

# **LETTER REPORT**

## **WASHING OF THE AN-107 ENTRAINED SOLIDS**

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## Introduction

BNFL Inc. (BNFL) is under contract with the U.S. Department of Energy, River Protection Project (DOE-RPP) to design, construct, and operate facilities for treating wastes stored in the single-shell and double-shell tanks at the Hanford Site, Richland Washington. The DOE-BNFL RPP contract identifies two feeds to the waste treatment plant: 1) primarily liquid low-activity waste (LAW) consisting of less than 2 wt% entrained solids and 2) high-level waste (HLW) consisting of 10 to 200 g/L solids slurry.

The RPP contract includes three options for disposition of the entrained solids contained in low-activity waste feed solutions: 1) washing to remove sodium, cesium, and technetium then returning *via* pipeline to DOE-RPP, 2) vitrification along with pretreated LAW solutions, or 3) vitrification along with pretreated high-level waste (HLW).

BNFL requested Battelle test inhibited water (0.01 M NaOH) and caustic leaching (3 M NaOH) as methods for pretreating the solids entrained in the AN-107 sample. These methods are meant to remove certain nonradioactive components (e.g., Na, Al, Cr, P, and S) from the HLW fraction so as to reduce the volume of immobilized HLW.

This report describes the results of a test conducted by Battelle to assess the effects of inhibited water washing on the composition of the entrained solids in the diluted AN-107 low-activity waste (LAW) sample. The objective of this work was to gather data on the solubility of the AN-107 entrained solids in 0.01 M NaOH, so that BNFL can evaluate whether these solids require caustic leaching. The work was conducted according to test plan BNFL-TP-29953-9, Rev. 0, *LAW Entrained Solids Water Wash and Caustic Leach Testing*. Some deviations from the test plan were required due to the nature of the AN-107 material. These deviations will be discussed in the Experimental Section. Based on the results of the 0.01 M NaOH washing, a decision was made by BNFL to not proceed with the caustic leaching test. The composition of the washed solids was such that caustic leaching would not result in significant reduction in the immobilized HLW volume.

## Personnel

The Battelle personnel and their responsibilities in performing this test are given below.

<u>Staff Member</u>	<u>Responsibilities</u>
G.J. Lumetta	Cognizant scientist. Prepared test plan and designed experiment. Supervised performance of the test. Prepared analytical service request. Interpreted data and reported results.
F. V. Hoopes	Hot cell technician. Performed test.
M.W. Urie	Managed chemical and radiochemical analytical work.
B.M. Rapko	Technical reviewer.
K.P. Brooks	Task Leader.

## Experimental

**Sample Description.** The sample used in this test was labeled as AN-107 CL-1. The homogenization, dilution, caustic adjustment, and representative subsampling were performed as described in test plan BNFL-29953-6, *Sub-Sampling and Characterization of AN-107 and AW-101 Diluted Feed Samples* (Urie 1999). The total volume of sample AN-107 CL-1 was 78 mL. This sample was half of the material indicated as the “Caustic Leach” sample in Figure 1.2 of Urie et al. (1999). Because the material was very dark, it was not possible to accurately determine the volume of settled solids in the sample.

**Apparatus.** The apparatus used consisted of an aluminum heating block placed on a hot plate/stirrer. The hot plate/stirrer was modified so that separate power could be applied to the heating and stirring functions. This allowed for continuous stirring, while the hot plate was powered by a temperature controller. The temperature controller used was a J-KEM Model 270 (J-KEM Electronics, Inc., St. Louis, MO). This temperature controller consists of two separate circuits. One is the temperature control circuit, while the other serves as an over-temperature device, which shuts down the system if a preset temperature is exceeded. The set point for the over-temperature circuit was set at 60°C for this test. A dual K-type thermocouple (model number CASS-116G-12-DUAL, Omega Engineering, Stamford, CT) was used to provide inputs to the temperature controller and over-temperature circuits. Both the J-KEM Model 270 and the dual thermocouple were calibrated before use. The aluminum heating block contained two wells. A vial containing water was placed in one of the wells, with the thermocouple wedged between this vial and the aluminum block. The vial containing the sample was placed in the other well.

**Procedure.**<sup>(a)</sup> The sample in AN-107 CL was mixed by shaking.<sup>(b)</sup> Previous experience with the AN-107 waste indicated that it was very difficult to filter through 0.45- $\mu\text{m}$  membranes. Accordingly, a 47-mm diameter 1.2- $\mu\text{m}$  nylon membrane filter held in an appropriate vacuum filter holder was used to filter the sample. The filter membrane was pre-wetted with 10 mL of 0.1 M NaOH (washing solution), then the homogenized slurry was poured into the filter funnel. As had been observed with previous attempts to filter the AN-107 waste, the filtration process was very slow. After pulling vacuum on the filter unit for 17 h, only about half of the material had filtered, and flow through the filter had essentially stopped. The fluid material remaining in the filter funnel was transferred to a centrifuge tube and centrifuged at 1,200G for 2 h. The centrifuged liquid was decanted.

Five 4-mL aliquots and one 2-mL aliquot of 0.01 M NaOH were used to transfer the filtered and centrifuged solids to a 30-mL high-density polyethylene (HDPE) vial (this vial also contained a Teflon®-coated magnetic stir bar). The weight of the washing slurry was 21.759 g. The vial was equipped with a condenser tube, which allowed the system to vent during heating, but minimized evaporation. The mixture was heated and stirred at  $85 \pm 2$  °C for 19 h. The washing slurry was filtered through a pre-weighed 0.45- $\mu\text{m}$  nylon filtration unit. The solution filtered rapidly, with no filter plugging as observed with the bulk diluted AN-107 sample. The weights of the filtrate and filtered solids were determined to be 20.230 g and 1.800 g, respectively. Two aliquots (~10-mL each)

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<sup>(a)</sup> See Appendix A for a copy of the test plan and procedural notes.

<sup>(b)</sup> The material foamed some upon shaking.

of the filtrate were taken for analysis. The washing solution remained clear after 11 days, indicating no precipitation after filtration.

The washing procedure described above was repeated three times for a total of four washes. The heating and mixing durations for the second, third, and fourth washing steps were 22, 22, and 18 h, respectively. There was no evidence of precipitation in the wash solutions after standing overnight. The weight of the wet filtered solids were 1.471, 1.226, and 1.266 g after the second, third, and fourth washing steps, respectively. These weights can be viewed as nearly constant given the potential for variable water content in the wet solids. After the fourth washing step, the solids were transferred to a pre-weighed glass vial using deionized water. Excess water was evaporated at 80°C, then the solids were dried overnight at 105°C. The final weight of the dried washed solids was 0.106 g. This low weight was surprising given the wet weight of ~1 g. The solids apparently have a strong propensity to retain water within the filter unit.

The wash solutions were subjected to the following analytical procedures: IC(anions), TOC/TIC, acid digestion, ICP/AES, ICP-MS(Tc-99), Sr-90, total alpha, total uranium, and GEA. The washed solids were dissolved for analysis by KOH and Na<sub>2</sub>O<sub>2</sub> fusion methods. The Na<sub>2</sub>O<sub>2</sub> fusion allowed for the determination of K and Ni, which could not be determined from the KOH fusion method alone.

## Results

Table 1 presents the concentration of the analyzed AN-107 components in each washing solution and in the washed solids. Table 2 lists the mass (or activity) of each analyzed component present in each wash solution and the washed solids and Table 3 gives the percentage of each component found in each solution and the washed solids. These values were obtained by dividing the amount of the given component found in a particular solution or the washed solids (i.e., the value in Table 2) by the total amount of that component found in all the wash solutions and the washed solids; the resulting fraction was multiplied by 100 to give the percentage values.

Aluminum, K, Na, Cs, and Tc were removed reasonably well from the AN-107 entrained solids. The Na concentration in the final wash solution (243 µg/mL = 0.0106 M) was essentially the same as that in the wash solution added (0.010 M NaOH) indicating that all soluble Na-containing components were removed. About 60% of the Cr was removed by dilute hydroxide washing. The washed solids contained ~1 wt% Cr. Improved Cr removal could likely be achieved by treatment of the washed solids with permanganate or other oxidant (Rapko et al. 1996 and 1998). The washed solids were dominated by the presence of Fe (25.9 wt%) and Mn (15.2 wt%). Other elements of note were Na (2.6 wt%), Al (1.9 wt%), and Pb (1.7 wt%).

The radiochemical data indicated nearly quantitative removal of <sup>137</sup>Cs from the AN-107 entrained solids. Approximately 90% of the <sup>99</sup>Tc was also washed from the solids, and a significant fraction (23%) of the <sup>90</sup>Sr was also removed. The wash solution could be processed along with the liquid fraction of the AN-107 LAW to remove these radioisotopes.

Because of the limited quantity available, TOC, TIC, and IC analyses could not be performed on the washed solids. Analyses of the washing solutions indicated a steady decrease in the TOC concentration such that the TOC in the washing liquid was below detection by the third washing step. The TIC concentration leveled out at about 100 µg/mL at the third washing step. The fact that

the TIC content did not decrease further might have been due to the presence of carbonate in the 0.01 M NaOH solution used in washing. The anion concentrations all decreased steadily from one wash step to the next. Consistent with the TOC results, IC indicated a steady decrease in the oxalate concentration with each subsequent washing step.

Much of the material found in the first wash solution can be attributed to dilution of the interstitial liquid rather than actual dissolution of entrained solids. Table 4 illustrates this. The volume of interstitial liquid in the filtered solids was estimated in the following manner. First, it was assumed that the Na present in the first wash solution was due only to dilution of the diluted AN-107 supernate and the 0.01 M NaOH (230  $\mu\text{g}/\text{mL}$  Na) used as the washing medium. The Na concentration in the first wash solution was 32,900  $\mu\text{g}/\text{mL}$ , of which  $32,900 - 230 = 32,670$   $\mu\text{g}/\text{mL}$  is attributed to dilution of the interstitial supernate. Given the wash solution volume of 18.84 mL and the Na concentration in the diluted AN-107 supernate was 173,500  $\mu\text{g}/\text{mL}$  (Urie 1999), the volume of the interstitial liquid was estimated as

$$V = (18.84 \text{ mL})(32,670 \mu\text{g}/\text{mL}) / (173,500 \mu\text{g}/\text{mL}) = 3.55 \text{ mL}$$

This value<sup>(a)</sup> was then used to determine the concentration expected for each AN-107 component expected in the first wash solution based on dilution (Table 4). For many components, the concentration determined in the wash solution was less than that expected based on dilution (negative percent difference). This is likely due to the inherent uncertainty associated with this analysis of the data. However, the concentrations were notably higher than expected for certain components (e.g., Al, Cr, Si, TOC, and  $\text{C}_2\text{O}_4^{2-}$ ), suggesting that these components were actually dissolved during the washing process. It appears that the concentration of U in the first wash solution is due primarily to dilution of U in the starting sample. This U is probably bound to either organic complexants or carbonate forming a soluble complex.

Table 5 presents further comparisons to the data for the entrained solids reported in Urie et al. (1999). The concentrations could not be compared directly because the composition for the untreated entrained solids were reported on a wet-weight basis, whereas the washed solids were analyzed on a dry-weight basis. For this reason, the data were normalized to the Fe content. The percent of each component was determined based on the differences in the component concentrations relative to Fe before and after washing. For certain components (e.g.,  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ,  $^{99}\text{Tc}$ , Al, Cr, Na, Ni, and P), the percent removals obtained in this manner agreed well with those reported in Table 3. However in most other cases, agreement between the two methods is not very good.

## Conclusions and Recommendations

The results of this test suggest that caustic leaching would not provide much benefit for processing the AN-107 entrained solids. Washing with 0.01 M NaOH appeared to remove >90% of the Al and ~90% of the P from the AN-107 solids. Iron and Mn appear to be the dominant elements present

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<sup>(a)</sup> It should be noted that there is an apparent discrepancy between the value of 3.55 mL of interstitial liquid and the total weight (21.7592 g) of the first washing slurry. Given the fact that 22 mL of 0.01 M NaOH was used in transferring the solids to the washing vessel, a slurry weight of ~26 g would be expected. This discrepancy is perhaps due to physical loss of liquid during the transfer; e.g., passage of liquid through the filter membrane.

in the washed AN-107 solids. Caustic leaching would not be expected to impact Fe and Mn (see Lumetta et al. 1996 and 1997; Rapko et al. 1995).

The Cr concentration (1 wt%) might present some problems in immobilizing the washed AN-107 solids. Previous studies we have done with other sludges suggest that caustic leaching might remove additional Cr, but a better strategy would be to add an oxidant during the washing process. Permanganate works very well, but sparging with air or ozone has also shown some promise (Rapko et al. 1996 and 1998). If the HLW volume is dictated by the Cr content, then an oxidative leaching process is recommended.

The concentrations of the major radionuclides contained in the washed solids were 68.6  $\mu\text{Ci/g}$   $^{241}\text{Am}$ , 4,330  $\mu\text{Ci/g}$   $^{90}\text{Sr}$ , and 61.3  $\mu\text{Ci/g}$   $^{137}\text{Cs}$ , indicating the solids should be treated as HLW. The washed solids represented only 0.1 wt% of the diluted AN-107 feed material. The blending of this material with the HLW sludge to be processed in Phase 1 Privatization should be considered.

