PNWD-3235
WTP-RPT-054, Rev 0

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J. J. Wagner

January 2003

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Test specification: 24590-PTF-TSP-RT-01-002, Rev. 1
Test plan: TP-RPP-WTP-111
Test exceptions: None
R&T focus area: Pretreatment
Test Scoping Statement(s): B-44

Battelle, Pacific Northwest Division
Richland, Washington, 99352

Completeness of Testing

This report describes the results of work and testing specified by 24590-PTF-TSP-RT-01-002, Rev. 1 and TP-RPP-WTP-111. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

Gordon H. Beeman, Manager WTP R&T Support Project	Date
G. Todd Wright, Manager Research and Technology	Date

Summary

The U.S. Department of Energy is tasked with the disposition of high-activity radioactive waste stored at the Hanford site. The waste is to be vitrified following specific pretreatment processing to separate the waste into a small-volume high-activity waste fraction, and a large-volume low-activity waste fraction. The River Protection Project-Waste Treatment Plant (RPP-WTP) baseline process for ^{137}Cs removal from Hanford high-activity tank waste is ion exchange. The current pretreatment flowsheet includes the use of Cs-selective, organic ion exchanger SuperLig® 644[a] (SL-644) material for cesium removal from the aqueous waste fraction. However, tests conducted at Savannah River Technology Center resulted in poor ion exchange performance when tested with Hanford Tank 241-AZ-102 (AZ-102) waste. It was postulated that the low Na molarity (2.77) of the AZ-102 supernatant contributed to the poor Cs ion exchange performance and that the ion exchange removal of Cs from AZ-102 concentrated to nominally 5 M Na would be more effective.

Battelle Pacific Northwest Division (PNWD) was contracted to perform Cs ion exchange studies under Contract 24590-101-TSA-W000-0004. In preparation for Cs ion exchange, PNWD was also contracted to perform AZ-102 characterization, concentration, and subsequent concentrate characterization. The Cs ion exchange activities are defined in Technical Scoping Statement B-44, which is included in Appendix C of the *Research and Technology Plan*.[b] These studies are to verify design and operating parameters for plant-scale ion exchange systems. Test results will also be used to validate ion exchange models.

Objectives

The objectives of this work were to composite the AZ-102 tank waste samples, perform limited characterization on the composite, concentrate the AZ-102 to nominally 5 M Na, perform limited characterization of the concentrate, and provide the concentrated waste to the Cs ion exchange task for follow-on Cs ion exchange processing. All objectives were met.

Conduct of Testing

Ten jars containing AZ-102 waste (retrieved from Tank AZ-102, cores 261 and 262) were provided to PNWD in October of 2001. All bottles were similar in appearance, containing clear liquid. An organic layer could not be discerned in these bottles. Some of the samples had a small amount of white precipitate.

The contents of the 10 jars (4659 g or 4078 mL) were filtered, combined into a single composite, and the composite mixed by stirring. Following stirring, the composite was sub-sampled and measured for density, inorganic analytes, and ^{137}Cs and total Cs. Characterization included:

- inductively coupled plasma-atomic emission spectrometry (ICP-AES)

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[a] This material has been developed and supplied by IBC Advanced Technologies, Inc., American Fork, UT.

[b] *Research and Technology Plan*, PL-W375-TE00007, Rev. 1, April 11, 2002, S. Barnes, R. Roosa, and R. Peterson, BNI, Richland, WA.

- inductively coupled plasma-mass spectrometry (ICP-MS) for total Cs and Cs isotopic abundances
- kinetic phosphorescence analysis (KPA) for total uranium
- ion chromatography (IC) analysis for inorganic anions
- titration for hydroxide
- total inorganic carbon (TIC) and total organic carbon (TOC)
- gamma energy analysis (GEA) for ^{137}Cs and ^{125}Sb.

After removing sub-samples, 3372 mL of the composite were then evaporated to a targeted Na concentration of 5 M (one half the volume). The AZ-102 concentrate density was determined to be slightly high. A small amount of dilute caustic was added to reduce the solution density to 1.25 g/mL (from 1.271 g/mL). The final volume was 1,808 mL corresponding to a concentration factor of 1.8. The concentrated AZ-102 was sub-sampled and characterized in a manner similar to the as-received supernatant (excluding ICP-MS).

Solids (35.5 g dry mass) precipitated from the solution during evaporative concentration. The solids were sub-sampled and characterized for inorganic analytes and ^{137}Cs. The solids characterization included

- ICP-AES on dissolved subsample
- IC on dissolved subsample
- GEA on dissolved subsample
- X-ray Diffraction (XRD) on solid subsample

Performance and Results

The compositions of the as-received and concentrated AZ-102 supernatants, as well as AZ-102 solids formed as a result of concentration are summarized in Table S1. The solids were largely composed of Na_3FSO_4 (kogarkoite) and $Na_2C_2O_4$ (natroxalate) mineral phases. Sample mass balance was maintained during processing operations. Furthermore , good mass balances of all significant anions and metals were obtained between the as-received AZ-102 and concentrated AZ-102 plus solids.

