

## **K Basin Sludge Conditioning Testing**

### **Nitric Acid Dissolution Testing of K East Area Sludge Composite, Small- and Large-Scale Testing**

C. D. Carlson  
C. H. Delegard  
I. E. Burgeson  
A. J. Schmidt  
K. L. Silvers

July 24, 1998

Prepared for  
Numatec Hanford Corporation

Work Supported by  
the U.S. Department of Energy  
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory  
Richland, Washington 99352

RECEIVED  
APR 19 1999  
OSTI

## DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY

*operated by*

BATTELLE

*for the*

UNITED STATES DEPARTMENT OF ENERGY

*under Contract DE-AC06-76RLO 1830*

Printed in the United States of America

Available to DOE and DOE contractors from the  
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;  
prices available from (615) 576-8401.

Available to the public from the National Technical Information Service,  
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161



This document was printed on recycled paper.

(9/97)

## **DISCLAIMER**

**Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.**

## Summary and Conclusions

This report describes work performed by Pacific Northwest National Laboratory (PNNL) for Numatec Hanford Corporation (NHC) to support the development of the K Basin Sludge Treatment System. For this work, testing was performed to examine the dissolution behavior of a K East Basin floor and Weasel Pit sludge composite, referred to as K East area sludge composite, in nitric acid at the following concentrations: 2 M, 4 M, 6 M and 7.8 M. With the exception of one high solids loading test, the nitric acid was added at 4X the stoichiometric requirement (assuming 100% of the sludge was uranium metal). The dissolution tests were conducted at boiling temperatures for 24 hours. Most of the tests were conducted with ~2.5 g of sludge (dry basis). The high solids loading test was conducted with ~7 g of sludge.

A large-scale dissolution test was conducted with 26.5 g of sludge and 620 mL of 6 M nitric acid. The objectives of this test were to 1) generate a sufficient quantity of acid-insoluble residual solids for use in leaching studies, and 2) examine the dissolution behavior of the sludge composite at a larger scale.

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

The dissolution tests were successfully completed in a controllable manner. While brown fumes (most likely  $\text{NO}_2$ ) were observed, offgas generation rates appeared to be low. Sludge additions to the dissolver flasks did not result in excessive reactions.

Throughout the dissolution tests, a significant quantity of fluffy, gel-like solids was observed floating in the solutions for all tests, except the 2 M test. A heavy build-up of a translucent solid on the thermowell (glass) was observed during the 7.8 M dissolution test. Similar solids accumulated, but to a lesser extent, on the thermowells in the 6 M (small-scale and scaled-up) and 4 M tests. Filtration of the residual solids from the small-scale testing took ~5 to ~45 min (7.8 M). Filtration of the rinsed solids from the large-scale test proceeded very rapidly (several minutes).

In general, it appears that dissolution reactions were greater than 85% complete within the first 2 hours at all acid concentrations. Within the first 30 minutes, many of the key analytes were more than 80% dissolved.

The quantity of residual solids remaining after 24 hours of dissolution ranged from 16% to 23%. Greater than 99% of the uranium and radionuclides were dissolved, with the exception of  $^{137}\text{Cs}$  in the high solids loading test (6.7% of the  $^{137}\text{Cs}$  remained with the residual solids). The residual solids were primarily composed of silicon ( $\text{SiO}_2$ ) and iron compounds.

The acid concentrations used for the dissolutions do not appear to have a dramatic effect on the radionuclide concentrations in the residual solids. The lowest radionuclide concentrations in the residual solids were obtained in both the large- and small-scale tests using 6 M  $\text{HNO}_3$ . This conclusion is tentative, since solids loadings were not kept constant for the dissolution tests.

Radionuclide and iron concentrations in the residual solids were greater (1.6X for  $^{241}\text{Am}$ , 5.3X for  $^{137}\text{Cs}$ , 6.9X for  $^{239/240}\text{Pu}$ , and 8.7X for Fe) when the initial sludge solids loading increased from 25 g/L to 115 g/L at 4 M  $\text{HNO}_3$ .

The results obtained from the large-scale dissolution test were comparable with those of the small-scale test performed at similar conditions. Some differences exist in the concentrations of radionuclides in the residual solids; however, the differences could be partially caused by inhomogeneity of the test material (sludge composite). The concentrations of radionuclides in the residual solids from the large-scale test are within an order of magnitude of the ERDF Waste Acceptance Criteria.

# Contents

Summary and Conclusions .....	iii
1.0 Introduction .....	1
2.0 Experimental .....	1
2.1 Composite Sample .....	1
2.2 Small-Scale Tests .....	2
2.3 Large-Scale Residual Preparation .....	4
3.0 Results .....	5
3.1 Small-Scale Testing; Qualitative Observations .....	5
3.2 Large-Scale Testing; Qualitative Observations .....	5
3.3 Small-Scale Testing; Quantitative Results .....	5
3.4 Large-Scale Testing; Quantitative Results .....	11
4.0 Discussion .....	11
5.0 References .....	13

## Figures

1. Syringe Delivery of Frozen Sludge Sample.....	15
2. 7.8 M Test at 2 Hours Showing Solid Formation of the Thermometer Well.....	16
3. Radiochemical Results for the 4 M Process Test.....	17
4. ICP-AES Results for the 4 M Process Test.....	18
5. Radiochemical Results for the 4 M Test.....	19
6. ICP-AES Results for the 4 M Test.....	20
7. Radiochemical Results for the 7.8 M Process Test.....	21
8. ICP-AES Results for the 7.8 M Process Test.....	22
9. Radiochemical Results for the 6 M Test.....	23
10. ICP-AES Results for the 6 M Test.....	24
11. Radiochemical Results for the 2 M Test.....	25
12. ICP-AES Results for the 2 M Test.....	26
13. Radiochemical Results for the Residual Solids.....	27
14. ICP-AES Results for the Residual Solids.....	28
15. The Residual from the 4 M Process Test.....	29
16. The Residual from the 4 M Test.....	29
17. The Residual from the 7.8 M Test.....	30
18. The Residual from the 6 M Test.....	30
19. The Residual from the 2 M Test.....	31
20. Comparison of the Uranium and Iron Results from Test with Different Solids Load, the 4M Process and the 4 M Test.....	32

## Tables

1. K East Weasel Pit Composite .....	2
2. K East Floor Composite.....	2
3. K East Area Composite.....	3
4. Testing Parameters.....	3
5. Comparison of the Composite Analysis to the Calculated Starting Material Composition.....	6
6. Analyte Removal for the 4 <u>M</u> Process Test .....	7
7. Analyte Removal for the 4 <u>M</u> Test.....	8
8. Analyte Removal for the 7.8 <u>M</u> Test.....	8
9. Analyte Removal for the 6 <u>M</u> Test.....	9
10. Analyte Removal for the 2 <u>M</u> Test.....	10
11. Residual Solids Following Dissolution.....	10
12. Analyte Removal for the 6 <u>M</u> Large-Scale Test .....	11
13. Comparison of Residual Results for the Large- and Small-Scale 6 <u>M</u> Tests.....	13

## 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 or 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 is 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 Pu criticality safety, and neutralized and made alkaline with NaOH. 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 area sludge composite (Basin floor and Weasel Pit) in nitric acid at various concentrations (i.e., 2 M, 4 M, 6 M, and 7.8 M) at boiling temperatures and to prepare residual solid material for further leach testing. The effectiveness of the dissolutions was evaluated by measuring the concentration of key species in the dissolution solutions as a function of reaction (dissolution) time, and by analyzing the final acid-insoluble 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 Composite Sample

The composite used in this testing was prepared as described in the test instruction. For the area composite, a Weasel Pit and a floor composite were prepared first, then combined. Table 1 shows the samples that were used to prepare the Weasel Pit composite. Table 2 shows the samples that were used to prepare the K East floor composite.

Table 1. K East Weasel Pit Composite

	Dry Solids	After Sieving
KES-P-16	54.79	51.97
KES-Q-17	13.04	12.37
KES-R-18	117.18	111.14
KES-S-19	57.39	54.43
KES-T-20	55.00	52.16
Total Solids	297.40	282.07
Water		114.39
Wt fraction Solids		0.71

Table 2. K East Floor Composite

	Dry Solids	After Sieving
KES-A-02	0.59	0.48
KES-B-03	2.11	1.73
KES-C-04	0.58	0.48
KES-F-10	15.82	12.99
KES-G-07	1.88	1.54
KES-I-15	2.40	1.97
KES-K-12	2.47	2.03
KES-L-01	0.54	0.44
KES-N-05	9.72	7.98
KES-E-11	26.52	21.77
KES-J-06	45.50	37.36
KES-D-14	11.64	9.56
Total Solids	119.77	98.34
Water		85.19
Wt fraction Solids		0.54

Both composites were dry sieved to remove organic ion exchange resin (OIER) beads present in some of the samples. After sieving, DI water was added to the composites to reconstitute the dry sludge to a wet "settled sludge." To make the final area composite, 148.91 grams of reconstituted K East floor composite were added to 144.42 grams of reconstituted K East Weasel Pit composite. Table 3 shows the calculated quantities of each sample that comprise the K East area composite. The resulting material was a brown slurry that flowed very easily.

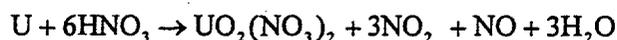
## 2.2 Small-Scale Tests

Small quantity samples of K East area composite were reacted for 24 hours in boiling nitric acid. Six tests (including one blank) were performed simultaneously using acid concentrations of 2 M, 4 M (two tests), 6 M, and 7.8 M. The tests were performed by adding ~2.5 grams of sample to the room-temperature nitric acid solutions. The initial plan was to perform all of the tests using ~5 grams of

Table 3. K East Area Composite

KES-A-02	0.39
KES-B-03	1.41
KES-C-04	0.39
KES-F-10	10.54
KES-G-07	1.25
KES-I-15	1.60
KES-K-12	1.65
KES-L-01	0.36
KES-N-05	6.48
KES-E-11	17.67
KES-J-06	30.31
KES-D-14	7.75
KES-P-16	18.93
KES-Q-17	4.51
KES-R-18	40.49
KES-S-19	19.83
KES-T-20	19.00
Total Solids	182.54
Water	110.79

composite material and a 4X stoichiometric excess of nitric acid (assuming the sample was all uranium and 6 moles of acid were required to dissolve each mole of uranium as shown in the reaction below).



During the actual testing, the 4 M process test was designated to emulate the actual process with a 120 g/L solids loading. The remaining tests were performed with the planned solids loading but with half of the solids and liquids, using the same moles of acid per gram of sample. Table 4 shows the parameters used for the dissolution testing, including the large-scale test.

Table 4. 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	60.97	6.9867	115
2	4	89.59	2.2457	25
3	7.8	46.09	2.5147	55
4	6	61.41	2.2870	37
5	7.8	61.27	Blank	--
6	2	175.9	2.3923	14
Large-Scale Test	6	623.7	26.59	43

For each test, the sludge dissolution apparatus consisted of a three-necked round bottom flask, a Graham condenser, a thermometer well, an inlet valve, and a ground glass plug. Inside a hot cell, each flask was placed into a heating mantle, and then the condenser was placed in the middle neck of the flask. The thermometer well was filled with sand and placed into one of the other necks. A plug was placed into the last neck to allow access for sample introduction and collection of liquid samples. At the top of the condenser, an inlet valve led to an air-filled trap, which was followed by a trap filled with sodium sodium hydroxide solution to react with any  $\text{NO}_x$  generated during the dissolution. Cooling water 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 was kept below  $20^\circ\text{C}$  by the addition of dry ice during the test since no capability for cooling the water existed.

Nitric acid was added to the apparatus. One glass thimble of sludge sample (four thimbles were required for the process test) was then dropped into each vessel through the access neck, and the mixture was heated to boiling. The 2 M  $\text{HNO}_3$  test, which contained a larger volume of solution, required about 45 minutes to reach reaction temperature, while the remaining reactions required between 15 and 25 minutes. Solution samples were collected at 30 minutes, 1, 2, 4, and 24 hours (measured from the addition of the K East area composite samples). These samples were first collected with a transfer pipette and allowed to cool, and then a 0.5 mL aliquot was filtered for analysis. Due to the high dose of the samples, a 500- $\mu\text{L}$  sample of each solution was diluted to 10 mL prior to removal from the hot cell. These samples were then analyzed by ICP-AES, gamma energy analysis, and alpha energy analysis.

After the tests were concluded, the vessels were allowed to come to room temperature and the solutions filtered immediately. The solutions were filtered through 0.45- $\mu\text{m}$  acetate/cellulose filters, and the resulting solids washed with two 10-mL aliquots of 2%  $\text{HNO}_3$  and one 10-mL aliquot of distilled deionized water. Samples of each residual solid were prepared by KOH fusion and analyzed by ICP-AES, gamma energy analysis, and alpha energy analysis.