## References

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**Table 1.** AN-107 Component Concentrations in the Wash Solutions and the Washed Solids.<sup>(a)</sup>

Analyte	First Wash	Second Wash	Third Wash	Fourth Wash	Washed Solids
	AN107-AQ-30	AN107-AQ-50	AN107-AQ-70	AN107-AQ-90	AN107-AQ-100
Cesium-137	4.13E+01	1.41E+01	1.92E-01	9.00E-02	6.13E+01
Strontium-90	7.68E+00	2.67E-02	2.70E-02	4.66E-02	4.33E+03
Technetium-99	1.17E-02	1.84E-03	5.03E-04	1.85E-04	1.86E-01
Americium-241	< 4E-02	< 8E-04	9.82E-04	1.82E-03	6.86E+01
Europium-154	1.17E-02	2.95E-04	1.04E-03	1.86E-03	5.70E+01
Europium-155	< 4E-02	< 8E-04	6.36E-03	1.39E-03	4.22E+01
Total Alpha	7.96E-03	6.86E-04	1.23E-03	2.02E-03	6.91E+01
Ag	< 0.1	< 0.1	< 0.1	< 0.1	(71)
Al	1140	83.4	44.6	28.2	19400
Ba	< 0.1	< 0.1	< 0.1	< 0.1	1440
Ca <sup>(b)</sup>	70.0	(1.3)	< 0.6	(0.62)	2200
Cd	7.26	(0.29)	< 0.1	< 0.1	(76)
Co	(0.55)	< 0.2	< 0.2	< 0.2	< 50
Cr	59.8	17.1	10.2	5.94	9630
Cu	3.76	(0.27)	(0.11)	< 0.1	(97)
Fe	3.06	(0.62)	4.86	9.02	259000
K	183	< 10	< 12	< 10	< 3800
La	(0.48)	< 0.2	< 0.2	< 0.2	1965
Mg	< 0.5	< 0.5	< 0.6	< 0.5	(970)
Mn	0.978	(0.15)	0.833	1.57	152500
Mo	< 0.2	< 0.2	< 0.2	< 0.2	< 60
Na	32900	1500	354	243	26500
Ni <sup>(c)</sup>	58.6	2.14	(0.2)	< 0.2	749
P	73.9	(3.0)	(2.8)	(1.7)	(1650)
Pb	46.0	(1.9)	< 0.35	(0.43)	17300
Si <sup>(d)</sup>	17.3	24.9	23.9	16.6	6930
Ti	(0.03)	< 0.03	< 0.03	< 0.03	197
U	(16)	< 10	< 12	< 10	1270
Zn	2.36	(0.26)	< 0.2	(0.14)	1290
Zr	< 0.2	< 0.2	< 0.2	(0.18)	2430
TOC	7550	244	< 35	< 35	(f)
TIC	3070	286	127	110	(f)
Cl <sup>-</sup>	230	12	2	3	(f)
F <sup>-</sup>	1050	75.0	23	12	(f)
NO <sub>3</sub> <sup>-</sup>	26150	960	58	7	(f)
SO <sub>4</sub> <sup>2-</sup>	1530	65	5	3	(f)
PO <sub>4</sub> <sup>3-</sup>	1240	55	3	3	(f)
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	9425	410	45	14	(f)

(a) For the liquids, concentrations for radionuclides are in units of  $\mu\text{Ci/mL}$ ; all other components are in units of  $\mu\text{g/mL}$ . For the washed solids, concentrations for radionuclides are in units of  $\mu\text{Ci/g}$  dry solids; all other components are in units of  $\mu\text{g/g}$  dry solids. Values in parentheses are within 10 times the analytical detection limit.

(b) Because of high process blank for the  $\text{Na}_2\text{O}_2$  fusion, only the Ca value from the KOH fusion was used.

(c) The Ni content of the washed solids was determined only through the  $\text{Na}_2\text{O}_2$  fusion method, because a Ni crucible is required for the KOH fusion. The process blank for the  $\text{Na}_2\text{O}_2$  fusion had a relatively high Ni content of  $439 \mu\text{g/g}$ .

(d) The process blank for the liquid samples had a relatively high Si content of  $22.4 \mu\text{g/mL}$ . For the analysis of the washed solids, only the Si value from the  $\text{Na}_2\text{O}_2$  fusion was used because of high process blank for the KOH fusion.

(f) Not determined because inadequate sample available.

**Table 2.** Quantities in Each Wash Solution and in the Washed Solids<sup>(a)</sup>

Analyte	First Wash	Second Wash	Third Wash	Fourth Wash	Washed Solids
Cesium-137	7.78E+02	2.51E+02	3.47E+00	1.65E+00	7.12E+00
Strontium-90	1.45E+02	4.76E-01	4.87E-01	8.54E-01	5.03E+02
Technetium-99	2.21E-01	3.27E-02	9.08E-03	3.40E-03	2.16E-02
Americium-241	< 8E-01	< 1E-02	1.77E-02	3.34E-02	7.97E+00
Europium-154	2.20E-01	5.26E-03	1.88E-02	3.41E-02	6.62E+00
Europium-155	< 8E-01	< 1E-02	1.15E-01	2.55E-02	4.90E+00
Total Alpha	1.50E-01	1.22E-02	2.22E-02	3.70E-02	8.03E+00
Ag	< 1	< 1	< 2	< 1	(8)
Al	21474	1487	805	517	2254
Ba	< 2	(1.8)	(1.8)	(1.8)	167
Ca	< 1319	< 23	< 11	< 11	256
Cd	< 137	< 5	< 2	< 2	(9)
Co	< 10	< 4	< 4	< 4	< 6
Cr	1126	305	184	(108.9)	1119
Cu	< 71	< 5	< 2	< 2	(11)
Fe	< 58	(11.1)	(87.7)	(165.3)	30096
K	3447	(178)	< 217	< 183	< 442
La	< 9	< 4	< 4	< 4	228
Mg	< 9	< 9	< 11	< 9	(113)
Mn	< 18	(2.7)	15.0	28.8	17721
Mo	< 4	< 4	< 4	< 4	< 7
Na	619724	26736	6391	4453	3079
Ni	(1104)	< 38	< 3	< 4	87
P	(1392)	(53)	(51)	< 31	(192)
Pb	< 866	< 34	< 6	< 8	2010
Si	326	444	431	304	805
Ti	< 1	< 1	(0.54)	(0.55)	23
U	301.4	178.2	216.7	183.3	(148)
Zn	< 44	< 5	< 4	(2.6)	150
Zr	< 4	< 4	(3.6)	(3.3)	282
TOC	142216	< 4349	< 632	< 641	(b)
TIC	57828	5089	2284	2016	(b)
Cl <sup>-</sup>	4332	214	36	55	(b)
F <sup>-</sup>	19778	1337	415	220	(b)
NO <sub>3</sub> <sup>-</sup>	492577	17111	1047	128	(b)
SO <sub>4</sub> <sup>2-</sup>	28820	1159	90	55	(b)
PO <sub>4</sub> <sup>3-</sup>	23357	980	54	55	(b)
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	177535	7308	812	257	(b)

(a) Radionuclides are given in  $\mu\text{Ci}$ ; other components are in  $\mu\text{g}$ . Values in parentheses are for components that were within 10 times the analytical detection limit.

(b) Not determined because inadequate sample available.

**Table 3.** Percentage of Each AN-107 Component in the Wash Solutions and in the Washed Solids<sup>(a)</sup>

Analyte	First Wash	Second Wash	Third Wash	Fourth Wash	Washed Solids
Cesium-137	75	24	0	0	1
Strontium-90	22	0	0	0	77
Technetium-99	77	11	3	1	8
Americium-241	< 9	0	0	0	> 91
Europium-154	3	0	0	0	96
Europium-155	< 13	0	2	0	98 > x > 84
Total Alpha	2	0	0	0	97
Ag	< 10	< 10	< 11	< 10	> 59
Al	81	6	3	2	8
Ba	< 1	(1.0)	(1.0)	(1.0)	96
Ca	< 81	< 1	< 1	< 1	> 16
Cd	< 89	< 3	< 1	< 1	> 6
Co	< 38	< 13	< 13	< 14	> 22
Cr	40	11	6	(3.8)	39
Cu	< 78	< 5	< 2	< 2	> 12
Fe	< 0	(0.0)	(0.3)	(0.5)	99
K	77	(4)	< 5	< 4	19 > x > 9
La	< 4	< 1	< 1	< 1	> 92
Mg	< 6	< 6	< 7	< 6	> 75
Mn	< 0	(0.0)	0.1	0.2	100
Mo	< 17	< 17	< 17	< 17	> 32
Na	94	4	1	1	0
Ni	(89)	< 3	< 0	< 0	11 > x > 7
P	(81)	(3)	(3)	< 2	11
Pb	< 30	< 1	< 0	< 0	> 69
Si	14	19	19	13	35
Ti	< 2	< 2	(2)	(2)	> 91
U	29.3	17.4	21.1	17.8	14
Zn	< 22	< 2	< 2	(1.3)	> 73
Zr	< 1	< 1	(1.2)	(1.1)	> 95

(a) Parentheses indicate that component was within 10 times the analytical detection limit.

**Table 4.** Expected Concentrations in the First Wash Solution Based on Dilution of the Interstitial Liquid<sup>(a)</sup>

Analyte	Diluted Supernate <sup>(b)</sup>	Concentration in First Wash		Difference, %
		Based on Dilution	Found	
Cesium-137	256	48	41	-14
Strontium-90	76	14.3	7.7	-46
Technetium-99	0.074	0.0139	0.0117	-15
Americium-241	0.379	0.0713	0.0400	-44
Europium-154	0.612	0.1152	0.0117	-90
Europium-155	0.356	0.0670	0.0400	-40
Total Alpha	0.447	0.0841	0.0080	-91
Ag	< 3	< 0.6	< 0.1	--
Al	3930	741	1140	54
Ba	(4.1)	(0.8)	< 0.1	--
Ca	439	83	70.0	-15
Cd	47	8.9	7.26	-18
Co	< 4	< 0.8	(0.55)	--
Cr	146	27	59.8	118
Cu	(21)	(4)	3.76	-5
Fe	1140	214.8	3.06	-99
K	(1270)	(239)	183	-24
La	(23)	(4)	(0.48)	-89
Mg	< 12	< 2	< 0.5	--
Mn	107	20.2	0.978	-95
Mo	< 6	< 1.1	< 0.2	--
Na	173500	32698	32900	1
Ni	392	74	58.6	-21
P	497	94	73.9	-21
Pb	256	48	46.0	-5
Si	< 44	< 8	17.3	109
Ti	< 3	< 0.6	(0.03)	--
U	73.1	13.8	(16)	16
Zn	(19)	(4)	2.36	-34
Zr	(43)	(8)	< 0.2	--
TOC	29900	5635	7550	34
TIC	16300	3072	3070	0
Cl <sup>-</sup>	1400	264	230	-13
F <sup>-</sup>	6350	1197	1050	-12
NO <sub>3</sub> <sup>-</sup>	161000	30343	26150	-14
SO <sub>4</sub> <sup>2-</sup>	7650	1442	1530	6
PO <sub>4</sub> <sup>3-</sup>	3000	565	1240	119
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	1300	245	9425	3747

(a) Radionuclides are reported in units of  $\mu\text{Ci/mL}$ ; all other components are in units of  $\mu\text{g/mL}$ .

(b) Values taken from Urie 1999. Each value is an average of duplicate measurements.

(c) It was assumed that there were 3.55 mL of interstitial liquid. This value was determined assuming the Na concentration in the wash solution was strictly due to dilution of the interstitial liquid plus the 0.01 M NaOH used as the wash medium.

**Table 5.** Comparison of the Compositions of the Washed AN-107 Solids to the Wet Untreated Solids

Analyte	Wet Entrained Solids <sup>(a)</sup>		Dry Washed Solids		Removed, %
	$\mu\text{Ci/g}$ or $\mu\text{g/g}$	$\text{Ci/g Fe}$ or $\text{g/g Fe}$	$\mu\text{Ci/g}$ or $\mu\text{g/g}$	$\text{Ci/g Fe}$ or $\text{g/g Fe}$	
Cesium-137	165	0.018	61	2.37E-04	99
Strontium-90	192	0.021	4330	1.67E-02	19
Technetium-99	0.065	0.00001	0.186	7.19E-07	90
Americium-241	1.47	0.00016	68.6	2.65E-04	-68
Europium-154	1.31	0.0001	57.0	2.20E-04	-57
Europium-155	0.82	0.0001	42.2	1.63E-04	-86
Total Alpha	1.830	0.00020	69.1	2.67E-04	-36
Ag	< 25	< 0.003	(71)	(0.0003)	--
Al	7500	0.805	19400	0.075	91
Ba	(44)	(0.005)	1440	0.006	-18
Ca	(650)	(0.070)	2200	0.008	88
Cd	(37)	(0.004)	(76)	(0.0003)	93
Co	< 50	< 0.005	< 50	< 0.0002	--
Cr	722	0.0775	9630	0.037	52
Cu	< 25	< 0.003	(97)	(0.0004)	86
Fe	9315	1	259000	1	--
K	(659)	(0.071)	< 3800	< 0.015	--
La	(63)	(0.0067)	1965	0.0076	-13
Mg	< 100	< 0.011	(970)	(0.0037)	--
Mn	5020	0.539	152500	0.589	-9
Mo	< 50	< 0.01	< 60	< 0.0002	--
Na	136500	14.7	26500	0.102	99
Ni	277	0.030	749	0.0029	90
P	(510)	(0.055)	(1650)	(0.0064)	88
Pb	(610)	(0.065)	17300	0.0668	-2
Si	< 510	< 0.1	6930	0.0268	--
Ti	< 25	< 0.003	197	0.0008	--
U	103	0.0111	1270	0.0049	56
Zn	< 50	< 0.01	1290	0.0050	--
Zr	(101)	(0.011)	2430	0.0094	13

(a) Urie et al. 1999.

(b) Percent removed =  $100 \cdot (C_o - C) / C_o$  where  $C_o$  is the Fe-normalized concentration in the wet centrifuged and C is the Fe-normalized concentration in the washed solids.

