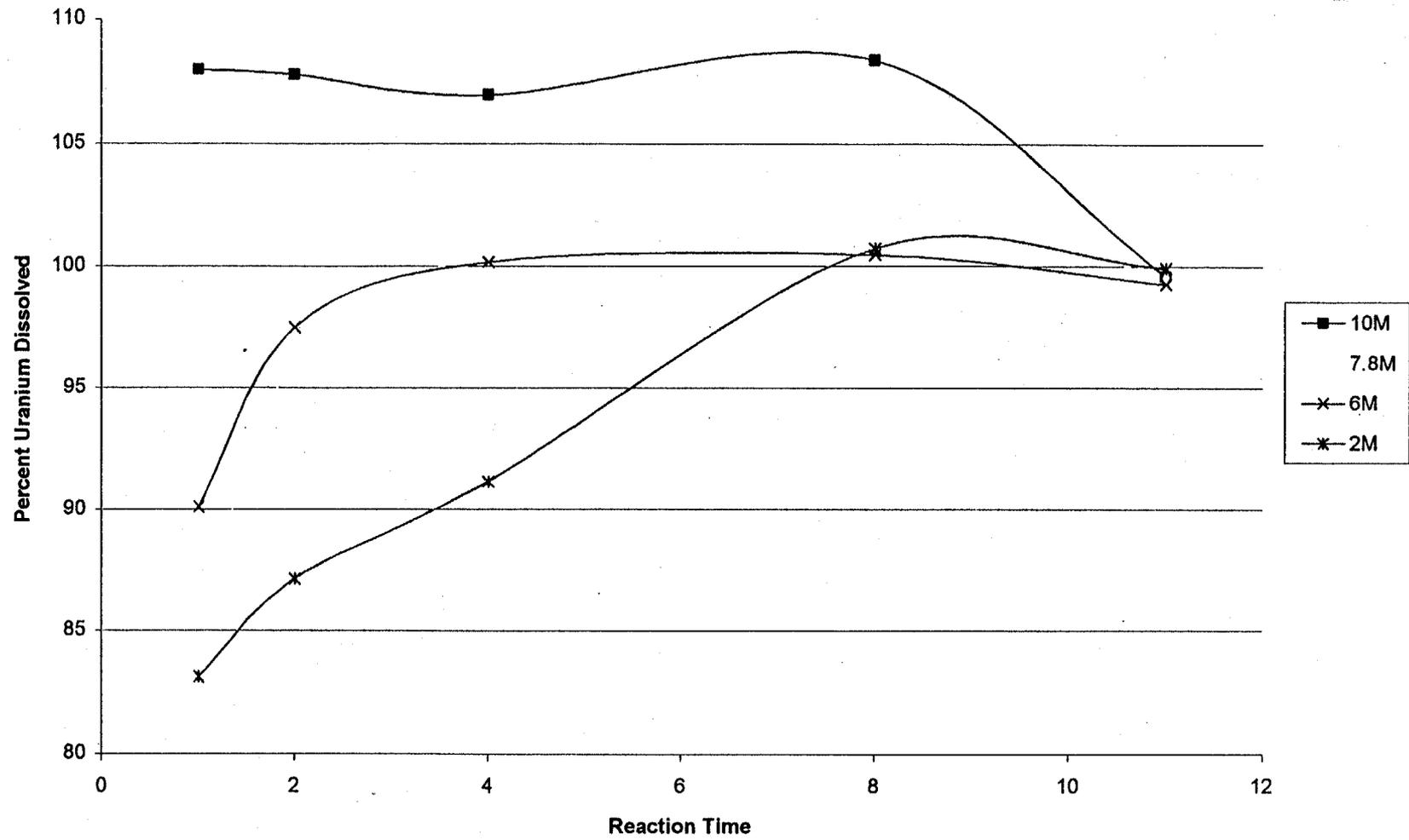


Figure 9. Uranium Dissolution Comparison by Acid Concentration

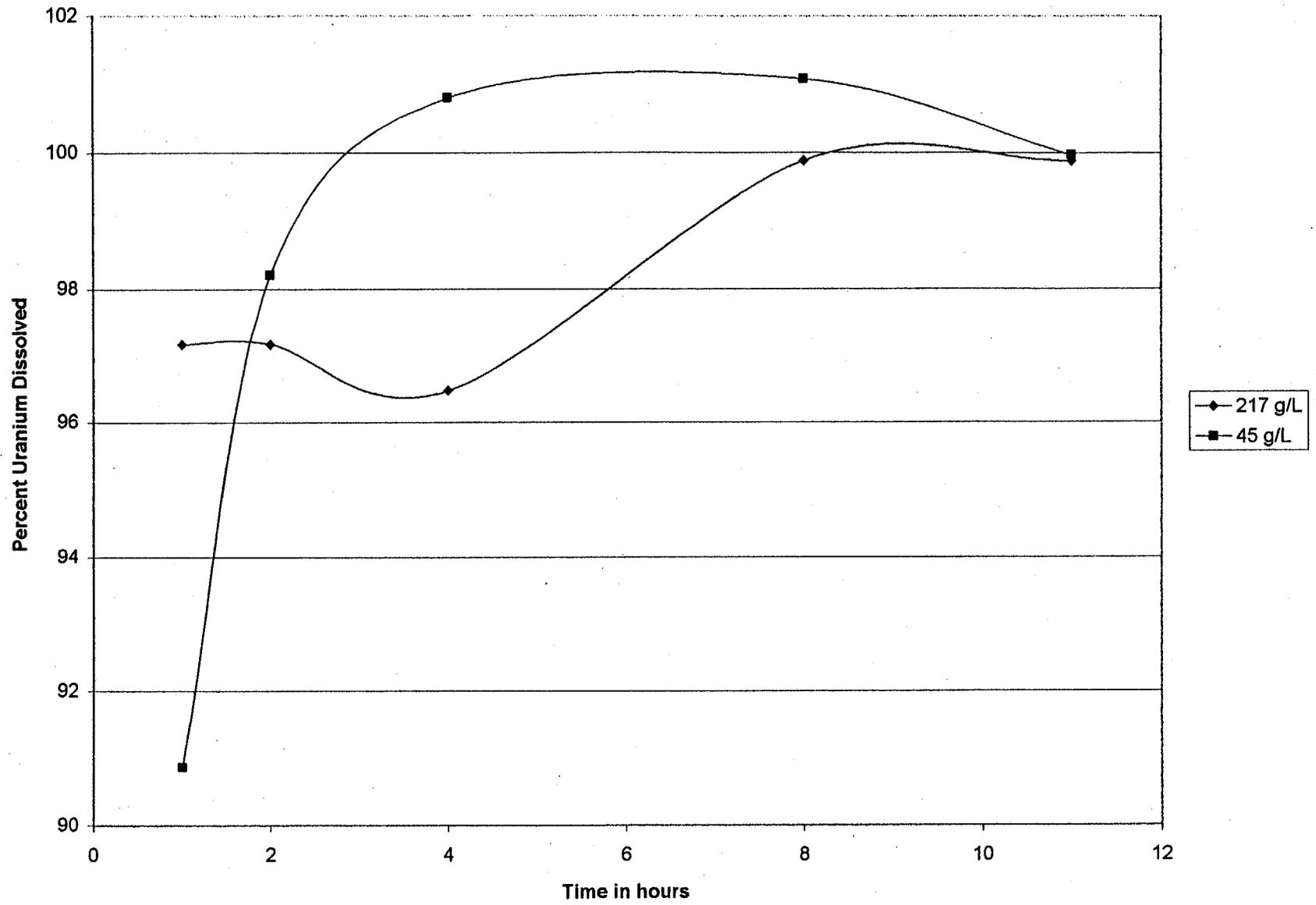


Figure 10. Uranium Dissolution as a Function of Solids Loading

## **Appendix**

### **Analytical Data for K East Canister Composite Sludge Residual Solids and Intermittent Dissolver Solution Samples**

**Table A.1** Data from the K East Canister Composite and the Residual Solids from the Dissolution Tests

	4 M		10 M		7.8 M		6 M		2 M		KECOMP	
	µg(µCi)/g	µg(µCi)	Wet µg(µCi)/g	Dry µg(µCi)								
U	50800	11100	53600	2600	37000	1760	24000	1300	29000	545	422000	685000
Fe	10500	2290	12300	598	10400	496	12100	653	181000	3400	7420	12000
Al	15000	3280	16500	802	16100	768	16000	864	24900	468	11350	18400
Si	195000	42600	332000	16100	356000	17000	313000	16900	172000	3230	4685	7600
Ca	5480	1200	11900	578	7910	377	8860	478	12000	226	725	1180
<sup>137</sup> Cs	155	33.9	69.7	3.39	46	2.19	42.2	2.28	94.6	1.78	498.5	809
<sup>60</sup> Co	1.03	0.225	0.56	0.0272	0.467	0.0222	0.508	0.0274	2.33	0.0438	0.233	0.378
<sup>125</sup> Sb	22.1	4.83	27.2	1.32	18	0.859	14.8	0.799	9.95	0.187		0
<sup>154</sup> Eu	0.874	0.191	0.769	0.0374	0.488	0.0233	0.335	0.0181	0.382	0.00718	5.38	8.73
<sup>155</sup> Eu	0.57	0.125	0.223	0.0108	0.34	0.0162	0.203	0.0110		0	2.55	4.14