### 2.3 Large-Scale Residual Preparation

A large-scale residual preparation was performed by placing 26.59 grams (dry weight) of solid into 624 mL of 6 M nitric acid (see Table 1 for test parameters). The reaction vessel setup was identical to that described above, using only a 1-L flask. Following the assembly of the reaction apparatus, a new method of sample addition was tested in an attempt to reduce sample loss and eliminate the addition of the glass thimbles. The samples were placed into modified disposable syringes, frozen in liquid nitrogen, and pushed into the reaction vessel (see Figure 1a and b). The new sample addition method left no residue in the addition syringe and did not introduce any foreign materials into the reaction vessel. Six plugs of sample were added during a 2-hour period, emulating a continuous feed operation. The heat to the vessel was turned on just prior to the addition of the first sample. By the addition of the third sample, the reaction was up to boiling. The volume of solution was such that the temperature was not noticeably affected by the additions of the frozen sample plugs. Upon melting in the solution, the solids quickly mixed into the solution. When the test was completed (24 hours), the reaction vessel was allowed to cool to room temperature. The slurry was allowed to settle, and the solution decanted onto a 0.45- $\mu\text{m}$  cellulose acetate filter. Two 150-mL aliquots of 2% nitric acid were then added to the residual solids, mixed well, and allowed to settle, and the solutions decanted onto the filter. Finally, 150 mL of deionized water were added to the solids, and the entire slurry was filtered through the 0.45- $\mu\text{m}$  cellulose acetate filter. The solids were air-dried and sampled for X-ray diffraction (XRD) analysis; particle size; total carbon, and a KOH fusion, which was analyzed by ICP metals, gamma energy analysis, and alpha energy

analysis. The solutions were collected separately as the final dissolution solution and the wash solution. The solutions were analyzed for ICP metals, gamma energy analysis, and alpha energy analysis. The results from the carbon analysis and X-ray diffraction were not available in time of this report and will be reported in an addendum.

## 3.0 Results

### 3.1 Small-Scale Testing; Qualitative Observations

For the small-scale tests, the solids were added to the reaction vessel, which was then heated to boiling. During the heating, some brown off-gases were observed, as expected for  $\text{NO}_2$  fumes. The off-gases were observed throughout the test, with more intense coloration occurring when the boiling was most vigorous. Throughout the tests, a large amount of fluffy solids were observed floating in the solutions for all of the tests except the 2 M  $\text{HNO}_3$ . For the 2 M test, the solids remained close to the bottom of the flask and the liquid remained clear yellow after an initial period of about 2 hours, when all of the solids were suspended. In the other tests, the solids remained suspended throughout the tests. The solids appeared to turn fluffy and gel-like, with this formation occurring later for the lower concentration acid solutions. The fluffy solids appeared first in the 7.8 M reaction after about 1 hour, in the 6 M reaction after about 7 hours, and in the 4 M reactions after about 12 hours. It was difficult to make an estimate of the amount of solids dissolved because the action of boiling kept all of the solids suspended.

After 2 hours of dissolution, solids began to collect on the thermometer well of the 7.8 M  $\text{HNO}_3$  test (see Figure 2). The solids started out white with a green tint. This material built up throughout the test and could not be removed by vigorous shaking of the flask. Similar solids began to appear on the thermometer well of the 6 M  $\text{HNO}_3$  test after 4 ½ hours and on the 4 M  $\text{HNO}_3$  process test after 15 hours. Filtration of the residual solids (0.45- $\mu\text{m}$  filter) was moderately slow, requiring between 5 and 45 minutes. Those tests in which solids accumulated on the thermometer well took the longest time to filter.

### 3.2 Large-Scale Testing; Qualitative Observations

For the large-scale test, the first K East area composite sample was added as heat was applied to the vessel, and the remaining samples were added after the vessel reached boiling temperature. As with the small-scale tests, brown fumes were observed throughout the test, with a slight increase in the fumes upon addition of the samples. Fluffy brown solids were also observed in this test, and the suspension of particulates in the solution made estimating the amount dissolved difficult. Late in the reaction (after 12 hours) solid began to collect on the thermometer well, just as in the small-scale test.

After the serial washes of the residual solids (Section 2.3) were performed, the residual solids were slurried and filtered through a 0.45- $\mu\text{m}$  filter. The slurry filtered rapidly (several minutes), indicating that extensive washing may improve the filterability of residual solid intermixed with gel.

### 3.3 Small-Scale Testing; Quantitative Results

Figures 3 through 12 show the percent of each analyte dissolved for each of the five small-scale tests (mass of analyte in solution divided by the sum of the mass of analyte in solution and the mass of analyte

in the residual solids times 100). Throughout the rest of this document, all comparisons will be made using the sum of the analyte in solution plus the analyte in the residual solids due to the inhomogeneity observed in the K East area sludge composite. Table 5 shows the comparison of the duplicate analyses for the composite material, the average and the calculated concentrations of the starting material using the analysis of the solutions and the residuals. The species with the greatest discrepancies are cesium and americium, which are also the species with the highest variability in the composite samples.

Figures 13 and 14 shows the percent of each analyte remaining in the residual solids (mass of analyte in residual solids divided by sum of the mass of analyte in solution and the mass of analyte in the residual solids times 100). The residual solids showed up as two distinct colors. The 4 M process residual sample was brown in color (see Figure 15) which is probably due to the high iron content found in this samples. The 7.8 M, 6 M, and 4 M residual solids (Figures 16, 17, and 18, respectively) were all gray with little tints of green. This lack of color is probably due to the silicon oxides that make up greater than 65% of all of these samples. The green may be due to the presence of some oxides of transition metals or possibly from plutonium compounds. The 2 M residual solid was collected as two separate fractions. The first fraction was the material that was poured directly out of the flask into the filter (see Figure 19a). This material was brown, indicating the presence of iron. The second fraction of the sample (see Figure 19b) was the material that had coated the outside of the flask and fell to the bottom after drying out. The second fraction of solids collected was gray and comprised about 55% of the total mass. The 2 M test was the only one to show an appreciable amount of solids retained in the reaction vessel. All of the remaining flasks had less than 0.01 grams of solids remaining. The filtration of all of the solids occurred fairly rapidly. This indicates that by the end of the test, very little gel was present in the mixture.

Figures 3 and 4 indicate that the dissolution for the 4 M process test (i.e., Test No. 1, Table 4) was about 80% complete by the time the first solution sample was collected (30 minutes), but the concentration of all analytes in the second solution sample decreased after 1 hour. This decrease was observed in four of the tests and could be due to a reprecipitation of material or an adsorption of the analytes onto a surface from which they are later released. By 4 hours, the reaction appears virtually complete. The majority of the residual solids were silicon and iron compounds. Table 6 lists the initial and final concentrations of selected analytes, the decontamination factor, percent of the total remaining undissolved, and the ERDF limits where applicable. The decontamination factor (DF) is the concentration of the analyte in the residual solids divided by the concentration of the analyte in the starting material, which was calculated from the sum of the analyte masses in the residual solids and dissolution solutions. If the DF is greater than 1, the nitric acid dissolution is selectively removing the analyte.

**Table 5.** Comparison of the Composite Analysis to the Calculated Starting Material Composition. All results are in mg/g or  $\mu\text{Ci/g}$ .

Analyte	Composite Sample	Duplicate Sample	Composite Average	4 MP Test	4 M Test	7.8 M Test	6 M Test	2 M Test
U	54.8	53.3	54.0	66.0	73.5	80.7	72.6	68.7
Fe	307	291	299	313	351	387	353	316
Al	47.1	46.0	46.6	53.2	55.2	60.6	56.4	53.4
Si	60.0	61.1	60.5	51.2	10.9	58.0	62.4	65.6
Ca	11.5	13.0	12.2	11.6	13.6	63.7	12.7	12.1
<sup>137</sup> Cs	410	1240	825	219	257	266	231	229
<sup>241</sup> Am	29.4	81.1	55.2	15.3	16.7	19.0	16.6	16.0
<sup>239/240</sup> Pu	11.9	16.3	14.1	17.9	19.1	21.3	19.1	18.8

Table 6. 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	66.0 mg/g	< 2.0 mg/g	> 33	< 0.68	2.6 mg/mL
Fe	313 mg/g	212 mg/g	1.5	15.3	--
Al	53.2 mg/g	14.7 mg/g	3.6	6.25	--
Si	51.2 mg/g	220 mg/g	0.23	97	--
Ca	11.6 mg/g	4.64 mg/g	2.5	9.05	--
<sup>137</sup> Cs	219 µCi/g	64.5 µCi/g	3.4	6.68	32 µCi/mL
<sup>241</sup> Am	15.3 µCi/g	0.592 µCi/g	26	0.877	0.05 µCi/g <sup>(c)</sup>
<sup>239/240</sup> Pu	17.9 µCi/g	2.99 µCi/g	6.0	3.79	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 total mass of the analyte in the products 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).

These results show that the residual solids will only meet the criterion for uranium, while the remaining analytes will require some additional leaching to meet the requirements. Since all of the analytes appear to be within an order of magnitude of the ERDF limits, the dilution factor realized from the grouting of the residual solids (assuming it will be around 10) may bring the concentrations of these analytes close to the limits.

Figures 5 and 6 show the dissolution results for the 4 M, low solids loading test (i.e., Test No. 2, Table 4). The dissolution profile looks similar to the 4 M process test where the first solution sample (after 30 minutes) shows about 90% dissolution followed by a drop in percent dissolution at 1 hour. As in the process test, the concentrations of the species in solution increases asymptotically until the reaction is complete after 4 hours. In this test, the majority of the residual solids were silicon (65% of the total as SiO<sub>2</sub>) with the majority of the remainder being made up by iron and aluminum compounds. The color of the residual solid was gray with a hint of green. Since the iron content of the solids is lower, some other species is dominating the color, probably the silicon. Table 7 lists the initial and final concentrations of selected analytes, the decontamination factor, percent of the total remaining undissolved, and the ERDF limits where applicable.

By decreasing the solids loading by a factor of 5 over the process test, it appears that the cesium concentration in the residual solids also meets the criterion and the americium content becomes slightly closer to the ERDF limit. Since the dissolution of cesium in aqueous solutions is not very difficult, the benefit of the lower solids loading will probably not overcome the additional costs associated with processing less solids per batch, since the solids will require some leaching to meet the TRU limits.

Figures 7 and 8 show that the dissolution for the 7.8 M test was approximately 80% complete after the first solution sample was taken at 30 minutes. The dissolution increased until the 4-hour sample when it decreased for all analytes. This is similar to what was observed in the 4 M tests, but the decrease occurred later. This could be due to a precipitation or adsorption onto a solid (e.g., a gel formed by silica)

Table 7. Analyte Removal for the 4 M Test

Analyte	Calculated Sludge Concentration <sup>(a)</sup>	Final Dry Residual Concentration	DF	% Residual <sup>(b)</sup>	ERDF Criterion
U	73.5 mg/g	< 2.0 mg/g	> 37	< 0.51	2.6 mg/mL
Fe	351 mg/g	24.4 mg/g	14.4	1.31	--
Al	55.2 mg/g	19.3 mg/g	2.86	11.7	--
Si	10.9 mg/g	326 mg/g	0.033	56.4	--
Ca	13.6 mg/g	6.29 mg/g	2.16	8.74	--
<sup>137</sup> Cs	257 µCi/g	12.2 µCi/g	21.1	0.896	32 µCi/mL
<sup>241</sup> Am	16.7 µCi/g	0.37 µCi/g	45.1	0.417	0.05µCi/g <sup>(c)</sup>
<sup>239/240</sup> Pu	19.1 µCi/g	0.432 µCi/g	44.2	0.426	0.029µCi/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 total mass of the analyte in the products 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).

during the reaction. Since the next sampling was not until 24 hours, it is difficult to determine the rate at which the redissolution occurs. Again, the majority of the residual solids was silicon (65 % of the total as SiO<sub>2</sub>) with some aluminum and iron with the color of the solids being gray. Table 8 lists the initial and final concentrations of selected analytes, the decontamination factor, percent of the total remaining undissolved, and the ERDF limits where applicable.

Table 8. Analyte Removal for the 7.8 M Test

Analyte	Calculated Sludge Concentration <sup>(a)</sup>	Final Dry Residual Concentration	DF	% Residual <sup>(b)</sup>	EDRF Criterion
U	80.7 mg/g	2.1 mg/g	38.4	0.43	2.6 mg/mL
Fe	387 mg/g	15.4 mg/g	25.1	0.66	--
Al	60.6 mg/g	20.2 mg/g	3.0	5.54	--
Si	58.0 mg/g	334 mg/g	0.17	95.6	--
Ca	63.7 mg/g	6.16 mg/g	10.3	7.47	--
<sup>137</sup> Cs	266 µCi/g	10.2 µCi/g	26.1	0.634	32 µCi/mL
<sup>241</sup> Am	19.0 µCi/g	0.385 µCi/g	49.4	0.336	0.05µCi/g <sup>(c)</sup>
<sup>239/240</sup> Pu	21.3 µCi/g	0.454 µCi/g	46.9	0.353	0.029µCi/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 total mass of the analyte in the products 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).

As with the 4 M, low solids loading test, the criteria for uranium and cesium are met, with the americium being within an order of magnitude of its criteria. Some form of residual leaching will likely be required for this material prior to disposal at ERDF.

Figures 9 and 10 show that the dissolution for the 6 M test was approximately 90-95% complete after the first 30 minutes, with the rest of the materials gradually dissolving over the next 24 hours. These figures show the decrease in analyte concentrations after the initial sample. The majority of the residual solid is silicon (71% of the total as SiO<sub>2</sub>) with some aluminum and iron, with the color of the solids being gray. Table 9 lists the initial and final concentrations of selected analytes, the decontamination factor, percent of the total remaining undissolved, and the ERDF limits where applicable.