## **Appendix A. Test Plan**

## Appendix B. Raw Data

## Appendix C. Calculations

## **Appendix A. Test Plan**

Work place Copy

<b>PNNL Test Plan</b>		Document No.: BNFL-TP-29953-9 Rev. No.: 0
Title: LAW Entrained Solids Water Wash and Caustic Leach Testing		
Work Location: RPL/SAL	Page 1 of 19	
Author: GJ Lumetta	Effective Date: December 14, 1998 Supersedes Date: New	
Use Category Identification: Mandatory		
Identified Hazards: <input type="checkbox"/> Radiological <input type="checkbox"/> Hazardous Materials <input type="checkbox"/> Physical Hazards <input type="checkbox"/> Hazardous Environment <input type="checkbox"/> Other:	Required Reviewers: <input checked="" type="checkbox"/> Technical Reviewer <input checked="" type="checkbox"/> Other: Client <input type="checkbox"/> Building Manage <input checked="" type="checkbox"/> Other: Project Manager <input type="checkbox"/> Radiological Control <input checked="" type="checkbox"/> Other: RPL Manager <input type="checkbox"/> ES&H <input checked="" type="checkbox"/> Quality Engineer	
Are One-Time Modifications Allowed to this Procedure? <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No		
NOTE: If Yes, then modifications are not anticipated to impact safety. For documentation requirements of a modification see SBMS or the controlling Project QA Plan as appropriate.		
On-The Job Training Required? <input type="checkbox"/> Yes or <input checked="" type="checkbox"/> No		
FOR REVISIONS: Is retraining to this procedure required? <input type="checkbox"/> Yes <input type="checkbox"/> No Does the OJT package associated with this procedure require revision to reflect procedure changes? <input type="checkbox"/> Yes <input type="checkbox"/> No <input type="checkbox"/> N/A		
Approval:		
	<u>Signature</u>	<u>Date</u>
Author	<u>G. J. Lumetta</u>	<u>1/5/99</u>
Technical Reviewer	<u>Brian Rapp</u>	<u>1-11-99</u>
RPL Manager	<u>[Signature]</u>	<u>1-12-99</u>
Project Manager	<u>D. S. Kurath</u>	<u>1/11/99</u>
RPG QE	<u>[Signature]</u>	<u>1/12/99</u>
BNFL	<u>[Signature]</u>	<u>1/19/99</u>

## Applicability

This test plan is to be used to determine 1) the aqueous-insoluble fraction of the entrained solids from BNFL LAW samples and 2) the caustic-insoluble fraction of the entrained solids from BNFL LAW samples. The work will be conducted in the SAL hot cells. The work will be conducted by Radiochemical Processing Group staff. This work is being done as part of the Technical Support to BNFL for Phase 1B project.

## Test Objectives

**Justification:** This activity supports confirmation of the process sequence, equipment performance, and design parameters for caustic leaching of solids separated from the low-activity waste (LAW) solutions.

**Objective:** This task will gather data on the inhibited water solubility of solids entrained in the LAW solutions. Caustic leaching experiments will estimate the removal efficiency for caustic soluble components and aid in determining the disposition of these solids.

## Definitions

BNFL	British Nuclear Fuels Ltd.
HDPE	High-density polyethylene
HLW	High-level waste
RPL	Radiochemical Processing Laboratory

## Emergency Response

In the event of building audible alarms (e.g., fire or criticality) personnel should proceed in accordance with the RPL Building Emergency Procedure. If time permits, ensure that test materials are secured from spilling prior to exiting the area.

## Quality Control

Quality assurance for work conducted under this Test Plan is governed by the Standards-Based Management System (SBMS). The quality control for each analysis will be established per Quality Assurance Plan MCS-033. MCS-033 specifies the minimum calibration and verification requirements for analytical systems, as well as batch processing quality control samples to monitor preparations (i.e., blanks, duplicates, matrix spikes, and laboratory control standards).

A work place copy of this document shall be present at the work location. Specific information regarding each test (e.g., sample numbers) will be recorded on the work place copy and kept as project records.

As discussed in the Prerequisites section, calibrated balances must be used in performing this test. Likewise, a calibrated temperature controller is required. The calibration ID, date of calibration, and calibration expiration date must be recorded on the work place copy for each balance used and for the temperature controller.

Measured weights will be recorded on the work place copy at the indicated spot in the work instructions.

Hand written changes or corrections made to the work place copy will be made by means of a single line-out. Such changes or corrections shall be initialed and dated by the staff member making the change and by the cognizant scientist.

### Equipment Description

A standard laboratory hot plate/magnetic stirrer will be used for this test. An aluminum heating block will be placed on the hot plate/stirrer to heat the sample. The apparatus will be equipped with two thermocouples. One of the thermocouples will be connected to a temperature controller, while the other will be connected to an over-temperature shut-off device. The latter will be used to ensure the sample is not over heated, which could result in lose of sample.

### Prerequisites

Staff performing the work must read and understand the entire test plan prior to beginning work.

The following are items that should be staged prior to start of the test.

Wide-mouth HDPE bottle; size to be determined (2)  
20-mL HDPE vial (14)  
30- to 40-mL glass vials (2)  
Hot plate/stirrer  
Aluminum heating block  
Temperature controller with temperature read-out  
Over-temperature shut-off device  
0.45- $\mu$ m nylon syringe filters (2)  
5-mL syringes (2)  
0.45- $\mu$ m nylon disposable filter units (9)  
Adjustable 5-mL pipette  
0.01 M NaOH  
3 M NaOH

The temperature controller shall be calibrated by maintenance services. Record the following information regarding the temperature controller used.

		<u>Thermocouples</u>	
Calibration ID:	<u>2093</u>	2899	2900
Calibration Date:	<u>1/12/99</u>	1/99	1/99
Expiration Date:	<u>1/2000</u>	1/2001	1/2001

A calibrated balance is required for this test. Record the following information regarding the balance(s) used.

Calibration ID:	<u>360-06-01-016</u>	Calibration ID:	_____
Calibration Date:	<u>2/2/99</u>	Calibration Date:	_____
Expiration Date:	<u>8/99</u>	Expiration Date:	_____

Before beginning work, a routine performance check should be performed and documented in the space below.

3/15/99	Check wt.	Measured
	1	1.0002
	5	5.0001
	10	10.0000
	<del>25</del> 20	19.9999
	50	50.0004
	100	100.0006
	150 (100+50)	150.0015

### Work Instructions

#### Notes

Where practical, catch pans should be used when working with the tank waste samples, so that they can be recovered if spilled.

Throughout this test plan bottle, vials, etc. are labeled as "        -XX-YY." The labels XX and YY are defined in the text. The tank number should be filled in the blank, e.g., "AW101."

### Part 1. Determination of Aqueous-Insoluble Fraction

- Sample # AN107 CL-1
- 1.1. Obtain a LAW sample containing ~5 mL of settled solids, as directed by the cognizant scientist. Stir to homogenize the sample. → Note: when shook the solution foamed a bit.
  - 1.2. Label a <sup>glass jar (capacity ≥ 100 mL)</sup> ~~disposable filter unit (0.45-µm nylon)~~ as AN107-AQ-10 n.k. 3/15/99
  - 1.3. Weigh AN107-AQ-10

$$\text{Wt. } \underline{\text{AN107 AQ-10}} = \underline{127.7522} \text{ g} \quad (1.3A)$$

Also weigh just the bottom part of the filter unit; i.e., the receiving bottle and cap

$$\text{Wt. receiving bottle \& cap} = \underline{\hspace{2cm}} \text{ g} \quad (1.3B) \quad \begin{matrix} n.k. \\ 3/15/99 \end{matrix}$$

- 1.4. Connect         -AQ-10 to the vacuum line <sup>filter apparatus with 1-2-µm nylon (47mm dia.) membrane to filter flask.</sup> ~~filter apparatus with 1-2-µm nylon (47mm dia.) membrane to filter flask.~~   
 Premoist filter by drawing 10 mL 0.1 M NaOH through the filter membrane. n.k. 3/15/99

Filtration process was very slow (as expected). Started at ~2:30 on 3/15. (a)  
 At 5:00 on 3/16, still had not all filtered. Filtration had essentially stopped.  
 Using a pipet, the remaining liquid remaining in the filter funnel was transferred to a  
 50-ml cent. tube. ~40 ml of material in the tube. Centrifuged 2500 rpm 9:20 → 11:25 (b)

1.5 Filter the homogenized sample through AQ-10 the 1.2-um membrane, collecting the filtrate in the glass vacuum flask. *M.I.E. 3/15/99*

1.6 Disconnect from the vacuum once the liquid has filtered

1.7 Place the cap on the top of the filter unit and weigh AN107-AQ-10 *M.I.E. 3/15/99*

*M.I. hummel 3/18/99*

Did not get this weight for two reasons:  
 1) It's not critical to the experiment.  
 2) It would likely exceed the capacity of the balance.  
 Wt. AN107-AQ-10 = \_\_\_\_\_ g (1.7A)

Carefully remove the funnel part of the apparatus from the receiving bottle, place the cap on the receiving bottle and weigh.

*M.I. hummel 3/15/99*

Wt. receiving bottle & cap = \_\_\_\_\_ g (1.7B)

Save the filtered solution.

1.8 Determine the total weight of the sample *M.I. hummel 3/15/99*  
 Wt. Sample = 1.7A - 1.3A = 104.112 g (1.8A)  
*According to information from Paul Bredt.*

Determine the weight of the filtered liquid *M.I.E. 3/18/99*  
 Wt. Liquid = 1.7B - 1.3B = \_\_\_\_\_ g (1.8B)

Determine the weight of the filtered solids  
 Could not determine the weight of the solids because some were filtered, some were centrifuged. *M.I. hummel 3/18/99*  
 Wt. Solids = 1.8A - 1.8B = \_\_\_\_\_ g (1.8C)

1.9 Measure out the appropriate volume of 0.01 M NaOH as instructed by the cognizant scientist into a plastic bottle *M.I.E. 3/16/99*  
 Vol. Used = 20 mL *We will use five 4-ml aliquots* (1.9A)

1.10 Label an appropriately sized wide-mouthed HDPE bottle as AN107-AQ-20. Place a stir bar in this bottle. (30ml)

1.11 Weigh AN107-AQ-20 including cap and stir bar  
 Wt. AN107-AQ-20 = 12.2570 g (1.11A)

1.12 Slurry the filtered solids using a portion of 0.01 M NaOH (volume = 1.9A + 5); transfer this slurry to AN107-AQ-20 *5 x 4ml each*

1.13 Repeat step 1.12 four times to ensure complete transfer of the solids to AN107-AQ-20

1.14 Place the cap back on AN107-AQ-20 and weigh  
 Wt. AN107-AQ-20 = 34.0162 g (1.14A)

Four ml 0.01M NaOH was placed in the filter funnel. The solids were slurried into a pipet & transferred to the centrifuge tube. Repeat slurried solids in cent. tube and transferred to AN107-AQ-20. This process was repeated four times. Four good measure another small vial (20ml) was done as well.  
 Note: There were some particles that were very dense and thus hard to transfer.

(a) Transferred the liquid that had filtered to AN107-AQ-10.  
 (b) Slowly poured centrifuged liquid back into AN107 CLI; set this aside.

*M.I. hummel 3/16/99*

Determine the weight of the slurry

$$\text{Wt. Slurry} = 1.14A - 1.11A = \underline{21.7592 \text{ g}} \quad (1.14B)$$

1.15 Equip AN107-AQ-20 with a condenser, then place in an aluminum heating block at 85°C

1.16 Stir the sample in AN107-AQ-20 at 85°C for a minimum of 8 hours

Start date/time: 3/16/99 12:15  
Stop date/time: 3/17/99 8:10

1.17 Allow to cool to ambient temperature

1.18 Remove the condenser and replace the original cap on AN107-AQ-20.  
Weigh AN107-AQ-20

*Note: Original cap from AN107-AQ-20 was inadvertently thrown away. Obtained new cap, then weighed.*  
Wt. AN107-AQ-20 = 33.8120 g (1.18A)

Determine mass loss due to evaporation

\* This is only an estimated value. Precise value could not be obtained because of loss of original cap.

$$\text{Wt. Lost} = 1.18A - 1.14A = \underline{0.2042 \text{ g}}^* \quad (1.18B)$$

1.19 Label a disposable filter unit (0.45- $\mu\text{m}$  nylon) as AN107-AQ-30

1.20 Weigh AN107-AQ-30

$$\text{Wt. } \underline{\text{AN107}}\text{-AQ-30} = \underline{64.3902 \text{ g}} \quad (1.20A)$$

Also weigh just the bottom part of the filter unit; i.e., the receiving bottle and cap

$$\text{Wt. receiving bottle\&cap} = \underline{41.5444 \text{ g}} \quad (1.20B)$$

1.21 Connect AN107-AQ-30 to the vacuum line

1.22 Filter the wash slurry

*Filtered ok. Rinsed stir bar off with a few mL of 0.01 M NaOH. Rinsed into filter funnel.*

1.23 Disconnect from the vacuum once the liquid has filtered

1.24 Place the cap on the top of the filter unit and weigh AN107-AQ-30

$$\text{Wt. } \underline{\text{AN107}}\text{-AQ-30} = \underline{86.4204 \text{ g}} \quad (1.24A)$$

Carefully remove the funnel part of the apparatus from the receiving bottle, place the cap on the receiving bottle and weigh.

$$\text{Wt. receiving bottle\&cap} = \underline{61.7749 \text{ g}} \quad (1.24B)$$

Transfer two 10-mL aliquots of the filtered solution to clean 20-mL HDPE sample vials labeled as AN107-AQ-30A and AN107-AQ-30B.

*(Left the remainder in -AQ-30 for observation).*

Note: Monitor the solution after ~24 h to determine if any solids form.

3/18/99 9:00

Solution was clear.

3/18/99 5:00

Solution was clear.