<sup>241</sup> Am	9.27	2.03	7.3	0.355	4.85	0.231	3.92	0.212	7.12	0.134	58.75	95.3
<sup>238</sup> U		0	0.0521	0.00253		0	0.0362	0.00196		0	0.256	0.415
<sup>239/240</sup> Pu	26.9	5.88	21.7	1.05	11	0.525	8.17	0.441	21.9	0.412	74.35	121
<sup>238</sup> Pu+ <sup>241</sup> Am	10.6	1.24	9.89	0.362	6.09	0.216	4.6	0.170	8.66	0.141	61.45	99.7
<sup>236</sup> Pu+ <sup>243/244</sup> Cm	1.42	0.310	0.0962	0.00468	0.046	0.00219	0.882	0.0476	2.83	0.0532	0.0764	0.124

A.1

**Table A.2.** Solution Data from the 4 M Process Test. The raw data does not include a 100 µL to 10 mL dilution performed in the hot cell. The volume of nitric acid added was 67.0 mL. The first column for each sample represents the raw data and the second column is the total milligrams in the sample.

	1-Hour Sample		2 Hour Sample		4-Hour Sample		8-Hour Sample		11-Hour Sample	
	µg(µCi)/mL	mg(µCi)	µg(µCi)/mL	mg(µCi)	µg(µCi)/mL	mg(µCi)	µg(µCi)/mL	mg(µCi)	µg(µCi)/mL	mg(µCi)
U	1350	9045	1350	9040	1340	8980	1390	9310	1390	9310
Fe	16.7	112	22.4	150	21.6	145	24	161	24	161
Al	36	241	42.9	287	36.4	244	37.3	250	36.5	245
Si	7.95	53.3	10.3	69.0	7.13	47.8	6.51	43.6	6.1	40.9
Ca	0.43	2.88	0.53	3.55	0.52	3.48	0.56	3.75	0.65	4.36
<sup>137</sup> Cs	0.973	6520	1.12	7500	1.11	7440	1.14	7640	1.13	7570