Table 9. 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	72.6 mg/g	< 2.0 mg/g	> 36.3	< 0.46	2.6 mg/mL
Fe	353 mg/g	10.9 mg/g	32.4	0.522	--
Al	56.4 mg/g	15.7 mg/g	3.59	4.71	--
Si	62.4 mg/g	355 mg/g	0.175	96.2	--
Ca	12.7 mg/g	4.44 mg/g	2.86	5.92	--
<sup>137</sup> Cs	231 µCi/g	5.18 µCi/g	44.6	0.380	32 µCi/mL
<sup>241</sup> Am	16.6 µCi/g	0.0821 µCi/g	202	0.0837	0.05 µCi/g <sup>(c)</sup>
<sup>239/240</sup> Pu	19.1 µCi/g	0.132 µCi/g	145	0.117	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 total mass of the analyte in the products 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).

The final concentrations in the residual solids show that all of the ERDF criteria are met except for the plutonium. The americium is slightly higher than the limit, but any dilution from waste form preparation would put the concentration below the limit.

The 2 M test appeared to be greater than 90% complete after 30 minutes but had the same decrease in solution analyte concentrations after 1 hour. As stated earlier, the residuals for this test were collected in two fractions. The first fraction was brown and comprised about 45% of the sample, while the second fraction was gray and comprised 55% of the sample. The final residual solids for this test were predominantly silicon (> 60%), but the first fraction probably consisted of a larger percentage of iron, and since plutonium associates with iron, the first fraction probably had a higher fraction of the TRU content. As can be seen in Figure 11, approximately 95% of the uranium was dissolved by 30 minutes into the reaction, while Figure 12 shows the radionuclides to be > 90% dissolved within the first 30 minutes. Table 10 lists the initial and final concentrations of selected analytes, the decontamination factor, percent of the total remaining undissolved, and the ERDF limits where applicable.

Table 10. Analyte Removal for the 2 M Test

Analyte	Calculated Sludge Concentration <sup>(a)</sup>	Final Dry Residual Concentration	DF	% Residual <sup>(b)</sup>	ERDF Criterion
U	68.7 mg/g	< 2.0 mg/g	> 34.4	< 0.45	2.6 mg/mL
Fe	316 mg/g	26.2 mg/g	12.1	1.29	--
Al	53.4 mg/g	8.49 mg/g	6.29	2.47	--
Si	65.6 mg/g	113 mg/g	0.581	26.8	--
Ca	12.1 mg/g	7.58 mg/g	1.67	9.75	--
<sup>137</sup> Cs	229 µCi/g	13.0 µCi/g	17.6	0.676	32 µCi/mL
<sup>241</sup> Am	16.0 µCi/g	0.125 µCi/g	128	0.122	0.05µCi/g <sup>(c)</sup>
<sup>239/240</sup> Pu	18.8 µCi/g	0.154 µCi/g	122	0.127	0.029µCi/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 total mass of the analyte in the products 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).

As with the 6 M test, the final concentrations for this test showed that all of the ERDF criteria are met except for the plutonium. The americium is slightly higher than the limit, but any dilution from waste form preparation would likely put the concentration below the limit.

Following the dissolution testing, the residual solids were collected and analyzed. Table 11 shows the mass of the residual solids for all of the tests. While these results show residuals higher than those observed during the dissolution of canister sludge, they were much lower than expected for the area composite. It was assumed that the high silicon content of many of the floor and Weasel Pit samples would provide 30 to 40% residual solids.

Figures 13 and 14 show the residual solids data for all of the tests. For all of the tests with low solids loadings, the most important analytes (TRUs and uranium) remain at less than 1% of their starting mass. This means that these analytes are removed from the solids at 99+%. While some additional treatment of the residual solids may be required to meet ERDF criteria, this dissolution was very effective at removing most of the radioactivity.

Table 11: Residual Solids Following Dissolution

Acid Concentration	Initial Solids (Dry Wt, g)	Residual Solids (g)	Percent Residual
4 M Process Test	6.9867	1.5824	22.6
4 M	2.2457	0.4238	18.9
7.8 M	2.5147	0.4174	16.6
6 M	2.2870	0.3867	16.9
2 M	2.3923	0.3722	15.6
6 M Large Scale	26.59	4.4211	16.6

### 3.4 Large-Scale Testing; Quantitative Results

As stated earlier, the large-scale test was performed using similar parameters to the 6 M test described above (see Table 4). Table 12 shows the analyte removals for the large-scale test. The percent residual solids remaining after the dissolution is within 5% of the small-scale test result. When the analytical results are compared between the large- and small-scale tests, the solution results have a relative percent difference of less than 20%. The residual solid results have large RPDs, but the radionuclides are generally lower for the large-scale test and the metals are all higher in the large-scale result. This indicates that the leaching of the radionuclides was more selective in the large-scale test.

The residuals exceed the ERDF criteria to a greater extent than the small-scale test for all analytes except plutonium. However, the plutonium is only eight times greater than the ERDF criterion, so waste form preparation may result in sufficient dilution to meet the acceptance criterion.

Five aliquots of the residual solids from the large-scale test were tested for total carbon using the furnace method. These results showed an average value of 10,700  $\mu\text{gC}$  per gram with a standard deviation of 1370  $\mu\text{gC/g}$ . A likely source of carbon is OIER. The 1% of the total carbon in the residual solids should not affect Waste Acceptance Criteria by itself, but could explain the high  $^{137}\text{Cs}$  results.

Table 12. Analyte Removal for the 6 M Large-Scale Test

Analyte	Calculated Sludge Concentration <sup>(a)</sup>	Final Dry Residual Concentration	DF	% Residual <sup>(b)</sup>	ERDF Criterion
U	70.4 mg/g	< 2.0 mg/g	> 36.3	< 0.11	2.6 mg/mL
Fe	352 mg/g	12.9 mg/g	32.4	0.610	--
Al	55.9 mg/g	23.3 mg/g	3.59	6.92	--
Si	61.3 mg/g	368 mg/g	0.175	99.9	--
Ca	12.9 mg/g	6.84 mg/g	2.86	8.79	--
$^{137}\text{Cs}$	219 $\mu\text{Ci/g}$	4.65 $\mu\text{Ci/g}$	44.6	0.353	32 $\mu\text{Ci/mL}$
$^{241}\text{Am}$	16.0 $\mu\text{Ci/g}$	0.0356 $\mu\text{Ci/g}$	202	0.0370	0.05 $\mu\text{Ci/g}$ <sup>(c)</sup>
$^{239/240}\text{Pu}$	19.3 $\mu\text{Ci/g}$	0.274 $\mu\text{Ci/g}$	145	0.237	0.029 $\mu\text{Ci/g}$ <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 total mass of the analyte in the products times 100.  
 (c) The limit for the total TRU elements is 0.1  $\mu\text{Ci/g}$ .  
 (d) The limit for each isotope ( $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ ).

### 4.0 Discussion

In general, it appears that all of the dissolutions were greater than 85% complete within the first 2 hours. All of the analytes showed continued dissolution in every acid concentration up until the end of the test at 24 hours. The dissolutions may have increased asymptotically after the 4-hour samples were taken, giving a 95% completion well before the 24 hours; however, no solution samples were collected between

4 and 24 hours. In addition, a large percentage (> than 80%) of the analytes were already dissolved by the time the first solution sample was taken at 30 minutes. As with the K-East Canister sludge dissolution, the dissolution increases with the amount of time in the solution.

The acid concentrations used for the dissolutions do not appear to have a dramatic effect on the radionuclide concentrations in the residual solids. The lowest radionuclide concentrations in the residual solids were obtained in both the large- and small-scale tests using 6 M HNO<sub>3</sub>. This conclusion is tentative, since solids loadings were not kept constant for the dissolution tests.

If the concentrations of the analytes present in the 30-minute sample are compared for the four different acid concentrations used, an interesting phenomenon is observed. The higher concentration acid solutions appear to dissolve a greater quantity of material, but the lower concentrations of acid dissolve the radionuclides and uranium more selectively. The range of percent metals dissolved for the 7.8 M test is 70% (Fe) to 84% (U), whereas the range for the 2 M test is 42% (Fe) to 95% (U). A greater percentage of the radionuclides are also dissolved for the lower acid concentrations: ~80% for the 7.8 M test and 82% to 98% for the 2 M test. The higher concentration acids are dissolving the bulk components of the material faster than the lower concentration acids. If a continuous feed system or short batch times are being considered, the lower concentration acids may be a better choice to keep the bulk materials as solids. If the amount of solids dissolved is not a driving factor in the process design, or minimization of solids to be sent to ERDF is a consideration, then the higher acid concentrations may be more useful.

Another variable tested was the solids loading. For the 4 M process test (Test 1, Table 4), the solids loading was increased greatly in comparison to the low solids loading test 4 M test (Test 2, Table 4). Radionuclide concentrations in the residual solids were greater (1.6X for <sup>241</sup>Am, 5.3X for <sup>137</sup>Cs, 6.9X for <sup>239/240</sup>Pu, and 8.7X for Fe) when the initial sludge solids loading increased from 25 g/L to 115 g/L at 4 M HNO<sub>3</sub>. Figure 20 shows the percent uranium and percent iron dissolved as a function of reaction time for the 4 M process test and 4 M low-solids loading test. The curves for uranium, as well as the radionuclides, are very close for the two different solid loadings.

In Tables 4 through 8 and 10, the decontamination factors for various analytes are shown. The DF is greater than 1 for all of the species except for silicon. While all of the species are dissolving to some extent in the nitric acid, the silicon is the least soluble and is the major constituent of the residual solids.

In addition to the DF information, the residual solids data are important to determine the effectiveness of the dissolution. As can be seen in Table 9, most of the solids have dissolved, leaving less than 20% residual solids in all cases, with the exception of the process test. It should be noted that in the 4 M process test, three glass boats were used to add the samples, while all of the other tests were conducted using only one glass weigh boat. If the boiling action was not vigorous enough to overturn the thimbles, it is possible that a portion of the samples was not adequately exposed to the nitric acid to allow for complete dissolution. Figures 13 and 14 show the percent of each analyte remaining in the residual solids. The radionuclides are greater than 99% removed from the solids, while the metals are removed at least 90%, with the exception of the silicon. Since most of the radionuclides are removed in the first 30 minutes, it may be feasible to consider several short, sequential dissolution steps to achieve an overall higher dissolution efficiency.

The final variable examined in these tests was the effect of scaling up the reaction. The large-scale test was a tenfold increase in volume over the small-scale test. Table 9 shows that there was very little

difference in the amount of solids dissolved (< 2% different), and the compositions of the residual solids are comparable. Some differences exist, particularly in the case of the radionuclide concentrations. Table 13 shows the direct comparison of the two tests.

**Table 13.** Comparison of Residual Results for the Large- and Small-Scale 6 M Tests

Analyte	Small-Scale Dry Residual Concentration	Large-Scale Dry Residual Concentration	Small-Scale % Residual <sup>(a)</sup>	Large-Scale % Residual <sup>(a)</sup>
U	< 2.0 mg/g	< 2.0 mg/g	< 0.46	< 0.11
Fe	10.9 mg/g	12.9 mg/g	0.522	0.610
Al	15.7 mg/g	23.3 mg/g	4.71	6.92
Si	355 mg/g	368 mg/g	96.2	99.9
Ca	4.44 mg/g	6.84 mg/g	5.92	8.79
<sup>137</sup> Cs	5.18 µCi/g	4.65 µCi/g	0.380	0.353
<sup>241</sup> Am	0.0821 µCi/g	0.0356 µCi/g	0.0837	0.0370
<sup>239/240</sup> Pu	0.132 µCi/g	0.274 µCi/g	0.117	0.237
(a) Mass of analyte in the residual solids divided by the total mass of the analyte in the products times 100.				

These data could be interpreted to indicate that scaling-up may provide a greater selectivity for the dissolution of radionuclides and uranium. However, the inhomogeneity of the K East area sludge composite may have contributed to the differences in radionuclide concentrations in the residual solids. Only two tests were run, so further study is required to verify this trend in larger scale operations.

Overall, the dissolution of the area (floor and Weasel Pit) composite was successful, dissolving virtually all of the uranium and leaving less than 1% of the radionuclides. Even with this efficiency, some additional treatment will likely be required prior to final disposal. This may mean further leaching of the residual solids is needed to remove the TRU species before the residual solids can be sent to disposal. If the results from the 2 M test can be achieved in a full-scale operation, the ERDF Waste Acceptance Criteria may be met after placing the residual solids into the final waste form (e.g., grout). A factor that has not yet been addressed in this dissolution testing is the fate of the PCBs known to be in some of the sludge samples that were used to make up the K East area composite. The fate of PCBs is being investigated in non-radioactive studies, and will most likely be studied during the validation testing, which will be concluded later in the fiscal year.

## 5.0 References

ERDF 1997. *ERDF Waste Acceptance Criteria*, BHI-00139, Rev. 2, Table 4-1.

Flament, T.A. 1998. *Testing Strategy to Support the Development of K Basin Sludge Treatment Process*, HNF-2574, Rev.0.

Makenas, B.J., T.L. Welsh, R.B. Baker, D.R. Hansen, and G.R. Golcar. 1996. *Analysis of Sludge from Hanford K East Basin Floor and Weasel Pit*. WHC-SP-1182, Westinghouse Hanford Company, Richland, Washington.