3/29/99 13:00 solution still clear

- 1.25 Determine the total weight of the slurry

$$\text{Wt. Slurry} = 1.24\text{A} - 1.20\text{A} = \underline{22.0302\text{ g}} \quad (1.25\text{A})$$

Determine the weight of the filtered liquid

$$\text{Wt. Liquid} = 1.24\text{B} - 1.20\text{B} = \underline{20.2305\text{ g}} \quad (1.25\text{B})$$

Determine the weight of the filtered solids

$$\text{Wt. Solids} = 1.25\text{A} - 1.25\text{B} = \underline{1.7997\text{ g}} \quad (1.25\text{C})$$

- 1.26 Measure out the appropriate volume of 0.01 M NaOH as instructed by the cognizant scientist into a plastic bottle

*Used 5 x 4 mL*

$$\text{Vol. Used} = \underline{20}\text{ mL} \quad (1.26\text{A})$$

- 1.28 Weigh AN107-AQ-20

$$\text{Wt. } \underline{\text{AN107}}\text{-AQ-20} = \underline{\hspace{2cm}}\text{ g} \quad (1.28\text{A})$$

*Forgot to weigh. M.F.Z. 3/17/99*

- 1.29 Slurry the filtered solids using a portion of 0.01 M NaOH (volume = 1.26A + 5); transfer this slurry to AN107-AQ-20 *HH*

- 1.30 Repeat step 1.29 four times to ensure complete transfer of the solids to AN107-AQ-20

- 1.31 Weigh AN107-AQ-20

$$\text{Wt. } \underline{\text{AN107}}\text{-AQ-20} = \underline{32.0751\text{ g}} \quad (1.31\text{A})$$

Determine the weight of the slurry

$$\text{Wt. Slurry} = 1.31\text{A} - 1.28\text{A} = \underline{19.8181\text{ g}} \quad (1.31\text{B})$$

*Use 1.11A instead (12.2570g)*

- 1.32 Equip AN107-AQ-20 with a condenser, then place in an aluminum heating block at 85°C

- 1.33 Stir the sample in AN107-AQ-20 at 85°C for a minimum of 8 hours

Start date/time: 3/17/99 9:45  
Stop date/time: 3/18/99 7:45

- 1.34 Allow to cool to ambient temperature

- 1.35 Remove the condenser and replace the original cap on AN107-AQ-20.  
Weigh AN107-AQ-20

$$\text{Wt. } \underline{\text{AN107}}\text{-AQ-20} = \underline{31.8704\text{ g}} \quad (1.35\text{A})$$

Determine mass loss due to evaporation

$$\text{Wt. Lost} = 1.35\text{A} - 1.31\text{A} = \underline{0.2047} \text{ g} \quad (1.36\text{B})$$

1.36 Label a disposable filter unit (0.45- $\mu\text{m}$  nylon) as AN107-AQ-50

1.37 Weigh AN107-AQ-50

$$\text{Wt. } \underline{\text{AN107}} \text{ AQ-50} = \underline{64.6172} \text{ g} \quad (1.37\text{A})$$

Also weigh just the bottom part of the filter unit; i.e., the receiving bottle and cap

$$\text{Wt. receiving bottle\&cap} = \underline{41.6631} \text{ g} \quad (1.37\text{B})$$

1.38 Connect AN107-AQ-50 to the vacuum line

1.39 Filter the wash slurry

1.40 Disconnect from the vacuum once the liquid has filtered

1.41 Place the cap on the top of the filter unit and weigh AN107-AQ-50

$$\text{Wt. } \underline{\text{AN107}} \text{ AQ-50} = \underline{84.0187} \text{ g} \quad (1.41\text{A})$$

Carefully remove the funnel part of the apparatus from the receiving bottle, place the cap on the receiving bottle and weigh.

$$\text{Wt. receiving bottle\&cap} = \underline{59.5940} \text{ g} \quad (1.41\text{B})$$

Transfer two 10-mL aliquots of the filtered solution to clean 20-mL HDPE sample vials labeled as AN107-AQ-50A and AN107-AQ-50B.

*(remainder kept in -AQ-50 for observation)*

2/19/99 9:00  
solution was clear  
3/29/99 13:00  
solution still clear

Note: Monitor the solution after ~24 h to determine if any solids form.

1.42 Determine the total weight of the slurry

$$\text{Wt. Slurry} = 1.41\text{A} - 1.37\text{A} = \underline{19.4015} \text{ g} \quad (1.42\text{A})$$

Determine the weight of the filtered liquid

$$\text{Wt. Liquid} = 1.41\text{B} - 1.37\text{B} = \underline{17.9309} \text{ g} \quad (1.42\text{B})$$

Determine the weight of the filtered solids

$$\text{Wt. Solids} = 1.42\text{A} - 1.42\text{B} = \underline{1.4706} \text{ g} \quad (1.42\text{C})$$

1.43 Measure out the appropriate volume of 0.01 M NaOH as instructed by the cognizant scientist into a plastic bottle

*will use 5 x 4 mL*

$$\text{Vol. Used} = \underline{20} \text{ mL} \quad (1.43\text{A})$$

*A. Smith  
2/18/99*

1.45 Weigh AN107-AQ-20

$$\text{Wt. } \underline{\text{AN107}}\text{-AQ-20} = \underline{17.3471} \text{ g} \quad (1.45\text{A})$$

1.46 Slurry the filtered solids using a portion of 0.01 M NaOH (volume = 1.43A + 5); transfer ~~the~~ this slurry to AN107-AQ-20 *NOTE: The solids came up off of the filter easily. Flaked off in fairly large chunks; these were easily broken into smaller pieces.*

1.47 Repeat step 1.46 four times to ensure complete transfer of the solids to AN107-AQ-20

1.48 Weigh AN107-AQ-20

$$\text{Wt. } \underline{\text{AN107}}\text{-AQ-20} = \underline{31.8130} \text{ g} \quad (1.48\text{A})$$

Determine the weight of the slurry

$$\text{Wt. Slurry} = 1.48\text{A} - 1.45\text{A} = \underline{19.4659} \text{ g} \quad (1.48\text{B})$$

1.49 Equip AN107-AQ-20 with a condenser, then place in an aluminum heating block at 85°C

1.50 Stir the sample in AN107-AQ-20 at 85°C for a minimum of 8 hours

Start date/time: 3/18/99 9:40  
Stop date/time: 3/19/99 7:45

1.51 Allow to cool to ambient temperature

1.52 Remove the condenser and replace the original cap on AN107-AQ-20.  
Weigh AN107-AQ-20

$$\text{Wt. } \underline{\text{AN107}}\text{-AQ-20} = \underline{31.7128} \text{ g} \quad (1.52\text{A})$$

Determine mass loss due to evaporation

$$\text{Wt. Lost} = 1.52\text{A} - 1.48\text{A} = \underline{0.1002} \text{ g} \quad (1.52\text{B})$$

1.53 Label a disposable filter unit (0.45- $\mu\text{m}$  nylon) as AN107-AQ-70

1.54 Weigh AN107-AQ-70

$$\text{Wt. } \underline{\text{AN107}}\text{-AQ-70} = \underline{64.9438} \text{ g} \quad (1.54\text{A})$$

Also weigh just the bottom part of the filter unit; i.e., the receiving bottle and cap

$$\text{Wt. receiving bottle\&cap} = \underline{41.5548} \text{ g} \quad (1.54\text{B})$$

1.55 Connect AN107-AQ-70 to the vacuum line

1.56 Filter the wash slurry *NOTE: A few drops of slurry stuck to threads of AN107-AQ-20. To recover this, rinsed them into filter funnel with 0.01M NaOH.*

1.57 Disconnect from the vacuum once the liquid has filtered

*M. J. Smith*  
3/19/99

1.58 Place the cap on the top of the filter unit and weigh AN107-AQ-70

$$\text{Wt. } \underline{\text{AN107}}\text{-AQ-70} = \underline{84.316}^{\text{43}} \text{ g} \quad \text{M.L. 3/19/99} \quad (1.58\text{A})$$

Carefully remove the funnel part of the apparatus from the receiving bottle, place the cap on the receiving bottle and weigh.

$$\text{Wt. receiving bottle\&cap} = \underline{59.6993} \text{ g} \quad (1.58\text{B})$$

Transfer two 10-mL aliquots of the filtered solution to clean 20-mL HDPE sample vials labeled as AN107-AQ-70A and AN107-AQ-70B. *Remainder kept in AN107-AQ-70 for observation.*

Note: Monitor the solution after ~24 h to determine if any solids form.

*3/29/99 13:00 solution clear.*

1.59 Determine the total weight of the slurry

$$\text{Wt. Slurry} = 1.58\text{A} - 1.54\text{A} = \underline{19.3705} \text{ g} \quad (1.59\text{A})$$

Determine the weight of the filtered liquid

$$\text{Wt. Liquid} = 1.58\text{B} - 1.54\text{B} = \underline{18.1445} \text{ g} \quad (1.59\text{B})$$

Determine the weight of the filtered solids

$$\text{Wt. Solids} = 1.59\text{A} - 1.59\text{B} = \underline{1.2260} \text{ g} \quad (1.59\text{C})$$

1.60 Measure out the appropriate volume of 0.01 M NaOH as instructed by the cognizant scientist into a plastic bottle

$$\text{Vol. Used} = \underline{20} \text{ mL} \quad \text{will use } 5 \times 4 \text{ mL} \quad (1.60\text{A})$$

1.62 Weigh AN107-AQ-20

$$\text{Wt. } \underline{\text{AN107}}\text{-AQ-20} = \underline{12.4195} \text{ g} \quad (1.62\text{A})$$

1.63 Slurry the filtered solids using a portion of 0.01 M NaOH (volume = 1.60A + 5); transfer this slurry to AN107-AQ-20 *###*

1.64 Repeat step 1.63 four times to ensure complete transfer of the solids to AN107-AQ-20

1.65 Weigh AN107-AQ-20

$$\text{Wt. } \underline{\text{AN107}}\text{-AQ-20} = \underline{32.4594} \text{ g} \quad (1.65\text{A})$$

Determine the weight of the slurry

$$\text{Wt. Slurry} = 1.65\text{A} - 1.62\text{A} = \underline{20.0399} \text{ g} \quad (1.65\text{B})$$

1.66 Equip AN107-AQ-20 with a condenser, then place in an aluminum heating block at 85°C

*Paused here (3/19/99). will resume on 3/29. M.L. Lumsden 3/19/99*

1.67 Stir the sample in AN107-AQ-20 at 85°C for a minimum of 8 hours

Start date/time: 3/29/99 13:10  
Stop date/time: 3/30/99 7:30

1.68 Allow to cool to ambient temperature

1.69 Remove the condenser and replace the original cap on AN107-AQ-20.  
Weigh AN107-AQ-20

$$\text{Wt. } \underline{\text{AN107}}\text{-AQ-20} = \underline{32.2298} \text{ g} \quad (1.69\text{A})$$

Determine mass loss due to evaporation

$$\text{Wt. Lost} = 1.65\text{A} - 1.69\text{A} = \underline{0.2296} \text{ g} \quad (1.69\text{B})$$

1.70 Label a disposable filter unit (0.45- $\mu\text{m}$  nylon) as AN107-AQ-90

1.71 Weigh AN107-AQ-90

$$\text{Wt. } \underline{\text{AN107}}\text{-AQ-90} = \underline{64.2538} \text{ g} \quad (1.71\text{A})$$

Also weigh just the bottom part of the filter unit; i.e., the receiving bottle and cap

$$\text{Wt. receiving bottle\&cap} = \underline{41.3462} \text{ g} \quad (1.71\text{B})$$

1.72 Connect AN107-AQ-90 to the vacuum line

1.73 Filter the wash slurry

1.74 Disconnect from the vacuum once the liquid has filtered

1.75 Place the cap on the top of the filter unit and weigh AN107-AQ-90

$$\text{Wt. } \underline{\text{AN107}}\text{-AQ-90} = \underline{83.9379} \text{ g} \quad (1.75\text{A})$$

Carefully remove the funnel part of the apparatus from the receiving bottle, place the cap on the receiving bottle and weigh.

$$\text{Wt. receiving bottle\&cap} = \underline{59.7647} \text{ g} \quad (1.75\text{B})$$

Transfer two 10-mL aliquots of the filtered solution to clean 20-mL HDPE sample vials labeled as AN107-AQ-90A and AN107-AQ-90B. *Reminder kept in AN107-AQ-90. N.H. 3/30/99*

Note: Monitor the solution after ~24 h to determine if any solids form.

*Solution still clear at 10:20 on 4/5/99*

1.76 Determine the total weight of the slurry

$$\text{Wt. Slurry} = 1.75\text{A} - 1.71\text{A} = \underline{19.6841} \text{ g} \quad (1.76\text{A})$$

*N.H. 3/30/99*

3/29/99  
A.1.2.

Determine the weight of the filtered liquid

$$\text{Wt. Liquid} = 1.75\text{B} - 1.71\text{B} = \underline{18.4185} \text{ g} \quad (1.76\text{B})$$

Determine the weight of the filtered solids

$$\text{Wt. Solids} = 1.76\text{A} - 1.76\text{B} = \underline{1.2654} \text{ g} \quad (1.76\text{C})$$

- 1.77 Label a glass vial as AN107-AQ-100
- 1.78 Dry AN107-AQ-100 at 105°C for a minimum of 1 h
- 1.79 Cool AN107-AQ-100 to ambient temperature in a desiccator
- 1.80 Weigh AN107-AQ-100

$$\text{Wt. AN107-AQ-100} = \underline{22.0353} \text{ g} \quad (1.80\text{A})$$

- 1.81 Using several <sup>4-ml portions (x5)</sup> portions of deionized water, quantitatively transfer the washed solids from the filter membrane to AN107-AQ-100. *Note: There was a small amount of solids that stuck to the magnetic stir bar.*

- 1.82 Weigh AN107-AQ-100

$$\text{Wt. AN107-AQ-100} = \underline{41.1294} \text{ g} \quad (1.82\text{A})$$

- 1.82 Heat AN107-AQ-100 at 80°C to evaporate excess water
- 1.83 Heat AN107-AQ-100 at 105°C overnight
- 1.84 Cool AN107-AQ-100 to ambient temperature in a desiccator
- 1.85 Weigh AN107-AQ-100

$$\text{Wt. AN107-AQ-100} = \underline{22.1414} \text{ g} \quad (1.85\text{A})$$

- 1.86 Determine the dry weight of the washed solids

$$\text{Wt. Dry Solids} = 1.85\text{A} - 1.82\text{A} = \underline{0.1061} \text{ g} \quad (1.86\text{A})$$

- 1.87 The washed solids are to be submitted for analysis. The cognizant scientist will prepare the required ASR.

A.1. Punnett  
4/5/99

(A) Note: Two aliquots of solids were taken for fusion preps. The combined weight of these was greater than 0.1061g. Specifically it was 0.0503 + 0.0659 = 0.1162g. This might have been due to reabsorption of water. The 0.1162g value was used for data work up due to the fact that this is what the

Per instructions from BFL, Part 2 (Constant Leaching, pp. 13-15) were not performed.