<sup>241</sup> Am	0.161	1080	0.175	1170	0.165	1110	0.168	1130	0.165	1110

**Table A.3.** Solution Data from the 10 M Test. The raw data does not include a 100uL to 10 mL dilution performed in the hot cell. The volume of nitric acid added was 69.76 mL. The first column for each sample represents the raw data and the second column is the total milligrams in the sample.

	1-Hour Sample		2-Hour Sample		4-Hour Sample		8-Hour Sample		11-Hour Sample	
	µg(µCi)/mL	mg(µCi)	µg(µCi)/mL	mg(µCi)	µg(µCi)/mL	mg(µCi)	µg(µCi)/mL	mg(µCi)	µg(µCi)/mL	mg(µCi)
U	528	3602	527	3595	523	3568	530	3616	487	3323
Fe	8.99	59.3	9.3	61.3	9.41	62.0	9.5	62.6	8.77	57.8
Al	12.9	90.0	13	90.7	13.1	91.4	13.2	92.1	12.2	85.1
Si	6.66	46.5	6.67	46.5	5.16	36.0	5.11	35.6	5.07	35.4
Ca	< 0.20	< 1.4	< 0.20	< 1.4	0.28	1.95	0.28	1.95	0.28	1.95
Cs-137	0.464	3237	0.479	3342	0.474	3307	0.471	3286	0.434	3028
Am-241	0.0604	421	0.0623	435	0.0609	425	0.0613	428	0.0562	392

A.2

**Table A.4.** Solution Data from the 7.8 M Test. The raw data does not include a 100 µL to 10 mL dilution performed in the hot cell. The volume of nitric acid added was 89.7 mL. The first column for each sample represents the raw data and the second column is the total milligrams in the sample.