Makenas, B.J., T.L. Welsh, R.B. Baker, E.W. Hoppe, A.J. Schmidt, J. Abrefah, J.M. Tingey, P.R. Bredt, and G.R. Golcar. 1997. *Analysis of Sludge from Hanford K East Basin Canisters*. HNF-SP-1201, DE&S Hanford, Inc., Richland, Washington.

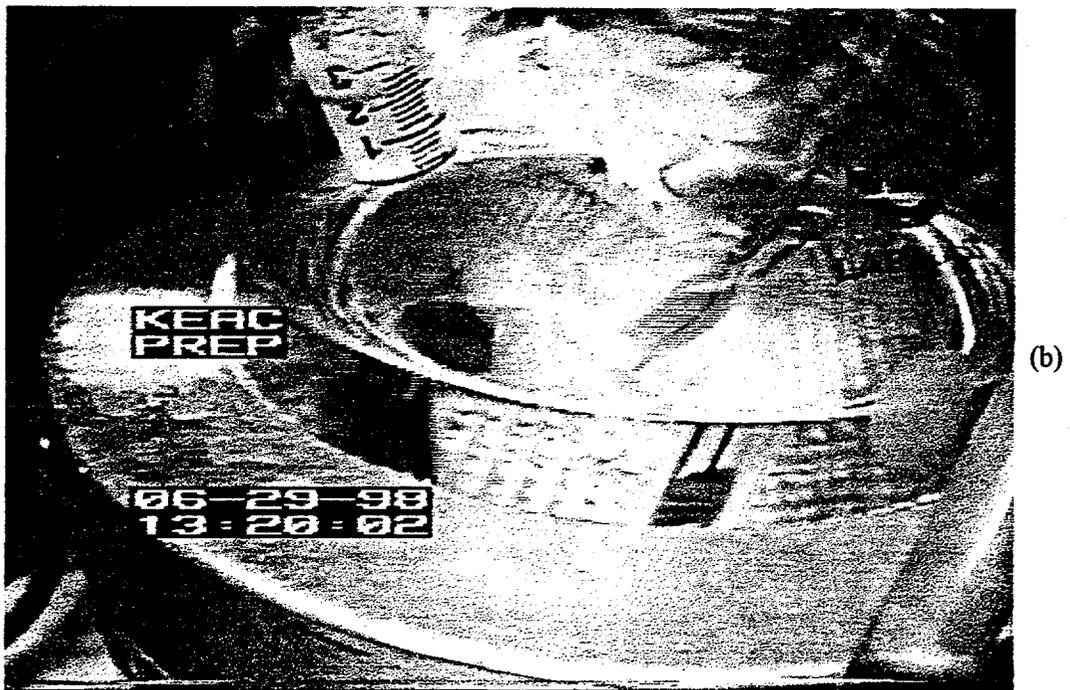
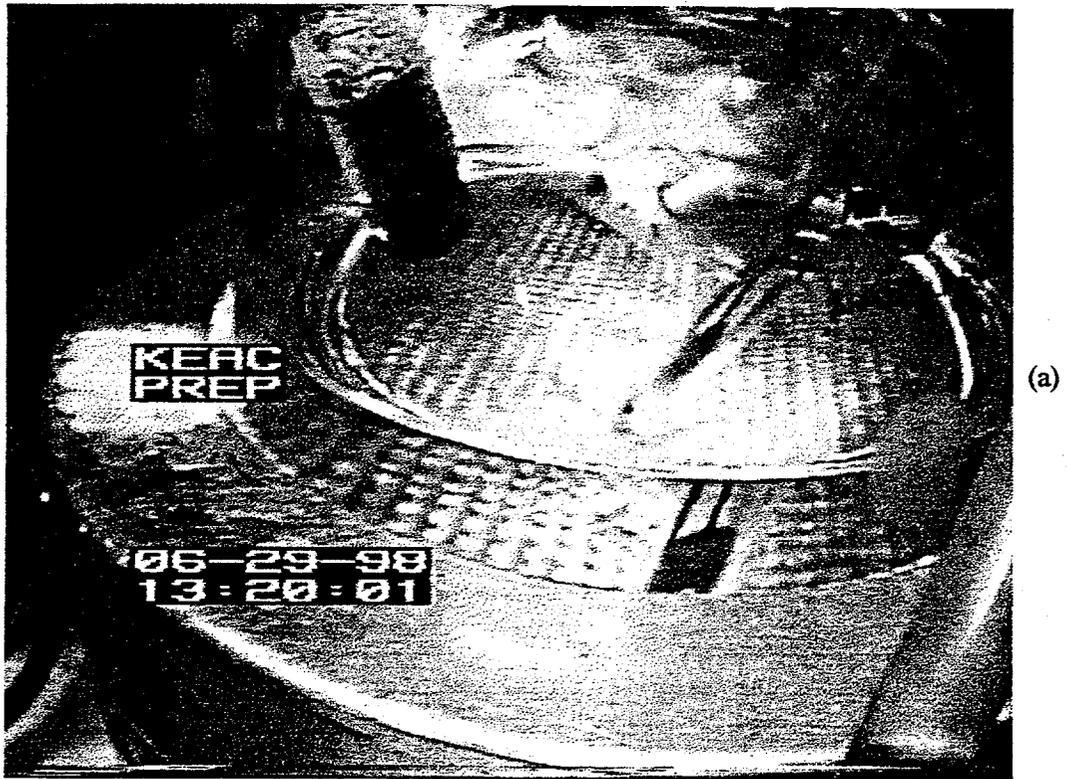