A.1. Punnett 8/11/99

## **Appendix B. Raw Data**

Analytical Chemistry Laboratory (ACL) Analytical Services Request (ASR)  
(Cover Page ... information applicable to all samples in series)

Requested By: Gregg J. Lumetta Gregg J. Lumetta 3/31/99 376-6911 P7-25  
Print Name Signature/Date Phone MSIN

Requester - Please Complete All Fields In This Section, Unless Specified "Optional" or ASR is a Revision

Request ID (optional): \_\_\_\_\_

PNL Project Number (if known): 29953

Work Order/Pkg.: W48481

Cost Estimate (\$): \_\_\_\_\_

Protocol Requirement:  None  RCRA  CERCLA, or

Other (specify): \_\_\_\_\_

Hold Time Requirement:  None  RCRA  CERCLA, or

Other (specify): \_\_\_\_\_

TPA Support:  No, or

Milestone No.: \_\_\_\_\_

QA Plan:  MCS-033, or

Other ACL QA Plan (specify): \_\_\_\_\_

Additional QA Requirements:  No, or

Reference Doc.: \_\_\_\_\_

ACL COC Req'd (PNL-ALO-010):  No  Yes

Sample Storage Requirements:  No  Refrigerate, or

Other (specify): \_\_\_\_\_

Date Sampled (optional): \_\_\_\_\_

Time Sampled (optional): \_\_\_\_\_

Matrix:  Samples vary (specify on Request Page), or

Liquid:  Aqueous  Organic  Multi-phasic

Solid:  Soil  Sludge  Sediment  Glass

Filter  Smear  Metal  Organic  Other Solids

Solid/Liquid Mixture:  Gas:

Biological:  Tissue  Urine  Feces

Process Knowledge:  Sample Information Check List, or

Reference Doc.: See ASR 5275

PCBs Present:  No  Yes

Sample Disposition ...

Untreated Sample(s):  Return  Dispose  Store, or

Reference Doc.: \_\_\_\_\_

Prep'd Sample(s):  Dispose  Return  Store, or

Reference Doc.: \_\_\_\_\_

Additional Instructions:  No, or

Reference Doc.: \_\_\_\_\_

Date Report Req'd: 5/14/99

Send Report to: G.J. Lumetta

MSIN: P7-25 Phone: \_\_\_\_\_

Fax (optional): \_\_\_\_\_

For ACL Use Only ... Do Not Complete This Section

Date Delivered: \_\_\_\_\_

Time Delivered (optional): \_\_\_\_\_

Deliv. By (if known): \_\_\_\_\_

Received By: \_\_\_\_\_

Resp. ACL Mgr.: \_\_\_\_\_

Signature/Date: \_\_\_\_\_

Job Group (optional): \_\_\_\_\_

Sample Group (optional): \_\_\_\_\_

PNL Impact Level:  1  2  3

DQ Review Req'd:  No  Yes ACL Waste:  No  Yes

ASR Number: \_\_\_\_\_ Revision:  Yes

ACL Numbers: \_\_\_\_\_



**Lumetta, Gregg J**

**From:** Lumetta, Gregg J  
**Sent:** Thursday, April 08, 1999 2:13 PM  
**To:** Steele, Rick T  
**Cc:** Urie, Michael W  
**Subject:** Sample AN107-AQ-100

Rick:

This message is to document our conversation this morning.

There is only ~0.1 g of solids in sample AN107-AQ-100, therefore you cannot do all the analyses originally requested on the ASR.

Regarding sample prep for this material, the priorities are to do the 1) KOH fusion and 2) the Na<sub>2</sub>O<sub>2</sub> fusion (forget about doing duplicates).

Accordingly, weigh out ~0.05 g for the KOH fusion and ~0.05 g for the Na<sub>2</sub>O<sub>2</sub> fusion. If you can't get the latter amount for the Na<sub>2</sub>O<sub>2</sub> fusion, get all that you can and use it for the KOH fusion. Note: To the extent possible, use reduced dilution volumes from the fusion preps so as not to over-dilute the samples.

Thanks.

Gregg

**Battelle PNNL/325 Bldg/RPG/Inorganic Analysis ...  
ICPAES Data Report**

**Project:** 29953  
**Client:** G. J. Lumetta

-----  
**ACL Number(s): 99-1295 through 99-1297, 99-1300 and  
99-1454 through 99-1457**  
-----

**Client ID: "AN107-SOL-30-1" through "AN107-SOL-40-1", "AN107-SOL-50-2" and  
"AN107-AQ-30" through "AN107-AQ-90"**  
-----

**ASR Number: 5294 & 5319**  
-----

**Total Samples: 8**  
-----

**Procedure:** PNL-ALO-211, "Determination of Elements by Inductively Coupled  
Argon Plasma Atomic Emission Spectrometry" (ICP-AES).

**Analyst:** J. J. Wagner

**Analysis Date (Filename):** 4-15-99 (A0523)

**See system file: "ICP-325-405-1" for traceability to Calibration,  
Quality Control, Verification, and Raw Data.**

**M&TE Number:** ICPAES instrument -- WB73520  
Mettler AT400 Balance -- Ser.No. 360-06-01-029

*Jerry Wagner* 4-20-99  
Reviewed by

*MW* 4/21/99  
Concur

4/20/99

**Battelle PNNL/325 Bldg/RPG/Inorganic Analysis ...  
ICPAES Data Report**

Four radioactive liquid samples, AN107-SOL-30-1 through AN107-SOL-50-2, were analyzed by ICPAES after preparation by the Sample Receiving and Preparation Laboratory (SRPL) using PNNL-ALO-128 Acid Digestion procedure. The liquid content of each sample vial was transferred to a digestion vessel prior to treatment using a plastic transfer pipette and distilled deionized water. Individual sample weights were obtained by subtracting the empty, dry sample vial weight from the weight of the vial containing the original liquid sample. Approximately 1.6 to 2.6 grams of aqueous sample (AN107-SOL-30-1 through AN107-SOL-50-2) was digested and diluted to a final volume of 25 ml. Sample AN107-SOL-50-2 contained a small amount of solids and liquid. The solids dissolved on contact with water during sample transfer. Additional dilution, up to 30 fold, was performed during ICPAES analysis. All measurement results reported have been corrected for preparation and analytical dilution. Analytical results are reported as  $\mu\text{g/g}$  as agreed to by the client. Analytes of interest (ASR 5294) include Al, Cr, Fe, Mn, Na, Ni, P, and Si.

Sample AN107-AQ-30 through AN107-AQ-90 was also prepared by SRPL using PNNL-ALO-128 Acid Digestion procedure. Approximately 4.5 or 5ml aliquots of aqueous sample was pipetted (and weighed), digested and diluted to a final volume of 25 ml. Additional dilution up to 10 fold was performed during ICPAES analysis. Analytes of interest for ASR 5319 include Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Ti, U, Zn, and Zr. All measurement results reported have been corrected for preparation and analytical dilutions and reported as  $\mu\text{g/ml}$ .

All quality control checks met MCS-033 QC tolerance requirements for analytes of interest except as noted below. Following is a list of quality control check measurement results relative to ICPAES analysis requirements under MCS-033.

**Five fold serial dilution:**

(Solid samples)      --

(Aqueous samples)

All results are within tolerance limit of  $\leq 10\%$  after correcting for dilution except sample 99-1296 @10 and 99-1296 @2 dilution (AN107-SOL-30-2). The following analyte concentration was recovered within 11% after dilution correction: Chromium, Iron, Manganese, and Nickel.

4/20/99

**Battelle PNNL/325 Bldg/RPG/Inorganic Analysis ...  
ICPAES Data Report**

**Duplicate RPD (Relative Percent Difference):**

(Solid samples) --  
(Aqueous samples) Duplicate samples were within MCS-033 tolerance limit of  $\leq 20\%$  RPD (Relative Percent Difference) except Silicon (32% RPD) in sample AN107-SOL-30-1. Silicon concentration in all samples was low and similar to the concentration found in the process blank. The source of Si is probably from labware used to digest samples.

**Post-Spiked Samples (Group A):**

(Solid samples) --  
(Aqueous samples) All analytes of interest were recovered within MCS-033 tolerance of 75 to 125%.

**Post-Spiked Samples (Group B):**

(Solid samples) --  
(Aqueous samples) All analytes of interest were recovered within MCS-033 tolerance of 75 to 125%.

**Blank Spike:**

(Solid samples) --  
(Aqueous samples) A blank spike was not prepared.

**Matrix Spiked Sample:**

(Solid samples) --  
(Aqueous samples) A matrix spike was not prepared.

**Quality Control Check Standards:**

Concentration of all analytes of interest, with one exception, was recovered within MCS-033 tolerance of  $\pm 10\%$  accuracy in the standards: QC\_MCVA, QC\_MCVB, and QC\_SSTMV. Calibration Blank (ICP98.0) concentration was less than two times IDL. The one exception was Silicon which was slightly high (about 11%) in QC\_SSTMV. All Si concentrations found in samples were about the same as that found in the preparation blank

**4/20/99**

**Battelle PNNL/325 Bldg./RPG/Inorganic Analysis ...  
ICPAES Data Report**

**High Calibration Standard Check:**

Verification of the high-end calibration concentration for all analytes of interest was within MCS-033 tolerance of  $\pm 5\%$  accuracy.

**Process Blank:**

(Solid samples)

--

(Aqueous samples)

All analytes of interest were within MCS-033 tolerance limit of  $\leq$  EQL or  $< 5\%$  of sample concentration except Silicon. The concentration of Silicon in all samples was about the same as that found in the process blank. Silicon contamination is low in concentration and probably due to labware (glass) used in preparing samples.

**Laboratory Control Standard:**

(Solid samples)

--

(Aqueous samples)

LCS not supplied.

Analytes other than those requested by the client are for information only. Please note bracketed values listed in the data report are within ten times instrument detection limit and have a potential uncertainty much greater than 15%.

**Comments:**

- 1) "Final Results" have been corrected for all laboratory dilution performed on the sample during processing and analysis unless specifically noted.
- 2) Detection limits (DL) shown are for acidified water. Detection limits for other matrices may be determined if requested.
- 3) Routine precision and bias is typically  $\pm 15\%$  or better for samples in dilute, acidified water (e.g. 2% v/v HNO<sub>3</sub> or less) at analyte concentrations greater than ten times detection limit up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000  $\mu\text{g/mL}$  (0.5 per cent by weight).
- 4) Absolute precision, bias and detection limits may be determined on each sample if required by the client.
- 5) The maximum number of significant figures for all ICP measurements is 2.

4/20/99

Multiplie#	10.0	19.6	19.7	23.2	31.3
ALO#	PROCESS BLANK	99-1295 @2	99-1296 @2	99-1297 @2	99-1300 @2
Client ID	(99-1295 & -1454 batch)	AN107-SOL-30-1	AN107-SOL-30-2	AN107-SOL-40-1	AN107-SOL-50-2
Det. Limit (ug/mL)	Run Date= (Analyte)	4/15/99 ug/g	4/15/99 ug/g	4/15/99 ug/g	4/15/99 ug/g
0.015	Ag	-	-	-	-
0.060	Al	[2.5]	2,900	3,000	3,320
0.080	As	-	[5.0]	[5.3]	[4.9]
0.050	B	26.8	41.5	38.4	63.2
0.010	Ba	-	2.33	2.47	[2.8]
0.010	Be	-	-	-	-
0.100	Bi	-	-	-	-
0.100	Ca	[3.2]	330	341	376
0.015	Cd	-	35.8	36.9	40.5
0.100	Ce	-	[19]	20.5	[22]
0.025	Co	-	[2.6]	[2.7]	[3.0]
0.020	Cr	-	106	110	123
0.015	Cu	-	15.4	16.0	17.8
0.050	Dy	-	-	-	-
0.100	Eu	-	-	-	-
0.025	Fe	-	709	752	833
2.000	K	-	894	931	1,030
0.025	La	-	14.3	15.0	16.6
0.005	Li	-	[0.39]	[0.39]	[0.47]
0.100	Mg	-	-	-	-
0.005	Mn	-	55.7	58.7	63.3
0.030	Mo	-	-	-	-
0.100	Na	30.6	133,000	143,000	147,000
1.100	Nd	-	48.4	50.5	53.7
0.030	Ni	-	289	298	328
0.100	P	-	375	389	420
0.060	Pb	-	181	189	207
0.300	Pd	-	[27]	[28]	[30]
0.300	Rh	-	[6.8]	[7.3]	-
0.075	Ru	-	21.1	21.8	24.0
0.050	Sb	-	[1.8]	[1.7]	[2.2]
0.050	Se	-	[2.4]	[2.6]	[2.9]
0.100	Si	44.8	55.3	40.2	79.9
1.000	Sn	-	-	-	-
0.005	Sr	-	1.81	1.87	2.09
0.500	Te	-	-	-	-
0.800	Th	-	-	-	-
0.005	Ti	-	[0.47]	[0.49]	[0.58]
0.250	Tl	-	-	-	-
2.000	U	-	[77]	[83]	[90]
0.015	V	-	[0.40]	[0.42]	[0.48]
0.500	W	-	[96]	99.5	[110]
0.010	Y	-	7.90	8.23	8.73
0.020	Zn	-	11.0	11.4	13.7
0.025	Zr	-	32.3	33.7	36.0

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.  
 2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.  
 3) "-" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

Multiplier= ALO#= Client ID= Run Date= (ug/mL) (Analyte)	5.0 PROCESS BLANK (99-1295 & -1454 batch) 4/15/99 (ug/mL)	5.0 99-1454 AN107-AQ-30 4/15/99 (ug/mL)	5.0 99-1455 AN107-AQ-50 4/15/99 (ug/mL)	5.6 99-1456 AN107-AQ-70 4/15/99 (ug/mL)	5.0 99-1457 AN107-AQ-90 4/15/99 (ug/mL)
0.015	Ag	-	-	-	-
0.060	Al	[1.2]	1,140	83.4	44.6
0.080	As	-	[1.3]	-	28.2
0.050	B	13.4	18.0	16.4	-
0.010	Ba	-	-	-	11.8
0.010	Be	-	-	-	-
0.100	Bi	-	-	-	-
0.100	Ca	[1.6]	70.0	[1.3]	-
0.015	Cd	-	7.26	[0.29]	[0.62]
0.100	Ce	-	-	-	-
0.025	Co	-	[0.55]	-	-
0.020	Cr	-	59.8	17.1	-
0.015	Cu	-	3.76	[0.27]	10.2
0.050	Dy	-	-	-	[0.11]
0.100	Eu	-	-	-	-
0.025	Fe	-	3.06	[0.62]	4.86
2.000	K	-	183	-	9.02
0.025	La	-	[0.48]	-	-
0.005	Li	-	[0.072]	-	-
0.100	Mg	-	-	-	-
0.005	Mn	-	0.978	[0.15]	0.833
0.030	Mo	-	-	-	1.57
0.100	Na	15.3	32,900	1,500	-
1.100	Nd	-	[1.1]	-	354
0.030	Ni	-	58.6	2.14	243
0.100	P	-	73.9	[3.0]	[0.18]
0.060	Pb	-	46.0	[1.9]	-
0.300	Pd	-	-	-	[0.43]
0.300	Rh	-	-	-	-
0.075	Ru	-	4.07	-	-
0.050	Sb	-	[0.44]	-	-
0.050	Se	-	[0.57]	-	-
0.100	Si	22.4	17.3	24.9	23.9
1.000	Sn	-	-	-	16.6
0.005	Sr	-	[0.25]	-	-
0.500	Te	-	-	-	-
0.800	Th	-	-	-	-
0.005	Ti	-	[0.029]	-	-
0.250	Tl	-	-	-	-
2.000	U	-	[16]	-	-
0.015	V	-	-	-	-
0.500	W	-	[24]	-	-
0.010	Y	-	0.530	-	-
0.020	Zn	-	2.36	[0.26]	-
0.025	Zr	-	-	-	[0.14]