	1-Hour sample		2-Hour Sample		4-Hour Sample		8-Hour Sample		11-Hour Sample	
	µg(µCi)/mL	mg(µCi)	µg(µCi)/mL	mg(µCi)	µg(µCi)/mL	mg(µCi)	µg(µCi)/mL	mg(µCi)	µg(µCi)/mL	mg(µCi)
U	354	3052	399	3439	417	3595	425	3664	413	3560
Fe	6.63	47.2	8.16	58.1	8.68	61.8	8.96	63.8	8.72	62.1
Al	9.81	80.3	11.1	90.9	11.5	94.2	11.8	96.6	11.6	95.0
Si	6.74	60.5	5.87	52.7	6.08	54.5	5.48	49.2	5.67	50.9
Ca	< 0.20	< 1.8	< 0.20	< 1.8	0.27	2.42	0.27	2.42	0.27	2.42
Cs-137	0.278	2494	0.342	3068	0.346	3104	0.355	3184	0.348	3122
Am-241	0.0419	376	0.0494	443	0.0505	453	0.0515	462	0.0503	451

**Table A.5.** Solution Data from the 6 M Test. The raw data does not include a 100  $\mu\text{L}$  to 10 mL dilution performed in the hot cell. The volume of nitric acid added was 119.2 mL. The first column for each sample represents the raw data and the second column is the total milligrams in the sample.

	1-Hour Sample		2-Hour Sample		4-Hour Sample		8-Hour Sample		11-Hour Sample	
	$\mu\text{g}(\mu\text{Ci})/\text{mL}$	mg( $\mu\text{Ci}$ )								
U	304	3283	329	3553	338	3650	339	3661	335	3618
Fe	5.2	50.3	6.1	59.0	6.51	63.0	6.61	64.0	6.51	63.0
Al	8.17	88.6	8.69	94.3	8.93	96.9	8.95	97.1	8.9	96.5
Si	8.11	96.7	7.76	92.5	6.78	80.8	6.57	78.3	7.06	84.2
Ca	< 0.20	< 2.38	< 0.20	< 2.38	< 0.20	< 2.38	< 0.20	< 2.38	< 0.20	< 2.38
Cs-137	0.241	2873	0.292	3481	0.318	3791	0.321	3826	0.32	3814
Am-241	0.0355	423	0.0395	471	0.0406	484	0.0405	483	0.0408	486

**Table A.6.** Solution Data from the 2 M Test. The raw data does not include a 100  $\mu\text{L}$  to 10 mL dilution performed in the hot cell. The volume of nitric acid added was 347.8 mL. The first column for each sample represents the raw data and the second column is the total milligrams in the sample.

	1-Hour Sample		2-Hour Sample		4-Hour Sample		8-Hour Sample		11-Hour Sample	
	$\mu\text{g}(\mu\text{Ci})/\text{mL}$	mg( $\mu\text{Ci}$ )								
U	104	2829	109	2965	114	3101	126	3427	125	3400
Fe	1.03	28.9	1.35	37.9	1.68	47.2	1.99	55.9	2.01	56.4
Al	2.7	78.3	2.82	81.8	2.84	82.4	3.2	92.8	3.14	91.1
Si	7.83	272	7.65	266	5.11	178	7.58	264	7.43	258
Ca	< 0.20	< 7.0	< 0.20	< 7.0	< 0.20	< 7.0	< 0.20	< 7.0	< 0.20	< 7.0
Cs-137	0.0712	2444	0.0759	2605	0.0904	3103	0.114	3913	0.117	4016
Am-241	0.0123	396	0.0125	403	0.0134	432	0.0148	477	0.0147	473