Figure 1. Syringe Delivery of Frozen Sludge Sample

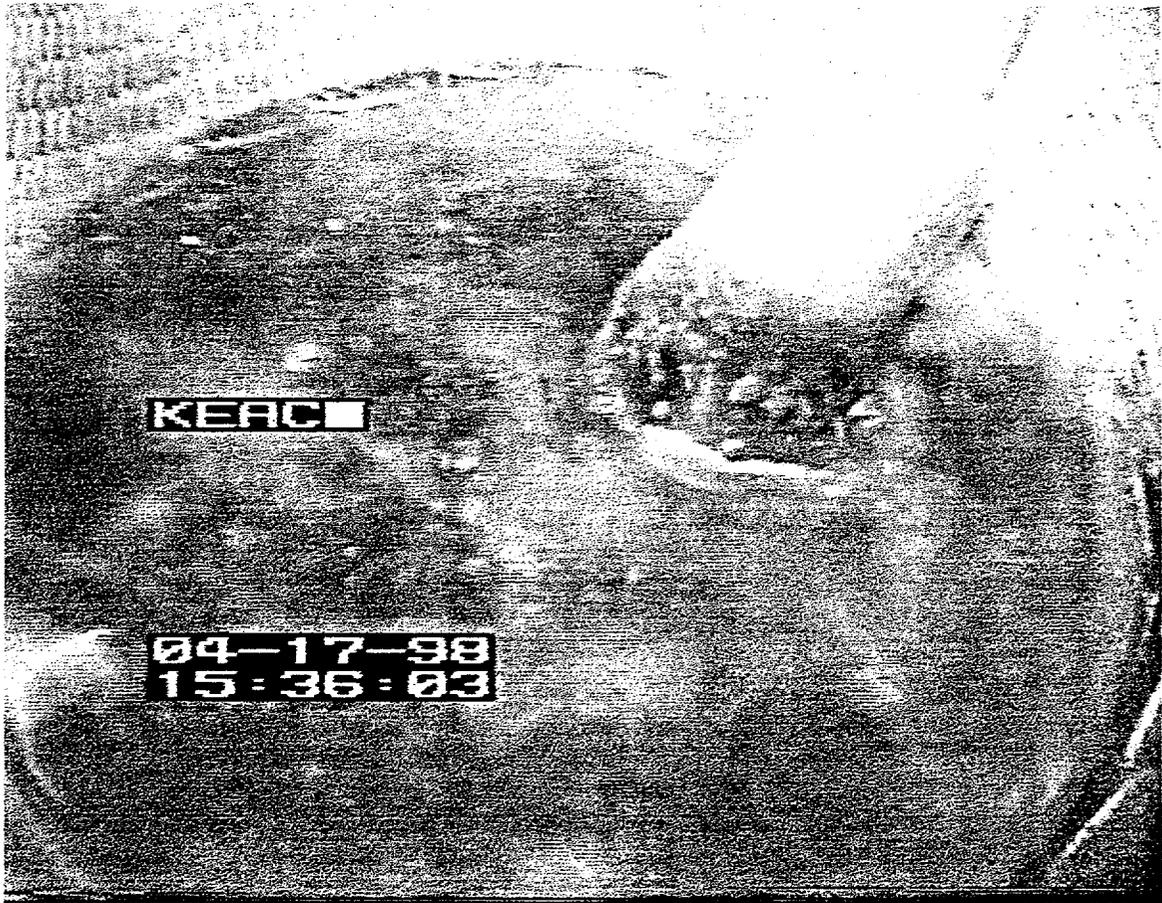


Figure 2. 7.8 M Test at 2 Hours Showing Solid Formation of the Thermometer Well

### 4 M Process Test, Dissolved Radionuclides

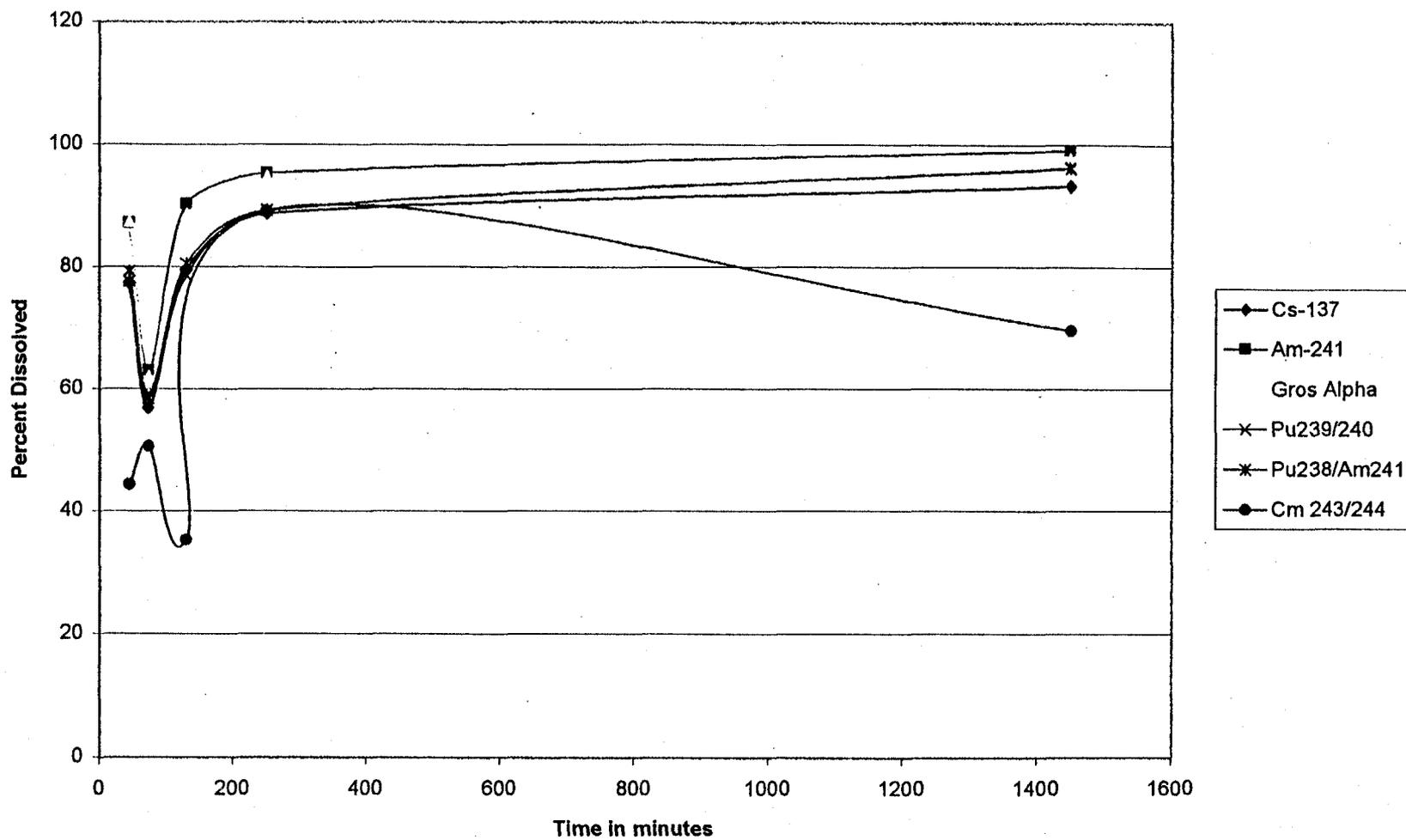


Figure 3. Radiochemical Results for the 4 M Process Test

### 4 M Process Test Solutions, Metals

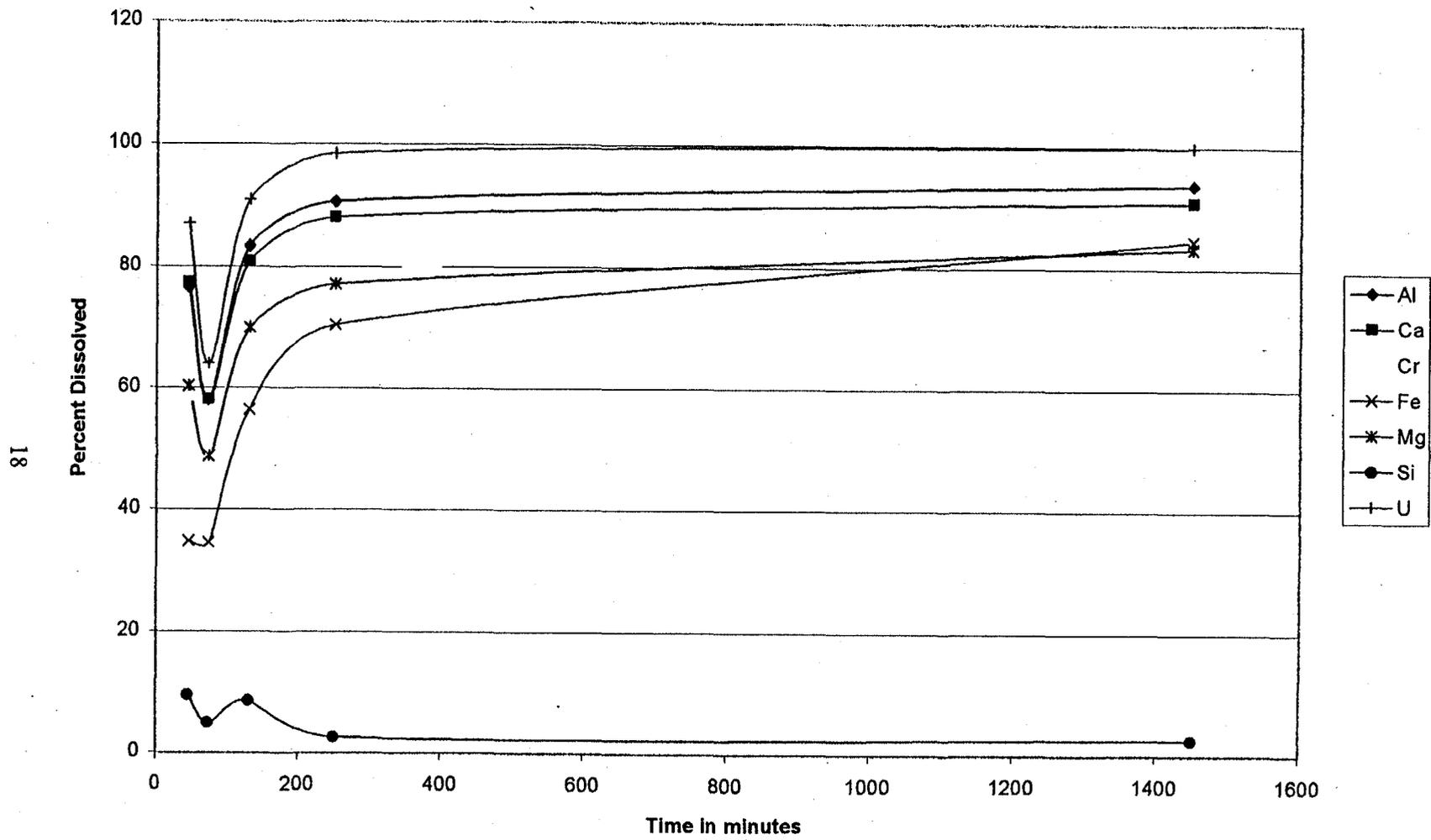