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.  
 2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.  
 3) "-" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

**SAMPLE PREP SHEET**  
**(325 SHIELDED ANALYTICAL LABORATORY)**

TI/ARF NO.: ASR 5319 PROJECT NO.: 29953 WBS NO.: \_\_\_\_\_ SAMPLE TYPE: Solids

ISSUED BY: RT Steele DATE: 4/14/99 PREP TYPE: Ni/KOH Fusion (ALO-115)

ANALYST: *[Signature]* DATE: 4-19-99 CHAIN OF CUSTODY RQD: No

REVIEW: *[Signature]* DATE: 4/20/99 QA PLAN: MCS-033 IMPACT LEVEL: \_\_\_\_\_

CLIENT: GJ Lumetta CORE ID: N/A TANK ID: AN107

WORK PACKAGE NUMBER	ALO NUMBER	SAMPLE IDENTIFICATION	ANALYTE OR ANALYSIS	SAMPLE WT	Sp.G. (g/mL)	WATER WT (g)	TOTAL VOL (mL)	SPIKE ID	SPIKE VOL (mL)	DILUTION FACTOR	DILUTION MATRIX	PIPET CALIB (mL)	MISC
W48481	99-1458-PB	PROCESS BLANK	SEE BELOW	0.0503			5.0						
	99-1458	AN107-AQ-100		0.0659									
	SRM 2710	LCS/99-1458/Ni											
			ICP-AES										
			ICP-MS (Tc-99)										
			GEA										
			Sr-90										
			GROSS ALPHA										
			U-LASER										

# PNL-ALO-115

## Solubilization of Metals from Solids Using a KOH-KNO3 Fusion

Client name: GJ Lumetta

Work package number: W48481

Work Auth. Doc (WAD): ASR 5319

Project number: 29953

Tank/Core/Project: BNFL

PNL QA plan: MCS-033

Special Instructions

PNL impact level:

Prep. lab (SAL/SRPL/other): SAL

Preparation batch number:

ACL Sample ID	ACL order number or Client sample ID	Crucible Identifier	Crucible weight (g)	Crucible + sample weight (g)	Sample weight (g)	Vol. (ml)	Spike added Weight (g)	Final solution Volume (ml)	Process Factor (1)
1 99-1458-PB	Process Blank	6						50	
2 99-1458	AN107-AQ-100	1	33.1257	33.1760	0.0503				994.04
3 SRM 2710	LCS/99-1458/Ni	2	31.1330	34.1989	0.0659				758.73
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									

Analyst's sample preparation comments:

DOSE RATE:

Spike source:

AN107 spl. was heavy dark reddish-brown color. Added An Additions ( PNL spike ID number: )  
ml of Hydroxylamine + heated & cleared up nicely  
Anal. balance M&TE360.06.01.016

HCl volume added (ml): 1 ml

Solution heated (yes/no): y-n

Sample filtered (yes/no): no

(1) Process factor = Final volume (ml) / [ Crucible & sample weight (g) - Crucible weight (g) ]

Other sample preparation worksheets may be substituted at the discretion of the Cognizant Scientist. Use one worksheet per client.

Analyst/Date: *[Signature]* 11.15.99 Reviewer/Date: *[Signature]* 4/20/99



**PNL-ALO-114**

**Solubilization of Metals from Solids Using a Na2O2-NaOH Fusion**

Client name: GJ Lumetta

Work Auth. Doc (WAD): ASR 5319

Tank/Core/Project: BNFL

Special instructions

Work package number: W48481

Project number: 29953

PNL QA plan: MCS-033

PNL impact level:

Prep. lab (SAL/SRPL/other): SAL

Preparation batch number:

1	ACL Sample ID	ACL order number or Client sample ID	Crucible Identifier	Crucible weight (g)	Crucible + sample weight (g)	Sample weight (g)	Vol. (ml)	Spike added		Process Factor (1)
								Weight (g)	Final solution Volume (ml)	
1	99-1458-Zr-PB	Process Blank	B					50		
2	99-1458-Zr	AN107-AQ-100	1	34.6694	34.7310	0.0614				814.33
3	SRM 2710-Zr	LCS99-1458Zr	2	34.3052	34.3602	0.0550				909.09
4										
5										
6										
7										
8										
9										
10										
11										
12										
13										
14										

Analyst's sample preparation comments:

DOSE RATE:

Spike source:

PNL spike ID number:

Anal. balance M&TE: 360-06-01-016

HCl volume added (ml): 1

Solution heated (yes/no): YES

Sample filtered (yes/no): NO

(1) Process factor = Final volume (ml) / (Crucible + sample weight (g) - Crucible weight (g))

Other sample preparation worksheets may be substituted at the discretion of the Cognizant Scientist. Use one worksheet per client.

Analys/Date: *[Signature]* 4-16-99. Reviewer/Date: *[Signature]* 4/20/99

**Battelle PNNL/325 Bldg/RPG/Inorganic Analysis ...  
ICPAES Data Report**

**Project:** 29953  
**Client:** G. J. Lumetta

-----  
**ACL Number(s):** 99-1161, 99-1458-Zr & 99-1458-Ni  
-----

**Client ID:** "AW101-AQ-100d", "AN107-AQ-100"(Zr) & "AN107-AQ-100"(Ni)  
-----

**ASR Number:** 5275 & 5319  
-----

**Total Samples:** 3  
-----

**Procedure:** PNL-ALO-211, "Determination of Elements by Inductively Coupled Argon Plasma Atomic Emission Spectrometry" (ICP-AES).

**Analyst:** J. J. Wagner

**Analysis Date (Filename):** 4-22-99 (A0524) and 4-27-99 (A0525).

**See system file:** "ICP-325-405-1" for traceability to Calibration, Quality Control, Verification, and Raw Data.

**M&TE Number:** ICPAES instrument -- WB73520  
Mettler AT400 Balance -- Ser.No. 360-06-01-029

 5-4-99  
Reviewed by

 5-4-99  
Concur

5/4/99  
!

**Battelle PNNL/325 Bldg/RPG/Inorganic Analysis ...  
ICPAES Data Report**

One radioactive solid sample AN107-AQ-100 (ASR 5319) was analyzed by ICPAES after preparation by the 325 Shielded Analytical Laboratory (SAL) using two fusion preparation procedures: PNNL-ALO-114 Na<sub>2</sub>O<sub>2</sub>-NaOH/Zr and PNNL-ALO-115 KOH/Ni. Approximately 0.05 to 0.06-gram aliquots were used for each procedure. After samples were fused they were diluted to a final volume of 50 ml. Additional dilution, up to 10 fold, was performed during ICPAES analysis. All measurement results reported have been corrected for preparation and analytical dilution. Because of limited sample material, duplicates were not prepared. Analytes of interest include Ag, Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Ti, U, Zn and Zr.

Sample AW101-AQ-100d (ASR 5275) was prepared by the client and analyzed by ICPAES without further processing other than necessary analytical dilution up to 5-fold. Analytes of interest are the same as those listed above. Measurement results have been corrected for analytical dilution only. Results are reported as µg/ml as agreed upon by the client.

All quality control checks met tolerance requirements for analytes of interest except as noted below. Following is a list of quality control check measurement results relative to ICPAES analysis tolerance requirements under MCS-033.

**Five fold serial dilution:**

(Solid samples) All results are within tolerance limit of  $\leq 10\%$  after correcting for dilution.

(Aqueous samples) All results were within tolerance limit of  $\leq 10\%$  after correcting for dilution except Mg in sample AW101-AQ-100d @5 and AW101-AQ-100d @1. Mg concentration was recovered within 13% after dilution correction. All other analytes of interest in the above sample were within 4% after dilution correction.

**Duplicate RPD (Relative Percent Difference):**

(Solid samples) No duplicates were prepared because of limited sample material.

(Aqueous samples) No duplicates were provided.

**Post-Spiked Samples (Group A):**

(Solid samples) All analytes of interest were recovered within tolerance of 75 to 125%.

(Aqueous samples) All analytes of interest were recovered within tolerance of 75 to 125%.

5/4/99

**Battelle PNNL/325 Bldg/RPG/Inorganic Analysis ...  
ICPAES Data Report**

**Post-Spiked Samples (Group B):**

(Solid samples) All analytes of interest were recovered within tolerance of 75 to 125%.

(Aqueous samples) All analytes of interest were recovered within tolerance of 75 to 125%.

**Blank Spike:**

(Solid samples) A blank spike was not prepared.

(Aqueous samples) A blank spike was not provided.

**Matrix Spiked Sample:**

(Solid samples) A matrix spike was not prepared.

(Aqueous samples) A matrix spike was not provided.

**Quality Control Check Standards:**

Concentration of all analytes of interest, except for Si, was recovered within tolerance of  $\pm 10\%$  accuracy in the standards: QC\_MCVA, QC\_MCVB, and QC\_SSTMVCV. Calibration Blank (ICP98.0) concentration was less than two times IDL. Silicon was slightly high (about 14%) in one determination of QC\_SSTMVCV. Silicon in QC\_MCVA check standard was within 5% of the true value of 20  $\mu\text{g/ml}$ , which was run several times during the analysis, thus, measurement results for Silicon in the samples are not likely to be affected.

**High Calibration Standard Check:**

Verification of the high-end calibration concentration for all analytes of interest was within tolerance of  $\pm 5\%$  accuracy except for Ca, Fe, and U. These three analytes were slightly high, between 6% and 7%, in the high-end cal. check standard. Measurement results for these analytes in the samples were closer to mid-range concentrations like those found in QC\_MCVA. Therefore, sample measurement results are not likely to be affected by the slightly high recovery for Ca, Fe, and U.

**5/4/99**

**Battelle PNNL/325 Bldg/RPG/Inorganic Analysis ...  
ICPAES Data Report**

**Process Blank:**

(Solid samples)

All analytes of interest were within tolerance limit of  $\leq$  EQL or  $<$  5% of sample concentration except Ca in ALO-114 prepared samples and Na in ALO-115 prepared samples. Concentration of Ca in the process blank for sample AN107-AQ-100 (Zr) was about 52% of that in the sample. Concentration of Na in the process blank for sample AN107-AQ-100 (Ni) was about 12% of that in the sample.

(Aqueous samples)

No preparation blank provided.

**Laboratory Control Standard:**

(Solid samples)

All analytes of interest at a concentration equal to or greater than EQL were recovered within tolerance of 75% to 125% in both fusion prepared LCS standards. SRM-2710 Montana Soil was used for the LCS in both ALO-114 and ALO-115 fusion preparations.

(Aqueous samples)

No LCS provided.

Analytes other than those requested by the client are for information only. Please note bracketed values listed in the data report are within ten times instrument detection limit and have a potential uncertainty much greater than 15%.

**Comments:**

- 1) "Final Results" have been corrected for all laboratory dilution performed on the sample during processing and analysis unless specifically noted.
- 2) Detection limits (DL) shown are for acidified water. Detection limits for other matrices may be determined if requested.
- 3) Routine precision and bias is typically  $\pm$  15% or better for samples in dilute, acidified water (e.g. 2% v/v HNO<sub>3</sub> or less) at analyte concentrations greater than ten times detection limit up to the upper calibration level. This also presumes that the total dissolved solids concentration in the sample is less than 5000  $\mu$ g/mL (0.5 per cent by weight).
- 4) Absolute precision, bias and detection limits may be determined on each sample if required by the client.
- 5) The maximum number of significant figures for all ICP measurements is 2.