Figure 4. ICP-AES Results for the 4 M Process Test

### 4 M Test Solutions, Radionuclides

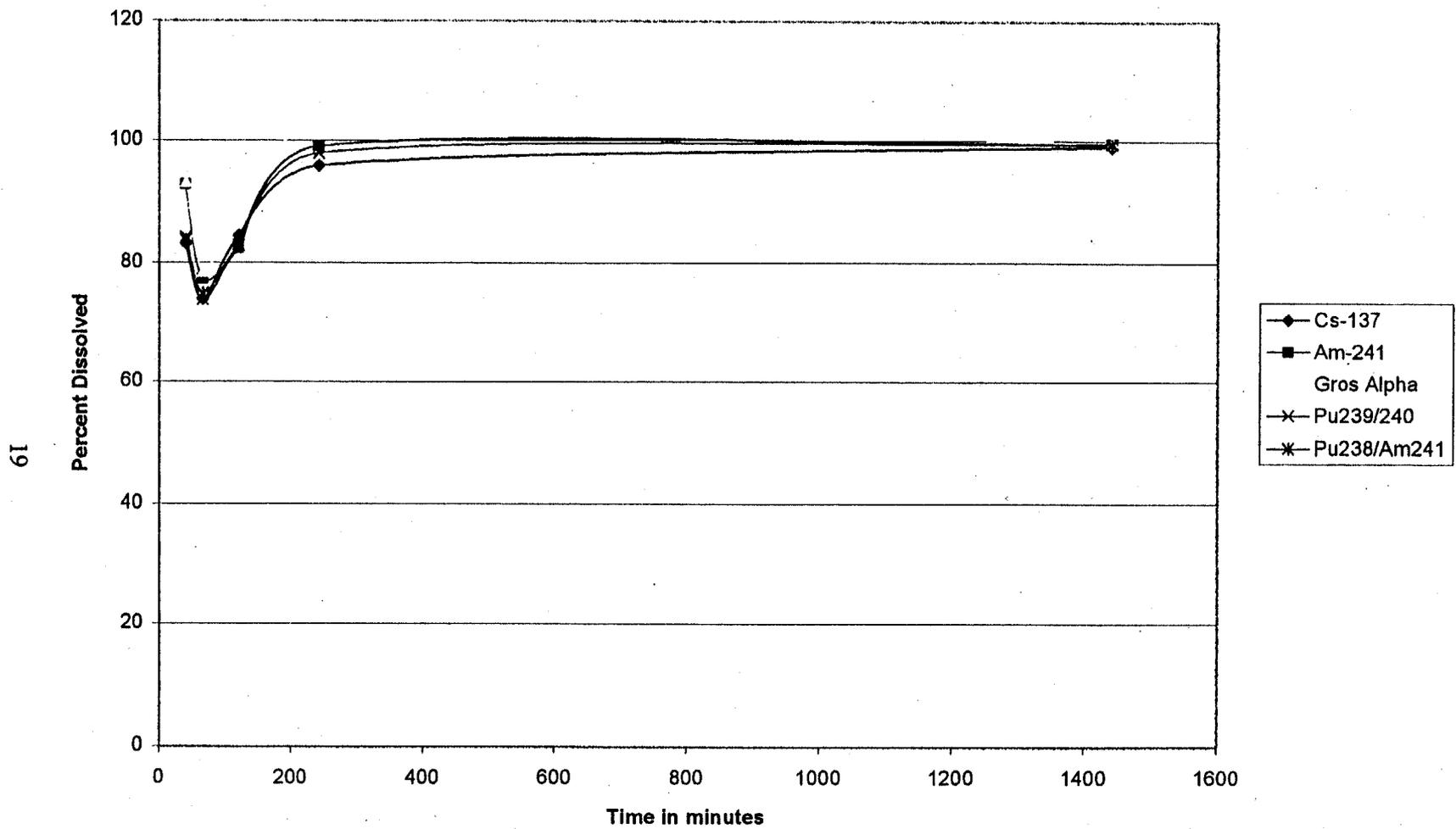


Figure 5. Radiochemical Results for the 4 M Test

### 4 M Test Solutions, Metals

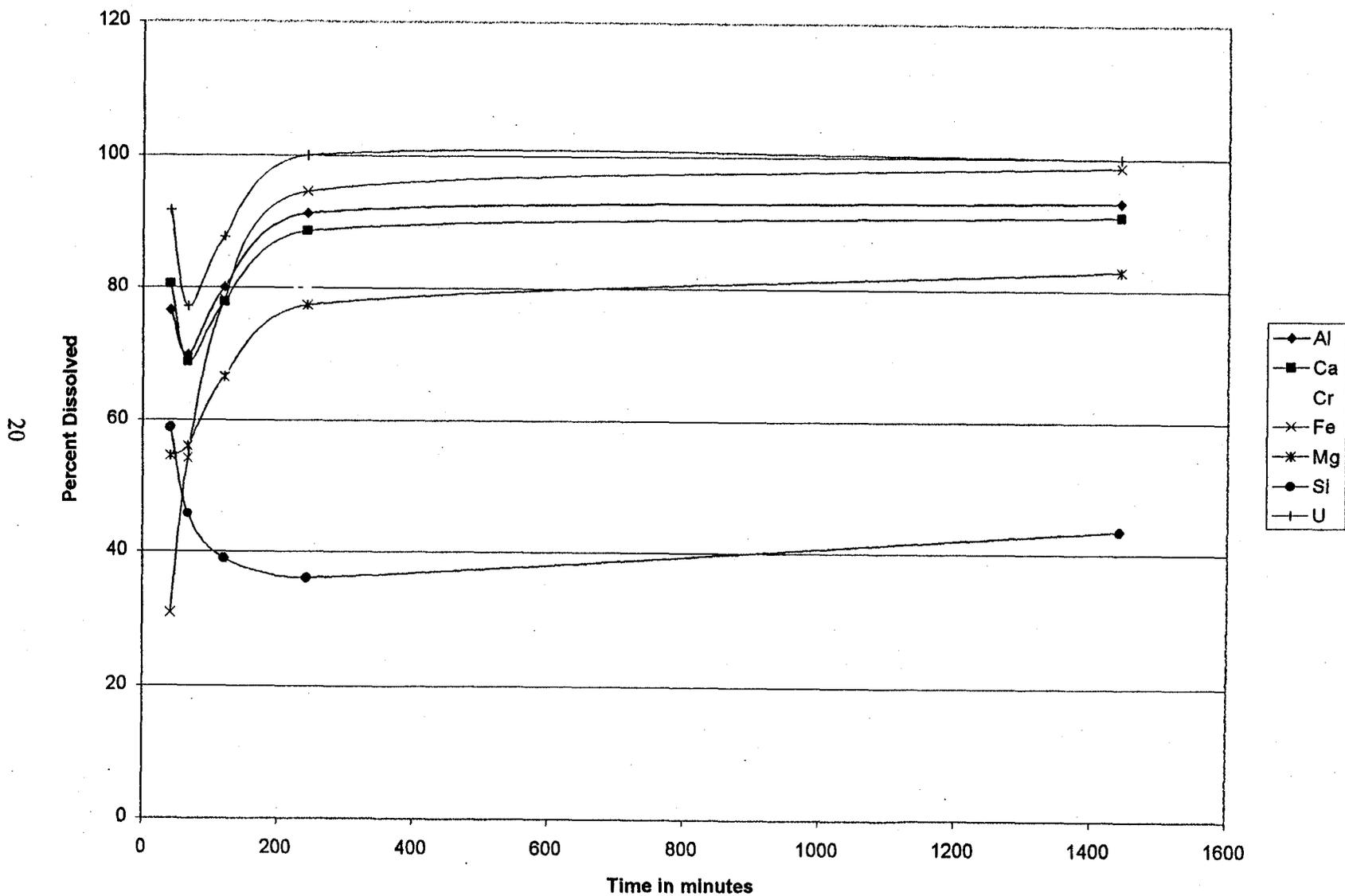


Figure 6. ICP-AES Results for the 4 M Test

### 7.8 M Test Solutions, Radionuclides

21

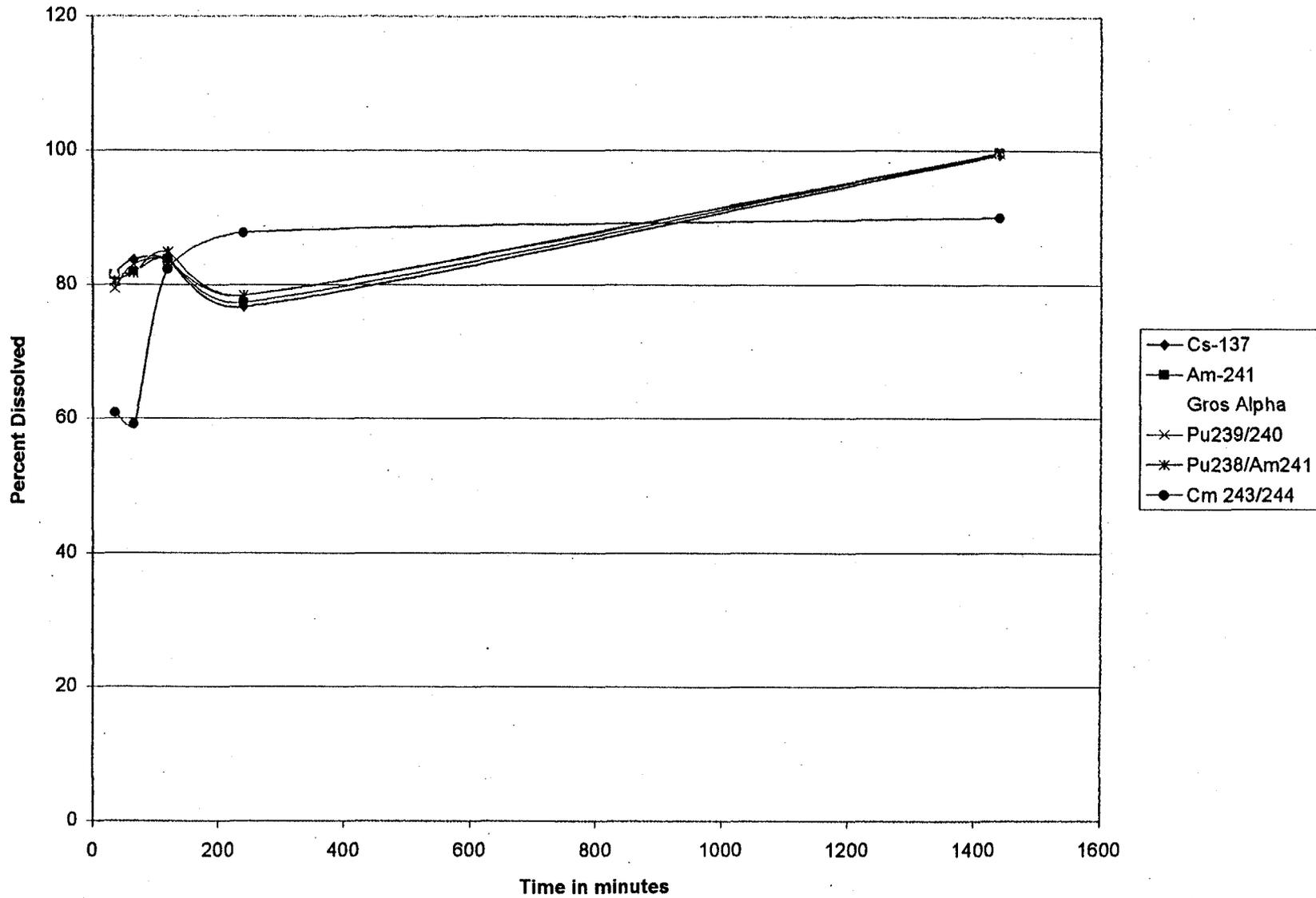
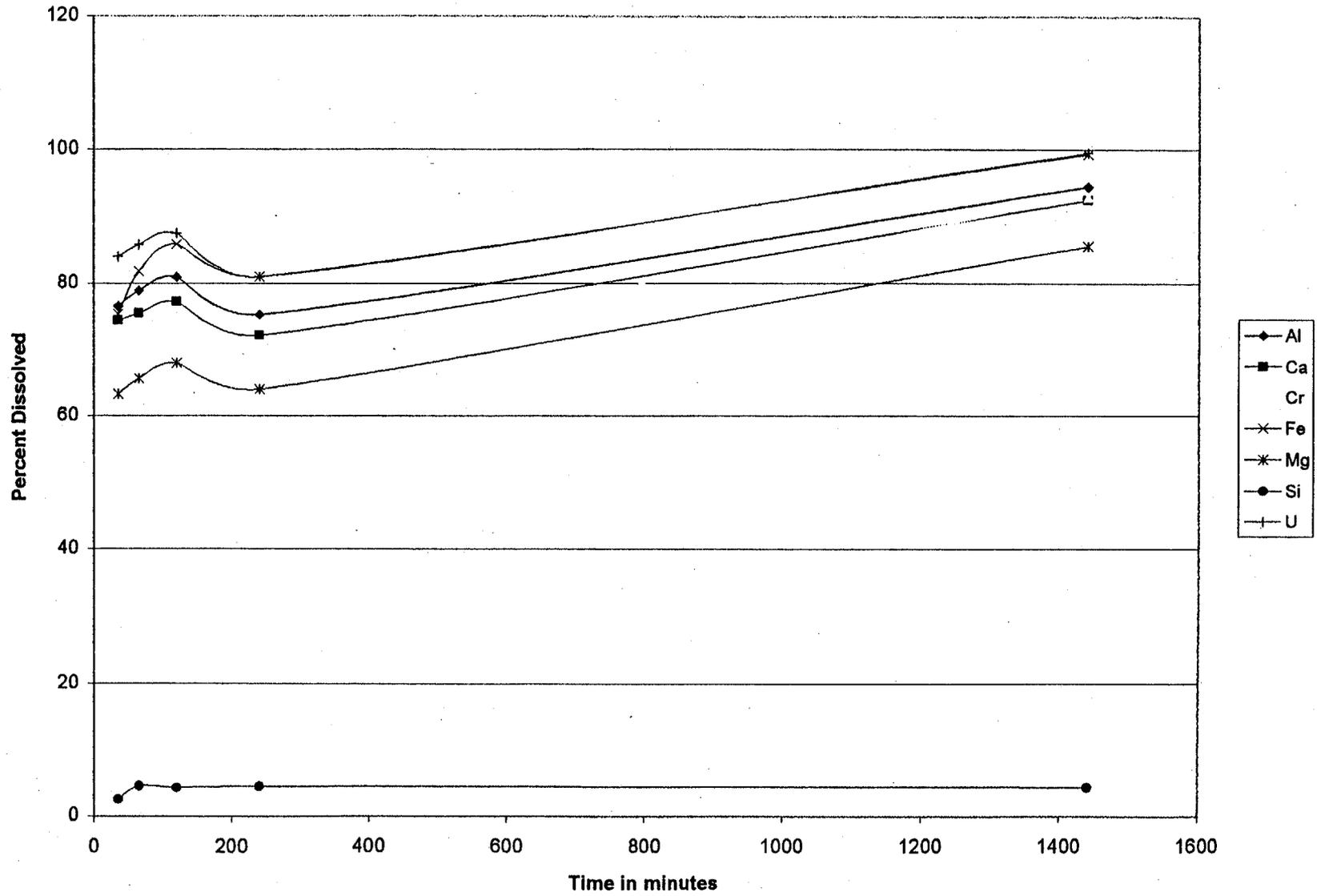


Figure 7. Radiochemical Results for the 7.8 M Process Test

7.8 M Test Solutions, Metals



22

Figure 8. ICP-AES Results for the 7.8 M Process Test

### 6 M Test Solutions, Radionuclides

23

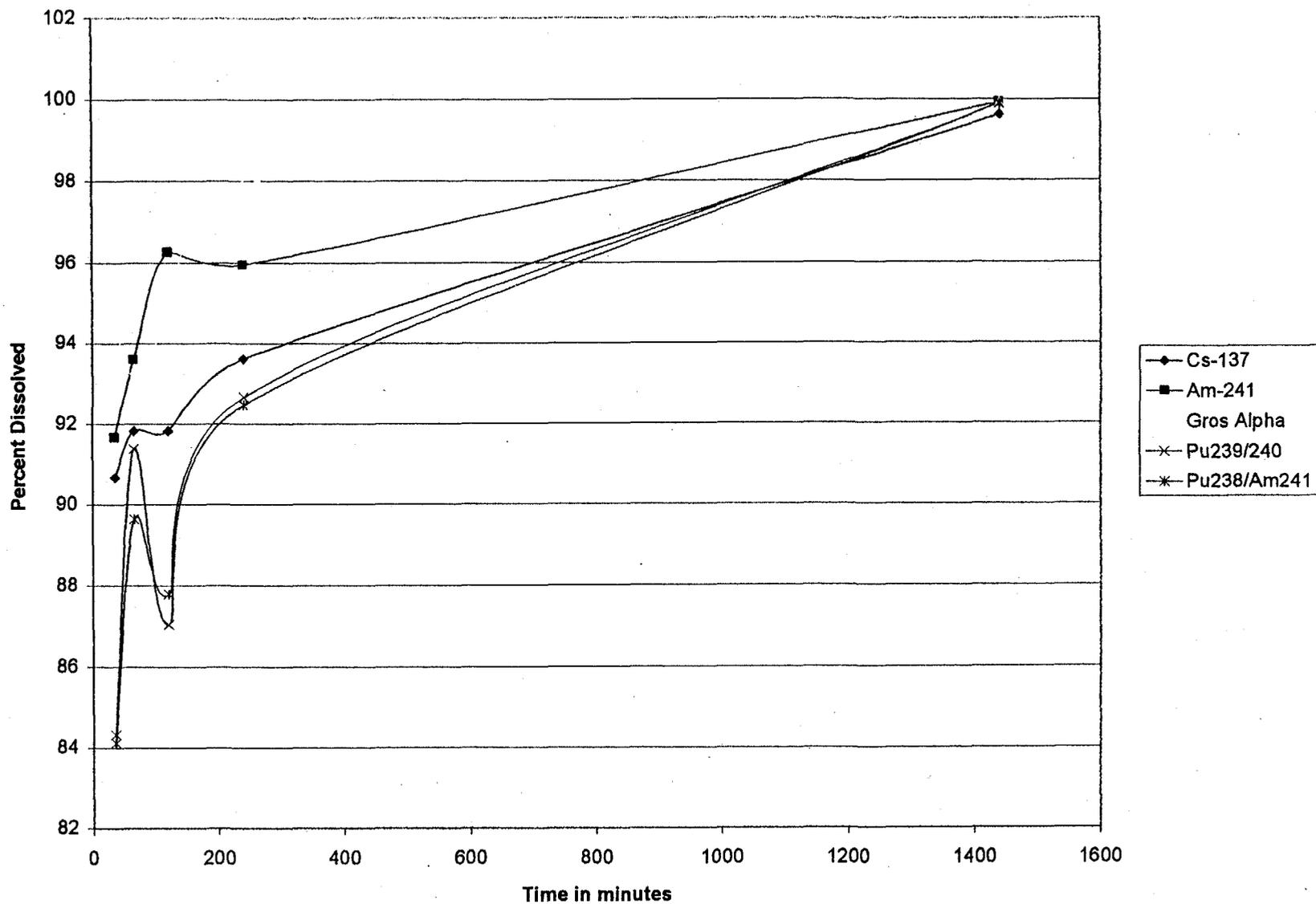


Figure 9. Radiochemical Results for the 6 M Test

### 6 M Test Solutions, Metals

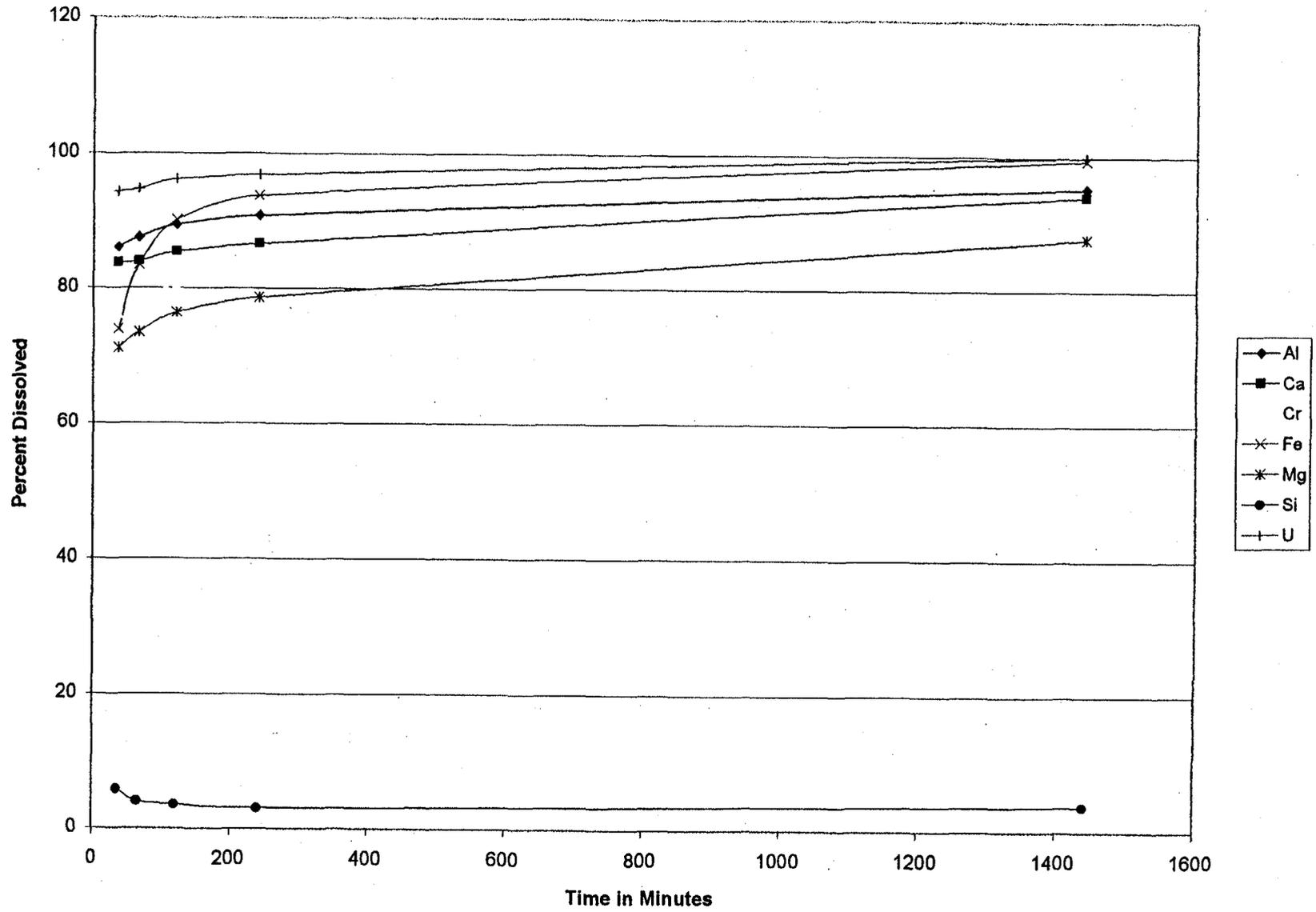
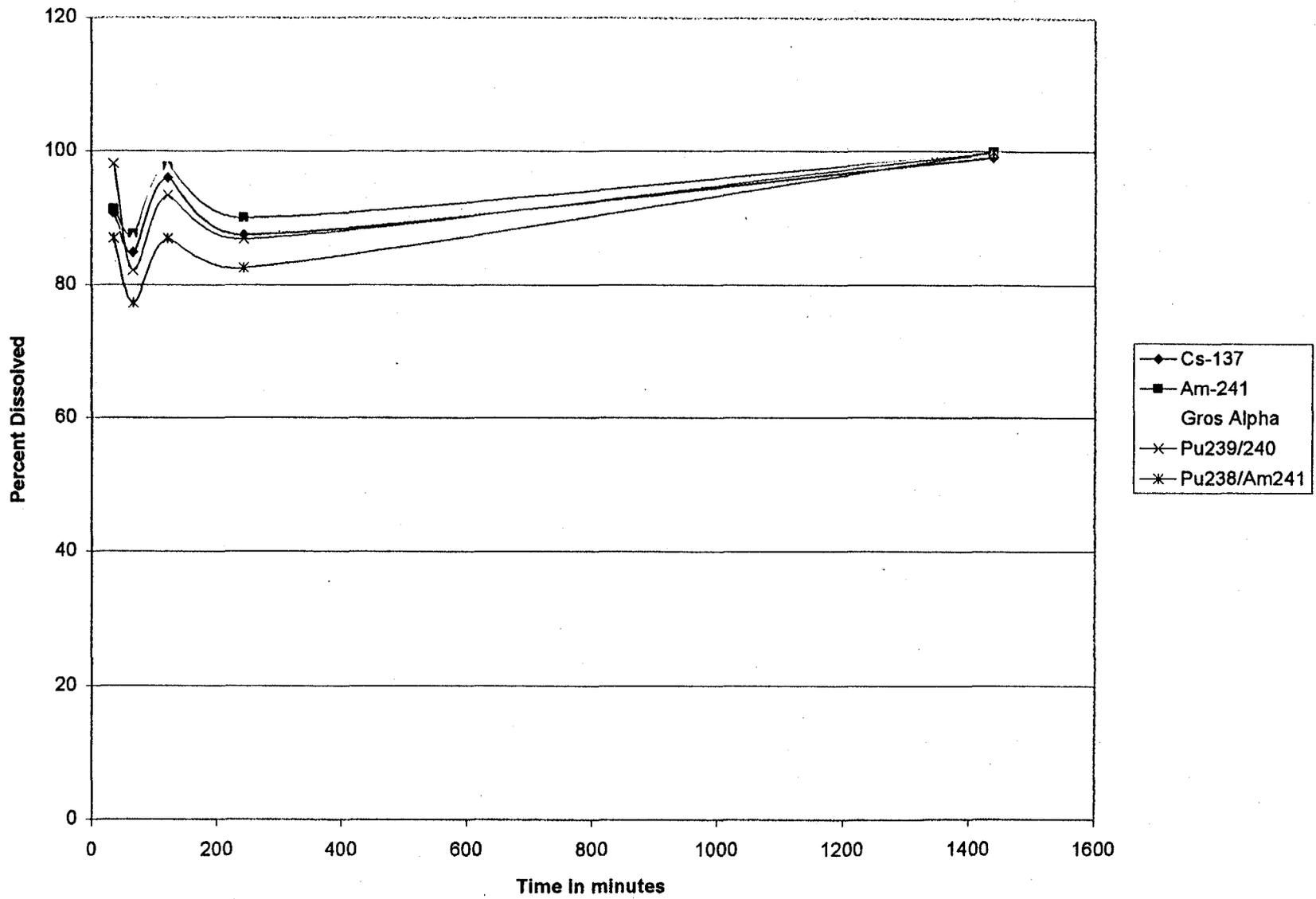