5/4/99

# Battelle PNNL/RPG/Inorganic Analysis ... ICPAES Data Report Page 1 of 1

Det. Limit (ug/mL)	Run Date= (Analyte)	Multiplier= ALO#= Client ID= 814.3 99-1458-Zr-PB AN107-AQ-100	1900.1 99-1458-Zr @ 2.3333 AN107-AQ-100		
		4/22/99 ug/g	4/22/99 ug/g		
0.015	Ag	[12]	[52]	-	-
0.060	Al	[200]	18,800	-	-
0.080	As	-	[200]	-	-
0.050	B	[49]	-	-	-
0.010	Ba	[9.0]	1,410	-	-
0.010	Be	-	-	-	-
0.100	Bi	-	-	-	-
0.100	Ca	3,540	6,820	-	-
0.015	Cd	-	[69]	-	-
0.100	Ce	[150]	5,820	-	-
0.025	Co	-	-	-	-
0.020	Cr	[35]	9,160	-	-
0.015	Cu	[28]	[94]	-	-
0.050	Dy	-	-	-	-
0.100	Eu	-	-	-	-
0.025	Fe	366	245,000	-	-
2.000	K	[2,000]	-	-	-
0.025	La	[30]	1,940	-	-
0.005	Li	[29]	[57]	-	-
0.100	Mg	-	[1,200]	-	-
0.005	Mn	[7.3]	143,000	-	-
0.030	Mo	-	-	-	-
0.100	Nd	[100]	6,710	-	-
0.030	Ni	439	749	-	-
0.100	P	[96]	[1,300]	-	-
0.060	Pb	[85]	18,700	-	-
0.300	Pd	-	[3,300]	-	-
0.300	Rh	-	-	-	-
0.075	Ru	-	[450]	-	-
0.050	Sb	[96]	[210]	-	-
0.050	Se	[76]	[350]	-	-
0.100	Si	[380]	6,930	-	-
1.000	Sn	-	[3,500]	-	-
0.005	Sr	56.0	220	-	-
0.500	Te	-	-	-	-
0.800	Th	-	-	-	-
0.005	Ti	[10]	185	-	-
0.250	Tl	-	-	-	-
2.000	U	-	[4,000]	-	-
0.015	V	[13]	[45]	-	-
0.500	W	-	-	-	-
0.010	Y	-	811	-	-
0.020	Zn	-	1,670	-	-

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.  
 2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.  
 3) "-" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

# Battelle PNNL/RPG/Inorganic Analysis ... ICPAES Data Report

Det. Limit (ug/mL)	Multiplier=	994.0	4970.2		
Run Date=	ALO#=	99-1458-Ni-PB	99-1458-Ni @5		
(Analyte)	Client ID=	AN107-AQ-100	AN107-AQ-100		
	Run Date=	4/22/99	4/22/99		
	(Analyte)	ug/g	ug/g		
0.015	Ag	[15]	[90]	-	-
0.060	Al	[320]	20,000	-	-
0.080	As	[100]	-	-	-
0.050	B	[200]	[400]	-	-
0.010	Ba	-	1,470	-	-
0.010	Be	-	-	-	-
0.100	Bi	-	-	-	-
0.100	Ca	[150]	[2,200]	-	-
0.015	Cd	-	[84]	-	-
0.100	Ce	-	[4,300]	-	-
0.025	Co	[30]	-	-	-
0.020	Cr	[22]	10,100	-	-
0.015	Cu	[24]	[100]	-	-
0.050	Dy	-	-	-	-
0.100	Eu	-	-	-	-
0.025	Fe	388	273,000	-	-
0.025	La	[25]	1,990	-	-
0.005	Li	[15]	[68]	-	-
0.100	Mg	[100]	[740]	-	-
0.005	Mn	191	162,000	-	-
0.030	Mo	-	-	-	-
0.100	Na	3,820	26,500	-	-
0.100	Nd	[100]	6,540	-	-
0.100	P	[120]	[2,000]	-	-
0.060	Pb	[110]	15,900	-	-
0.300	Pd	-	[3,300]	-	-
0.300	Rh	-	-	-	-
0.075	Ru	-	[530]	-	-
0.050	Sb	[82]	[330]	-	-
0.050	Se	[110]	[570]	-	-
0.100	Si	1,640	7,470	-	-
1.000	Sn	-	-	-	-
0.005	Sr	-	[170]	-	-
0.500	Te	-	-	-	-
0.800	Th	-	-	-	-
0.005	Tl	[14]	[210]	-	-
0.250	Tl	-	-	-	-
2.000	U	-	-	-	-
0.015	V	-	-	-	-
0.500	W	-	-	-	-
0.010	Y	-	652	-	-
0.020	Zn	[39]	1,770	-	-
0.025	Zr	-	3,190	-	-

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.  
 2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.  
 3) "-" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

Det. Limit (ug/mL)	Multiplier= ALO#= Client ID= Run Date=	1.0 99-1161 @1 AW101-AQ-100d 4/22/99	(Analyte)	(ug/mL)				
0.015	Ag	0.881		-		-		-
0.060	Al	67.3		-		-		-
0.080	As	[0.12]		-		-		-
0.050	B	34.3		-		-		-
0.010	Ba	6.47		-		-		-
0.010	Be	[0.057]		-		-		-
0.100	Bi	2.61		-		-		-
0.100	Ca	53.2		-		-		-
0.015	Cd	2.62		-		-		-
0.100	Ce	[0.46]		-		-		-
0.025	Co	0.366		-		-		-
0.020	Cr	80.7		-		-		-
0.015	Cu	1.30		-		-		-
0.050	Dy	[0.11]		-		-		-
0.100	Eu	[0.15]		-		-		-
0.025	Fe	113		-		-		-
2.000	K	[5.0]		-		-		-
0.025	La	0.257		-		-		-
0.005	Li	0.098		-		-		-
0.100	Mg	4.80		-		-		-
0.005	Mn	105		-		-		-
0.030	Mo	-		-		-		-
0.100	Na	131		-		-		-
0.100	Nd	[0.46]		-		-		-
0.030	Ni	16.5		-		-		-
0.100	P	4.72		-		-		-
0.060	Pb	8.60		-		-		-
0.300	Pd	-		-		-		-
0.300	Rh	-		-		-		-
0.075	Ru	[0.34]		-		-		-
0.050	Sb	[0.090]		-		-		-
0.050	Se	[0.23]		-		-		-
0.100	Si	398		-		-		-
1.000	Sn	[3.5]		-		-		-
0.005	Sr	0.734		-		-		-
0.500	Te	-		-		-		-
0.800	Th	[4.5]		-		-		-
0.005	Ti	0.766		-		-		-
0.250	Tl	-		-		-		-
2.000	U	428		-		-		-
0.015	V	[0.058]		-		-		-
0.500	W	-		-		-		-
0.010	Y	[0.021]		-		-		-
0.020	Zn	15.5		-		-		-
0.025	Zr	17.3		-		-		-

Note: 1) Overall error greater than 10-times detection limit is estimated to be within +/- 15%.  
 2) Values in brackets [] are within 10-times detection limit with errors likely to exceed 15%.  
 3) "-" indicate measurement is below detection. Sample detection limit may be found by multiplying "det. limit" (far left column) by "multiplier" (top of each column).

**ENGINEERING WORKSHEET**

Prepared By: M.J. Smith Date: 4/23/88 Project: \_\_\_\_\_  
 Title/Subject: Analysis of AW107-AB-100

Component	Na <sub>2</sub> O <sub>2</sub> Prep.	KOH Prep.	Mean Value	
Ag	(52)	(90)	(71)	
Al	18800	20000	19400	
Ba	1410	1470	1440	
Cu	6820 <sup>(a)</sup>	(2200)		(c) Process blank high - Use 2200 value
Cd	(69)	(84)	(76)	
Cr	5820	(4300)	(5060)	
Co	< 48	< 125	Sur < 50	
Cv	9160	<del>10,100</del> 10100	9630	
Cu	(94)	(100)	(97)	
Fe	245000	273000	259000	
K	< 3800	—	< 3800	
La	1940	1990	1965	
Mg	(1200)	(740)	(970)	
Mn	143000	162000	152500	
Mo	< 57	< 150	Sur < 60	
Ni	—	26500	26500	
NH	6710	6540	6625	
Ni	749 <sup>(b)</sup>	—	749	(b) Process blank high 439 mg/g
P	1300	(2000)	(1650)	
Pb	18700	15900	17300	
Si	6930	7470 <sup>(c)</sup>		(c) High process blank 1640 mg/g; Use 6930 value
Ti	185	(210)	197	
U	(4000)	< 9940	(4000)	
Zn	811	1770	1290	} quite a discrepancy between the two fusions
Zv	1670	3190	2430	

# Battelle PNNL/RPG/Inorganic Analysis --- IC Report

WO/Project: W48481/29953  
Client: G. Lumetta

-----  
ACL Nmbr(s): 99-1454 through 99-1457  
-----

Client ID: AN-107 AQ series  
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ASR Nmbr 5319  
-----

Total Samples: 4 liquids  
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Procedure: PNL-ALO-212, "Determination of Inorganic Anions by Ion Chromatography" (IC).

Analyst: MJ Steele

Analysis Date: May 7, 1999

See Chemical Measurement Center 98620: IC File for Calibration and Maintenance Records.

M&TE Number: IC instrument -- WD25214  
Mettler AT400 Balance - Cal. No. 360-06-01-031

Analyst: Marilyn J. Steele 5-13-99

Approval: M. J. Steele 5-13-99

## Battelle PNNL/RPG/Inorganic Analysis --- IC Report

### Final Results:

Four liquid samples were analyzed by ion chromatography (IC) for inorganic anions as specified in ASR 5319. The liquid samples were diluted at the IC workstation up to 200-fold to ensure that all anions were within the calibration range. The anion results are presented in the table below.

Sample ID	Client ID	F, $\mu\text{g/ml}$	Cl, $\mu\text{g/ml}$	NO <sub>2</sub> , $\mu\text{g/ml}$	Br, $\mu\text{g/ml}$	NO <sub>3</sub> , $\mu\text{g/ml}$	PO <sub>4</sub> , $\mu\text{g/ml}$	SO <sub>4</sub> , $\mu\text{g/ml}$	C <sub>2</sub> O <sub>4</sub> , $\mu\text{g/ml}$
99-1454	AN107-AQ-30	1,050	230	7180	<50	26,300	1,220	1,510	9,620
99-1454 Rep	AN107-AQ-30	1,050	230	7150	<50	26,000	1,260	1,550	9,230
	RPD	0.1	0.8	0.5	NA	1.0	3.6	2.8	4.2
99-1454 Spike	% Rec	94	94	92	94	103	97	100	102
Blank Spike	% Rec	98	98	101	100	98	97	99	103
99-1455	AN107-AQ-50	75	12	31	<3	960	55	65	410
99-1456	AN107-AQ-70	23	2	19	<1	58	3	5	45
99-1457	AN107-AQ-90	12	3	5	<1	7	3	3	14

RPD = Relative Percent Difference (between sample and duplicate)

### Q.C. Comments:

Following are results of quality control checks performed during IC analyses. In general, quality control checks met the requirements of the governing QA Plan, MCS-033.

Working Blank Spike/Process Blank Spike: Process Blank Spike recoveries ranged from 98% to 103%, well within the acceptance criteria of 75% to 125%.

Matrix Spiked Sample: The matrix spike recovery for samples AN107-AQ-30 ranged from 92% to 103%. Again, this is well within the acceptance criteria of 75% to 125%.

Duplicate: No duplicates were provided. However, the laboratory-dilution of sample AN107-AQ-30 was analyzed in replicate (i.e., two different analysis injections) at the IC workstation from two different IC workstation dilutions. The RPDs ranged from 0% to 4%, which is within the acceptance criteria of 20%.

System Blank/Processing Blanks: No anions were detected above reportable concentrations in the system blanks or in the processing/dilution blank.

Quality Control Calibration Verification Check Standards: Four mid-range verification standards were analyzed throughout the analysis run. For all reported results, the concentrations of all analytes of interest were recovered within the governing QA Plan acceptance criteria of  $\pm 10\%$  for the verification standard.

## **Battelle PNNL/RPG/Inorganic Analysis --- IC Report**

### **Notes:**

- 1) "Final Results" have been corrected for all laboratory dilution performed on the sample during processing and analysis.
- 2) The low calibration standards are defined as the estimated quantitation limit (EQL) for the reported results and assume non-complex aqueous matrices. Actual detection limits or quantitation limits for specific sample matrices may be determined, if requested.
- 3) Routine precision and bias is typically  $\pm 15\%$  or better for non-complex aqueous samples that are free of interference and have similar concentrations as the measured anions. Sample-specific precision and bias may be determined on each sample if required.

Date May 14, 1999

File/LB

To G. Lumetta

From M. Urie 

Subject Carbon Analysis Results for AN107 AQ  
Samples

The analysis of the AN-107-AQ liquid samples submitted under ASR 5319 was performed by the hot persulfate wet oxidation method, PNL-ALO-381, rev. 1. The hot persulfate method uses acid decomposition for TIC and acidic potassium persulfate oxidation at 92-95 °C for TOC, all on the same weighed sample, with TC being the sum of the TIC and TOC.

The samples were analyzed on May 12, 1999 and Table 1 below shows the results, rounded to three significant figures. The raw data bench sheets and calculation work sheets showing all calculations are attached. All sample results are corrected for average percent recovery of system calibration standards and are also corrected for contribution from the blank.

All samples were analyzed directly (i.e., no preparative or analytical dilution), and are reported in microgram of carbon per milliliter of original sample. The samples are reported on a weight per weight basis due to the difficulty in pipetting the liquids (i.e., there appeared to be significant residuals remaining in the pipet tips). Since there was insufficient sample to perform density measurement on the samples, the pipet volume are provide along with the weights for your evaluation.

### QC Narrative

The TIC standard is calcium carbonate and TOC standard is  $\alpha$ -Glucose (the certificates of purity are attached). The standard materials were used in solid form for system calibration standards as well as matrix spikes. TIC and TOC percent recovery are determined using the appropriate standard (i.e., calcium carbonate for TIC or glucose for TOC).

The QC for the methods involves calibration blanks, system calibration standards, sample duplicates, and one matrix spike per matrix type. The QC system calibration standards were all within acceptance criteria, with the average recovery being 98.5% for TIC and 94.6% for TOC. The calibration blanks were acceptable, averaging 12.3  $\mu\text{gC}$  for TIC and 56.5  $\mu\text{gC}$  for TOC.

The accuracy of the carbon measurements can be estimated by the recovery results from the matrix spike. The matrix spike recoveries from sample 99-1454 were 98% for TIC and 103% for TOC, well within the acceptance criteria of 75% to 125%. The precision (estimated by the Relative Percent Difference between duplicates where the carbon concentration is greater than 5 times the method detection limit) was good, with RPDs being well within the acceptance criteria of 20%.

Some results are reported as less than (" $<$ ") values. These less than values represent the sample MDL (method detection limit), which is the system MDL adjusted for the volume of sample used for the analysis. The system MDL is based on the attached pooled historical blank data.

**Table 1: TIC, TOC, and TC Results**

ALO Number	Sample ID	Vol (mL)	Wt (g)	TIC ( $\mu\text{gC/g}$ )	TIC RPD (%)	TOC ( $\mu\text{gC/g}$ )	TOC RPD (%)	TC ( $\mu\text{gC/g}$ )	TC RPD (%)
99-1454	AN107-AQ-30	0.10	0.1086	2,970		7,090		10,100	
99-1454 Dup	AN107-AQ-30	0.10	0.0929	3,170	6	8,010	12	11,200	11
99-1454 Spike	AN107-AQ-30 MATRIX SPIKE	0.10	0.1087	98		103		100	
99-1455	AN107-AQ-50	0.30	0.3022	291		233		524	
99-1455 Dup	AN107-AQ-50	0.30	0.3002	280	4	255	n/a	535	2
99-1456	AN107-AQ-70	0.50	0.5028	127		<35		127	
99-1456 Dup	AN107-AQ-70	0.35	0.3532	126	n/a	<50	n/a	126	n/a
99-1457	AN107-AQ-90	0.50	0.4983	99		<35		99	
99-1457 Dup	AN107-AQ-90	0.30	0.2986	121	n/a	<59	n/a	121	n/a

RPD = Relative Percent Difference: Calculated when sample and duplicate results exceed five times the method detection limit

Review/Approve:  5/24/99

Archive Information:

Files: ASR 5319 Lumetta.doc, ASR 5319 Lumetta.xls



**Battelle**

Pacific Northwest Laboratories

Project Number

Internal Distribution

329/4 File

Date April 22, 1999  
To Greg Lumetta  
From Tom Farmer  
Subject ICP/MS Analysis of Submitted Samples

Pursuant to your request, the samples that you submitted for analysis were analyzed by ICPMS for  $^{99}\text{Tc}$ . The results of this analysis are reported on the attached page.

An Amersham  $^{99}\text{Tc}$  was used to generate the calibration curve. An independent Amersham  $^{99}\text{Tc}$  standard was used as the continuing calibration verification (CCV) standard. Unless otherwise specified, the overall uncertainty of the values is conservatively estimated at  $\pm 10\%$ , and is based on the precision between consecutive analytical runs as well as the accuracy of the CCV standard results.

The  $^{99}\text{Tc}$  values reported assume that the Ru present is exclusively fission-product Ru, and therefore does not have an isotope at  $m/z$  99; i.e., everything observed at  $m/z$  99 is due to  $^{99}\text{Tc}$ . The fingerprint we're seeing for Ru is obviously not natural, and is consistent with that observed in previous tank waste analyses. Approximate  $^{101}\text{Ru}$  concentrations are provided for your information.

If you have any questions regarding this analysis, feel free to call me at 372-0700 or James Bramson at 372-0624

# Lumetta Tc-99 Analysis

April 22, 1999

*J. Brown*  
4/22/99

The uncertainty of the results is estimated at  $\pm 10\%$ .

Sample Number	ICP/MS Number	ALO Number	Tc-99	$^{101}\text{Ru}/^{102}\text{Ru}$ (*.541)	$\dagger^{101}\text{Ru}$
1%HNO3	9421a_B1		<0.05 ng/ml		
1%HNO3	9421a_B7		<0.05 ng/ml		
1%HNO3	9421a_B19		<0.05 ng/ml		
Process Blank	9421a_PB2	99-1458-PB	<500 ng/g		
SRM 2170	9421a20	LCS/99-1458/Ni	<500 ng/g		
AN107-AQ-100	9421a13	99-1458	11400 ng/g	1.182	3000 ng/g
AN107-AQ-100 Dup.	9421a15	99-1458	10500 ng/g		
AN107-AQ-100 + spike	9421a18	99-1458	31900 ng/g		
<b>Spike Recovery</b>			<b>87%</b>		
Blank	9421a21	DDI-H20	2.2 $\pm$ 0.9 ng/ml	1.175	0.4 ng/ml
AN107-AQ-90	9421a9	99-1457	10.9 $\pm$ 1.4 ng/ml	1.161	2.4 ng ml
AN107-AQ-70	9421a10	99-1456	29.6 ng/ml	1.161	40 ng/ml
AN107-AQ-50	9421a11	99-1455	108 ng/ml	1.192	1400 ng/ml
AN107-AQ-30	9421a14	99-1454	693 ng/ml		
AN107-AQ-30 Dup.	9421a16	99-1454	688 ng/ml		
AN107-AQ-30 + spike	9421a23	99-1454	918 ng/ml		
<b>Spike Recovery</b>			<b>90%</b>		
2.5ppb Tc-99 CCV	9421a_C5		2.53 ng/ml		
2.5ppb Tc-99 CCV	9421a_C22		2.75 ng/ml		
20ppb Co			<0.05 ng/ml		

\* Natural  $^{101}\text{Ru}/^{102}\text{Ru}$  ratio.

$\dagger$  Based on response from indium

## DATA REVIEW

Reviewed by *Paul Thomas Lumetta*

Battelle Pacific Northwest National Laboratory  
 Radiochemical Processing Group  
 Radioanalytical Applications Team - 325 Bldg.

99-1454U  
 4/27/99

Client : G. Lumetta  
 Wp#: W48481

*J. Sheppard*

Cognizant Scientist:

Date : 4/27/99

*T. Trang*

Concur:

Date : 4/27/99

Measured Activities (uCi/ml)

Sample	Client ID	Alpha Error +/-	Sr-90 Error +/-	Uranium ug/ml	Co-60 Error +/-	Cs-137 Error +/-	Eu-154 Error +/-	Eu-155 Error +/-	Sb-125 Error +/-	Am-241 Error +/-
99-1454	AN107-AQ-30	7.96E-3 11%	7.68E+0 5%	1.52E+1 4%	1.89E-2 3%	4.13E+1 2%	1.17E-2 11%	<4.0E-2	<4.0E-2	<4.0E-2
99-1455	AN107-AQ-50	6.86E-4 13%	2.67E-2 13%	1.83E+0 4%	5.55E-4 4%	1.41E+0 2%	2.95E-4 10%	<8.0E-4	<1.6E-3	<8.0E-4
99-1456	AN107-AQ-70	1.23E-3 3%	2.70E-2 5%	3.11E-1 2%	7.07E-5 7%	1.92E-1 2%	1.04E-3 3%	6.36E-4 8%	6.28E-4 15%	9.82E-4 10%
99-1457	AN107-AQ-90	2.06E-3 2%	4.73E-2 5%	2.63E-1 8%	2.41E-5 9%	9.00E-2 2%	1.86E-3 1%	1.39E-3 3%	3.61E-4 8%	1.82E-3 5%
99-1457 Rep	AN107-AQ-90	1.98E-3 2%	4.59E-2 5%	<3.E-5						
RPD		4%	3%							
Blank		<3.E-6								
Process Blank		<2.E-4	<2.E-5							
Matrix Spike		110%	104%							
Blank Spike		106%	97%	100%						



## ENGINEERING WORKSHEET

Prepared By: S.J. Kuntz Date: 4/13/99 Project: 29553

Subject: Measurement of AN101 and AN107 Solution Densities

Pipet Used: 1141166 (see attached calibration information)

1.00-ml aliquots were weighed on balance # (Cal. expires 8/99)

Sample ID	# 1	# 2	# 3	# 4		Mean	Std Dev
AN101-AQ-30B	1.036	1.030	1.035	<del>1.036</del>	1.036 S.I.L.	1.034	0.003
-50B	1.005	1.006	1.003	1.006	4/13/99	1.005	0.001
-70B	1.001	0.996	1.002	1.006		1.001	0.004
-90B	1.006	1.003	1.005	1.003		1.004	0.002
AN107-AQ-30A	1.070	1.076	1.077	1.073		1.074	0.003
-50A	1.011	1.000	1.008	1.003		1.006	0.005
-70A	1.0045	1.008	1.001	1.006		1.005	0.003
-90A	1.005	1.002	1.003	1.008		1.005	0.003

Dose rate on AN107-AQ-30A (hottest sample): Contact: 145 B 238 Wade Sheets  
6" : 45 B 58 RCT

DATA SHEET FOR PIPETTOR CALIBRATION

Procedure Number: PCS-TP-511-2      Revision Number: 1

1. Date Performed: 4/9/99

2. Pipettor ID: 1141166 (1-ml capacity)

3. Balance Calibration Code: 384.06-01-005

4. Balance Calibration Due Date: 8/99

5. Thermometer Control Number: 384.79-04-005

6. Volume 1 = 0.20

7. Volume 2 = 0.50

8. Volume 3 = 1.00

9. Ambient Temperature at Start of Procedure: 23 °C

Aliquot No. =	1	2	3	4	5	6
10. Mass Volume 1, g	0.202	0.196	0.199	0.197	-	-
11. Mass Volume 2, g	0.498	0.499	0.495	0.494	0.489	0.492
12. Mass Volume 3, g	1.002	1.002	0.996	0.998	1.004	-

13. Ambient Temperature at End of Procedure: 23 °C

Performed by: [Signature]

Date: 4/9/99

Reviewed by: [Signature]

Date: 8-10-99

## CALCULATION SHEET FOR PIPETTOR CALIBRATION

Procedure Number: PCS-TP-511-2

1. Mean Temperature: 23 °C

2. Density of Water: 0.9976 g/mL

	<u>Mean Mass, g</u>	<u>Std. Dev., g</u>	<u>Accuracy, %</u>	<u>Precision, %</u>
3. Volume 1	0.199	0.003	± 0.26	± 1.51
4. Volume 2	0.495	0.004	± 0.76	± 0.81
5. Volume 3	1.000	0.003	± <del>0.22</del> 0.24 A.I.K.	<del>± 0.10</del> ± 0.30 A.I.K.

Performed by: B.J. Smith Date: 4/9/99  
 Reviewed by: Brian Ryle Date: 8-10-99

**ENGINEERING WORKSHEET**

Prepared By: M.J. Smith      Date: 4/27/99      Project: 29953  
 Title/Subject: AN107 Entrained Solids Wash/Leach

Excel spreadsheets were used to perform the required calculations. Aluminum is considered here as an example of these calculations.

Solution Volume Volumes: Determined from solution densities & weights.

1 <sup>st</sup> Wash	(20.2305 g) / (1.074 g/mL)	= 18.8366 mL
2 <sup>nd</sup> Wash	(17.9309 g) / (1.006 g/mL)	= 17.8240 mL
3 <sup>rd</sup> Wash	(18.1445 g) / (1.005 g/mL)	= 18.0542 mL
4 <sup>th</sup> Wash	(18.1185 g) / (1.005 g/mL)	= 18.0269 mL

Aluminum in Each Solution:

1 <sup>st</sup> Wash (AN107-AA-30)	: (1140 mg/mL) (18.8366 mL)	= 21474 mg Al
2 <sup>nd</sup> Wash (AN107-AA-50)	: (83.4 mg/mL) (17.8240 mL)	= 1487
3 <sup>rd</sup> Wash (AN107-AA-70)	: (44.6 mg/mL) (18.0542 mL)	= 805
4 <sup>th</sup> Wash (AN107-AA-90)	: (28.2 mg/mL) (18.0269 mL)	= 517

21474
1487
805
517
<u>2254</u>
26537 mg Al total

Aluminum in Washed Solids (AN107-AA-100):

$$(19400 \text{ mg/g}) \left( \frac{0.1162}{1.14 \cdot 4/23/99} \right) = 2254 \text{ mg Al}$$

(see note at the bottom of p. 12 of test plan)

Al Distribution:

1 <sup>st</sup> Wash:	100 (21474 / 26537)	= 80.9 %
2 <sup>nd</sup> Wash:	100 (1487 / 26537)	= 5.6
3 <sup>rd</sup> Wash:	100 (805 / 26537)	= 3.0
4 <sup>th</sup> Wash:	100 (517 / 26537)	= 1.9
Washed Solids:	100 (2254 / 26537)	= <u>8.5</u>
		99.9

Prepared By: <u>M. J. Smith</u>	Date: <u>4/27/99</u>	Project: <u>    </u>
Title/Subject: <u>AN107 Entrained Solids Wash/Leach</u>		

Technetium

Technetium concentrations were converted from ng/mL to uCi/mL (or ng/g to uCi/g)

AN107-AQ-100 -100 DUP	(11400 ng/g) (10000 ng/g)	(0.017 Ci/g) "	$(10^6 \text{ uCi/Ci}) (5/10^9 \text{ ng}) = 0.1738 \text{ uCi/g}$ $= 0.1785 \text{ uCi/g}$	} mean = 0.186 uCi/g
AN107-AQ-30 -30 DUP	(693 ng/mL) (688 ng/mL)	" "	= 0.0118 uCi/mL = 0.0117	} mean = 0.0117 uCi/mL
-50	(108 ng/mL)	"	= 0.00184 uCi/mL	
-70	(29.6 ng/mL)	"	= 0.000503 uCi/mL	
-90	(10.9 ng/mL)	"	= 0.000185 uCi/mL	

So,

First wash	(0.0117 uCi/mL) (18.8366 mL) =	0.2204 uCi	76.7 %
Second wash	(0.00184 uCi/mL) (17.820 mL) =	0.0328 uCi	11.4 %
Third wash	(0.000503 uCi/mL) (18.0542 mL) =	0.0091 uCi	3.2 %
Fourth wash	(0.000185 uCi/mL) (18.3265 mL) =	0.0034 uCi	1.2 %
washed Solids	$\frac{0.186 \text{ uCi}}{0.1162 \text{ g}}$ (0.1162 g) =	0.0216 uCi	7.5 %
	Total	0.2873 uCi	↑

See Tables 1 → 3

Prepared By: <u>M.A. Hewitt</u>	Date: <u>8/10/99</u>	Project:
Title/Subject: <u>AN107 Wash/Leach</u>		

The filtered, <sup>/centrifuged</sup> solids apparently retained considerable liquid. The concentrations in solution might just reflect dilution of the interstitial liquid rather than actual dissolution of solid entrained solids.

To assess this possibility, we consider the first wash step.

First, we need to estimate the amount of interstitial liquid. To do this, we assume that the Na concentration in the first wash solution is due only to dilution of the interstitial liquid and the 0.01 M NaOH used.

$$\rightarrow 230 \text{ ng Na/ml}$$

32900 ng Na/ml in first wash solution (determined by ICP)

$$32900 - 230 = 32670 \text{ ng/ml due to dilution}$$

From Urie et al. 1999, PNWD-2463  $\rightarrow$  173500 ng Na/ml in the <sup>liquid fraction of</sup> AN107 sample

Thus,

$$V (173500) = (32670)(18.84 \text{ mL})$$

$\rightarrow$  vol. of wash solution

$$V = 3.55 \text{ mL}$$

Taking Cr as an example:

$$(145.5 \text{ ng/ml})(3.55 \text{ mL}) / 18.84 \text{ mL} = 27.4 \text{ ng Cr/ml expected based on dilution}$$

(59.8 ng/ml found)

$^{137}\text{Cs} \rightarrow$

$$(255.5 \text{ uCi/ml})(3.55 \text{ mL}) / 18.84 = 48.1 \text{ uCi/ml expected (41.3 uCi/ml found)}$$