Figure 10. ICP-AES Results for the 6 M Test

### 2 M Test Solutions, Radionuclides



25

Figure 11. Radiochemical Results for the 2 M Test

### 2 M Test Solutions, Metals

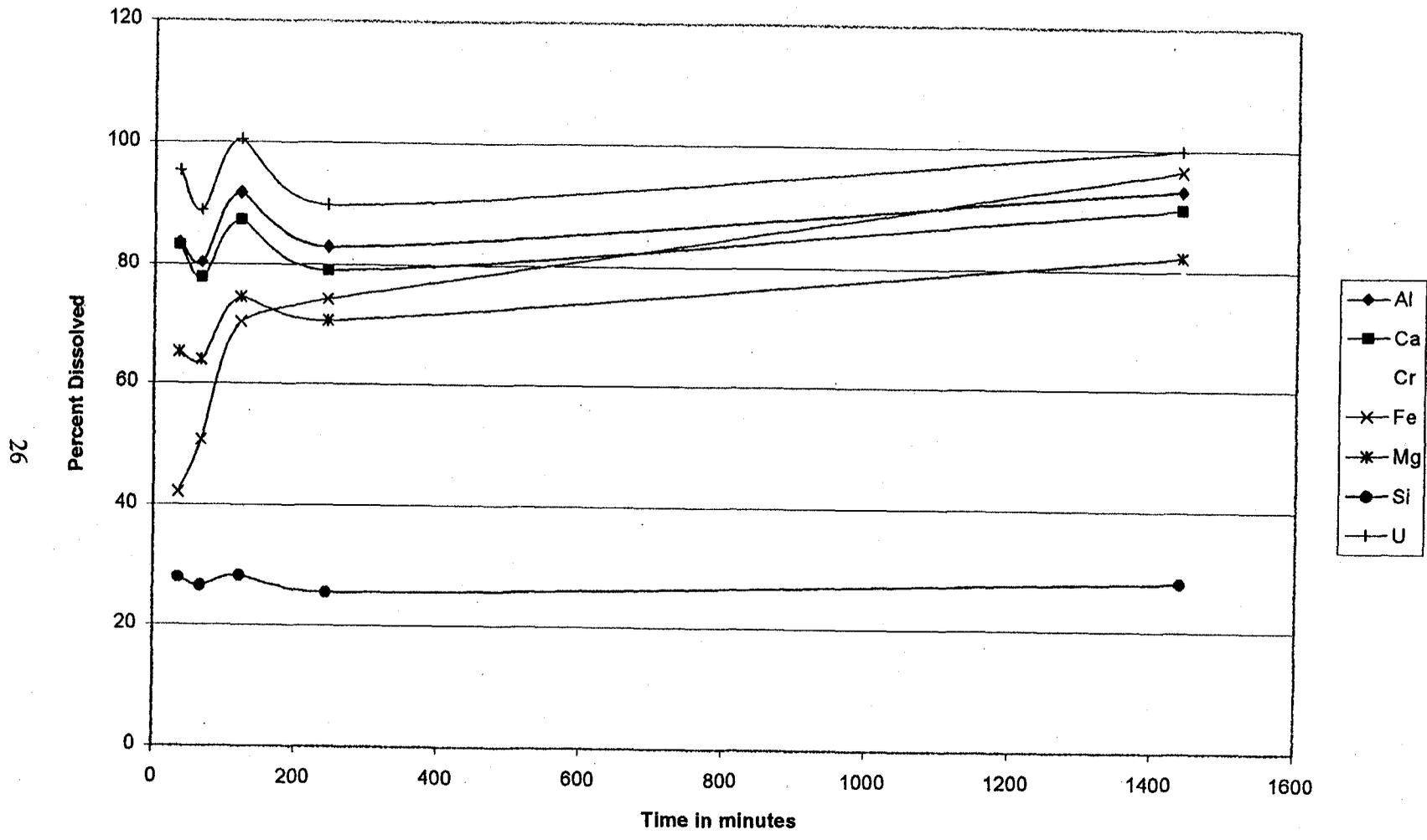


Figure 12. ICP-AES Results for the 2 M Test

### Percent of Analytes in Residual Solids

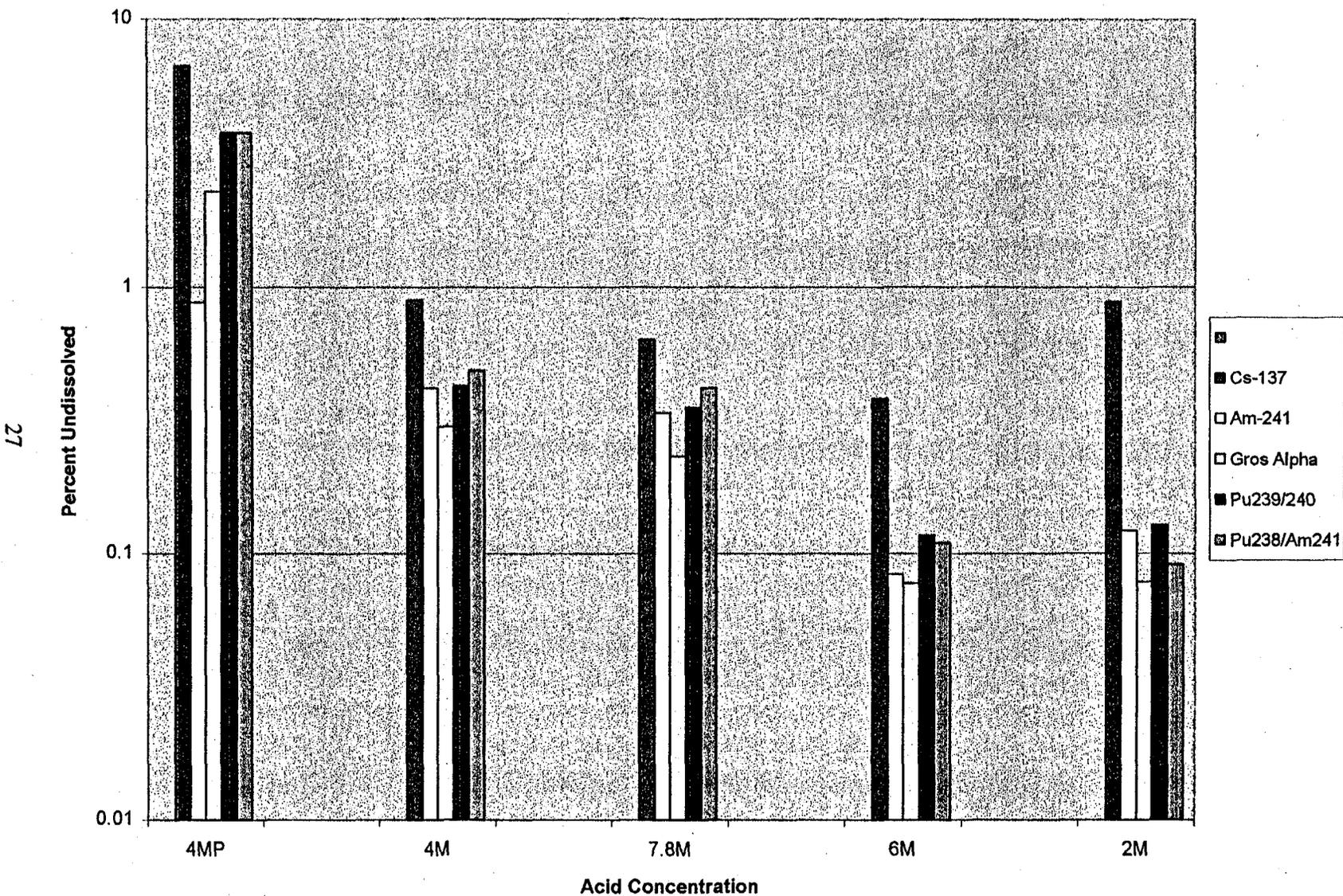


Figure 13. Radiochemical Results for the Residual Solids

Percent of Analytes in Residual Solids

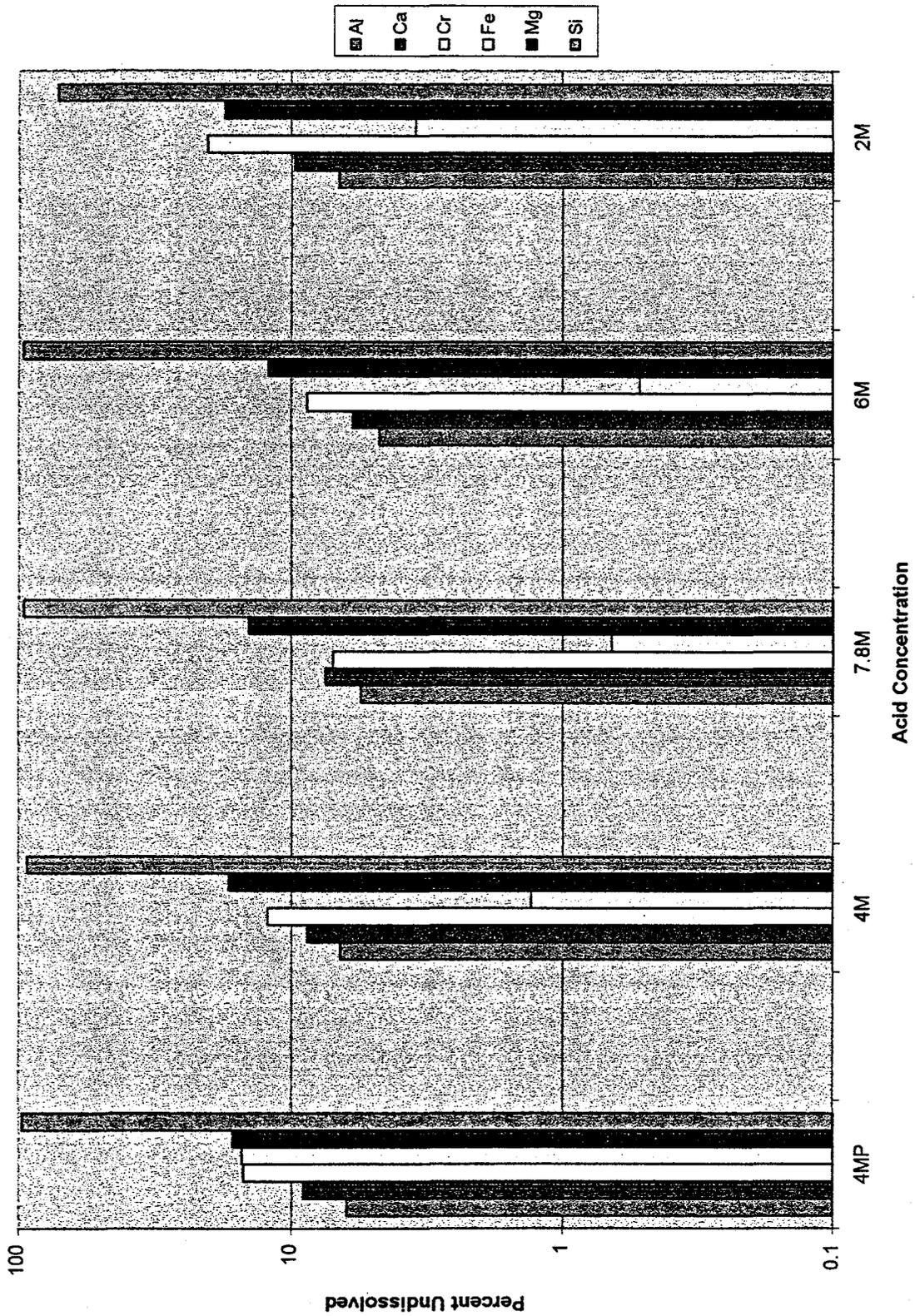


Figure 14. ICP-AES Results for the Residual Solids

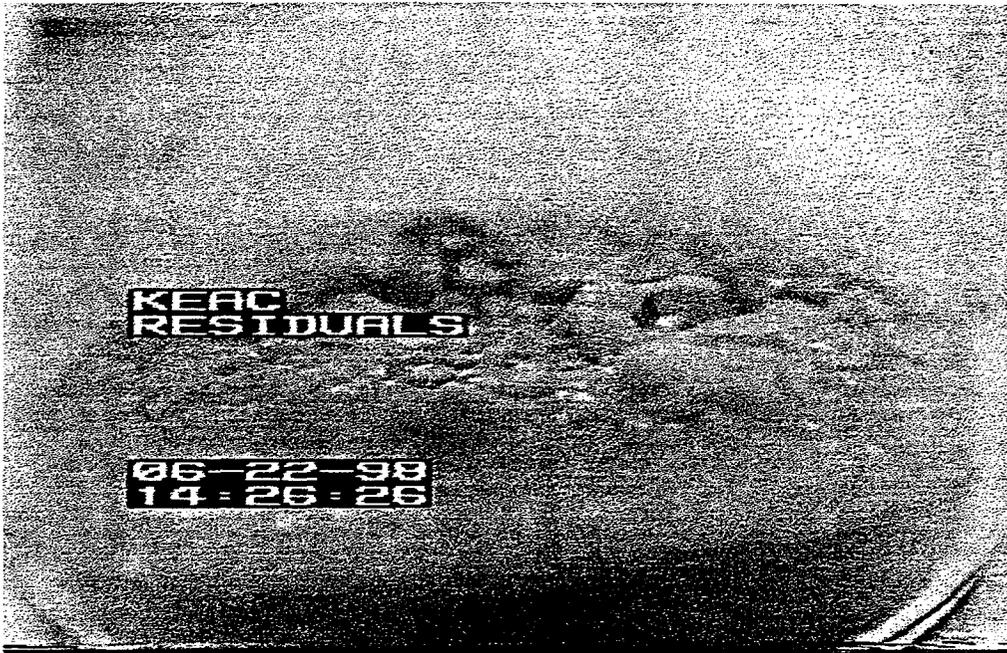


Figure 15. The Residual from the 4 M Process Test

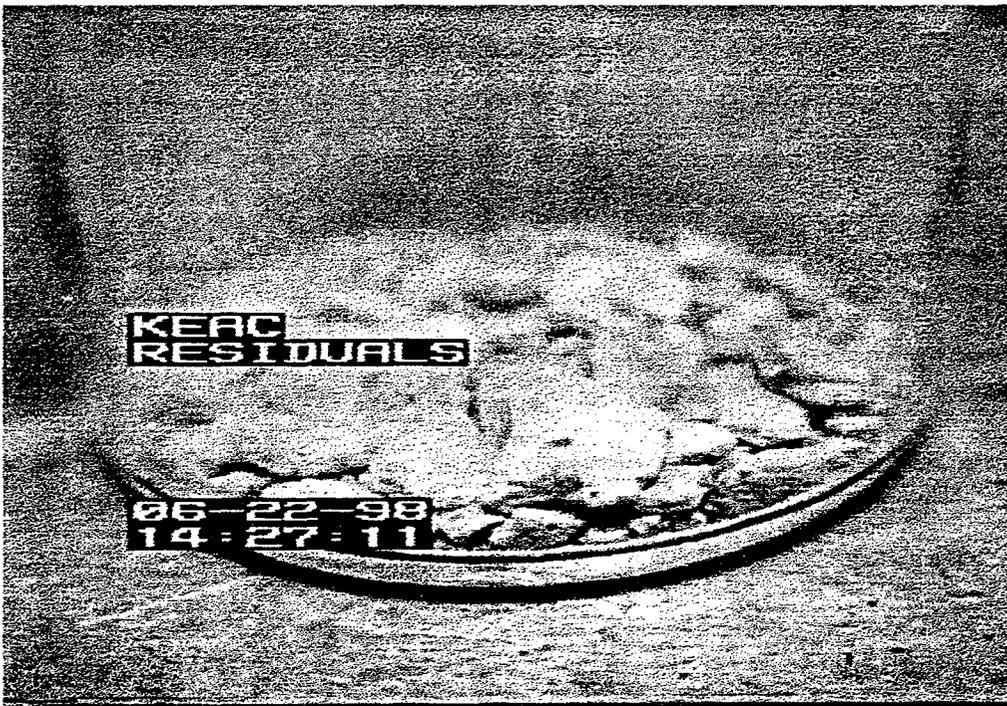


Figure 16. The Residual from the 4 M Test



Figure 17. The Residual from the 7.8 M Test

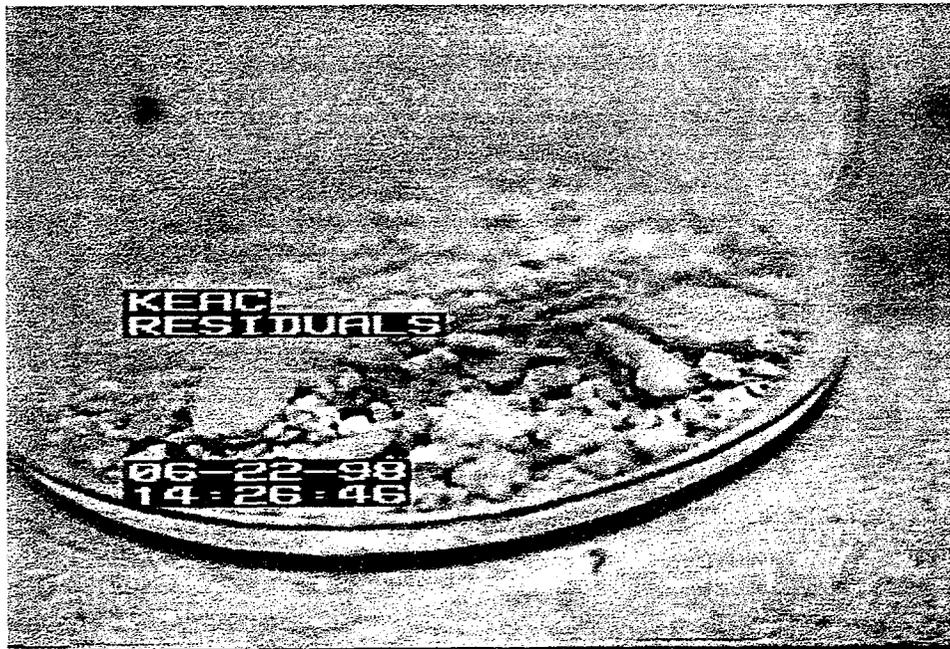


Figure 18. The Residual from the 6 M Test



Figure 19. The Residual from the 2 M Test

### Solids Loading Comparison

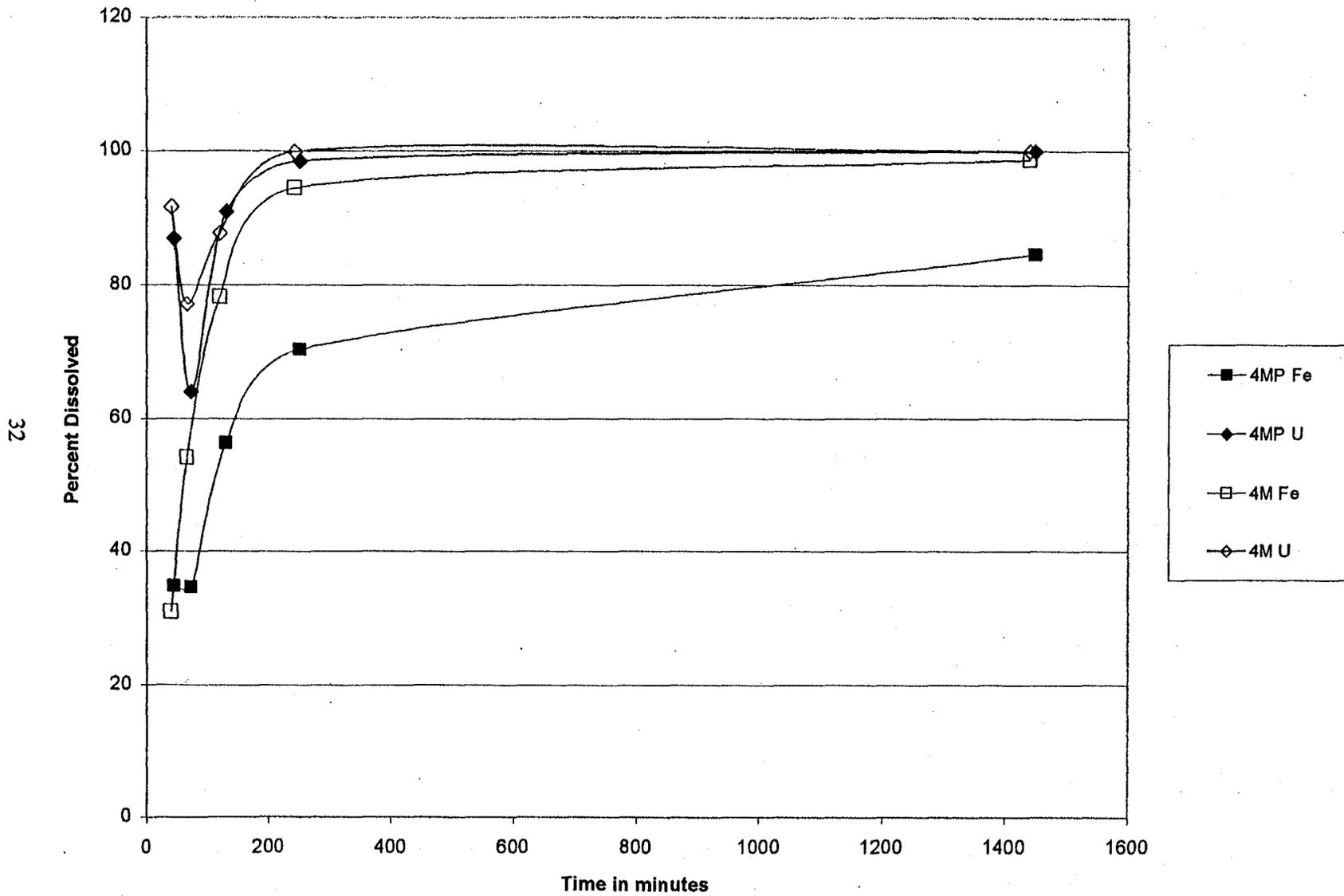


Figure 20. Comparison of the Uranium and Iron Results from Test with Different Solids Load, the 4 M Process and the 4 M Test