Table S1. Summary of AZ-102 As-Received and Concentrated Supernatants and Solids Compositions

	AZ-102 As-Received Supernatant		AZ-102 Concentrate Supernatant		AZ-102 Precipitated Solids		
	02-366		02-751		02-1299		Mass Balance %
Analyte	Average µg/mL(a)	Data Flag	Average µg/mL(a)	Data Flag	Average µg/g(a)	Data Flag	
Test Specification Analytes							
Al	**518**		**929**		**1,080**		99.2
Ca	33	U	34	U	**[260]**	J	NA
Cr	**856**		**1,510**		**1,210**		96
Cs (total)(b)	**36.6**		**71.6**		**48**		115
^{137}Cs	**946** µCi/mL		**2,005** µCi/mL		**1,345** µCi/g		115
Li	3.9	U	4	U	3.5	U	NA
K	**3,340**		**6,660**		**5,460**	X	108
Na	**64,400**		**106,000**		**364,500**	X	94.3
^{125}Sb	4 µCi/mL	U	4 µCi/mL	U	4 µCi/g	U	NA
U(KPA)	**10.1**		**15.2**	X	NM		80.5
F (c)	**1,050**		**1,760**		**40,150**		130
Cl	140	U	140	U	72	U	NA
NO_2	**37,500**		**78,000**		**47,000**		113
NO_3	**19,600**		**37,700**		**25,800**		105
PO_4(d)	**820**		**1,340**		**595**		88.2
SO_4	**20,000**		**35,400**		**219,000**		107
OH	**10,200**		**18,800**		NM		99.2
Density	**1.143** g/mL		**1.246** g/mL		NM		
Other Measured Analytes							
C_2O_4	**3,160**	X	**1,680**		**221,000**		102
Mo	**[60]**	J	**110**		**91**		99.5
P	**150**		**286**		**229**		104
Si	**[280]**	JB	**[255]**	JB	**6,050**	BX	72.9
TOC/F (e)	**10,200**		**13,800**		NM		(f)
TIC/F (e)	1,400	U	**1,400**		NM		(f)
TOC/P (e)	1,000	U	**1000**		NM		NA
TIC/P (e)	**7,340**		**14,600**		NM		106

Analytes detected are bolded for clarity and better readability.
NM = not measured; NA = not applicable

U signifies undetected analyte; the concentration provided represents the instrument detection limit (IDL) multiplied by the sample dilution factors.

B signifies associated preparative blank concentration resulted in 5% or more of the sample concentration.

X signifies a quality control parameter (e.g., precision, blank spike recovery, etc.) was exceeded.

J signifies an estimated concentration; the concentration was within 10-times the detection limit.

Table S.1 (Notes Contd)

The overall error for bolded values without brackets is estimated to be within ±15% (analytes greater than 10 times the method detection limit [MDL]). Bracketed values identify sample concentrations that are <10 times the MDL, and errors likely exceed ±15%.
The total Cs concentration was calculated based on the ^{137}Cs concentration and the isotopic distribution determined from the AZ-102 as-received sample by ICP-MS
Fluoride results should be considered the upper-bound concentration. Significant peak distortion of the F peak suggests the presence of co-eluting anion(s), possibly formate or acetate.
The P determined as PO_4 by IC was higher than the P determined by ICP-AES. The IC chromatograms had many other anions at much higher concentrations and peak tailing may have biased the PO_4 high.
For TOC and TIC: P=by hot persulfate method; F=by furnace method/TIC by difference (TIC = TC-TOC).
Furnace TIC and TOC results questionable; hot persulfate results used for mass balance calculation.

Quality Requirements

PNWD implemented the RPP-WTP quality requirements by performing work in accordance with the quality assurance project plan (QAPjP) approved by the RPP-WTP Quality Assurance (QA) organization. This work was conducted to the quality requirements of NQA-1-1989 and NQA-2a-1990, Part 2.7, as instituted through PNWD's *Waste Treatment Plant Support Project Quality Assurance Requirements and Description* (WTPSP) Manual.

PNWD addressed verification activities by conducting an Independent Technical Review of the final data report in accordance with Procedure QA-RPP-WTP-604. This review verified that the reported results were traceable, that inferences and conclusions were soundly based, and that the reported work satisfied the Test Plan objectives.

Issue/Observation

Solids formed upon evaporation are composed primarily of Na_3FSO_4 (57%) and $Na_2C_2O_4$ (28%). The precipitated solids were nominally 1 wt% of the AZ-102 as-received solution mass.

Terms and Abbreviations

ASR	Analytical Service Request
BNI	Bechtel National Inc.
BS	blank spike
DI	deionized
DRD	Development Requirements Document
EQL	estimated quantitation limit
GEA	gamma energy analysis
HASQARD	Hanford Analytical Services QA Requirements Document
HPIC	high-performance ion chromatography
IC	ion chromatography
ICP-AES	inductively coupled plasma-atomic emission spectrometry
ICP-MS	inductively coupled plasma-mass spectrometry
IDL	instrument detection level
KPA	kinetic phosphorescence analysis
LCS	laboratory control standard
MDA	minimum detectable activity
MDL	method detection limit
MRQ	minimum reportable quantity
MS	matrix spike
MSD	matrix spike duplicate
NA	not applicable
ND	not detected
NM	not measured
n/r	not recovered
nr	not reported
%D	percent difference
OH	hydroxide
PB	preparation blank
PNWD	Battelle - Pacific Northwest Division
QA	quality assurance
QC	quality control
RPD	relative percent difference
RPL	Radiochemical Processing Laboratory
RPP	River Protection Project
SAL	Shielded Analytical Laboratory
TC	total carbon

TIC	total inorganic carbon
TOC	total organic carbon
TP	test plan
TS	test specification
WTP	Waste Treatment Plant

Units

°C	degree Celsius
g	gram
kV	kilovolt
ma	milliamp
μCi	microcurie
μg	microgram
μm	micrometer
mL	milliliter
M	molarity
wt%	weight percent

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Tables

1.0 Introduction

The U. S. Department of Energy plans to vitrify tank wastes at the Hanford Site in preparation for permanent disposal. Before vitrification, tank wastes will be divided into low-activity and high-activity fractions through specific pretreatment processes. The pretreatment flowsheet for the Hanford high-activity tank wastes includes the use of SuperLig® 644 (SL-644) material for ^{137}Cs removal from the aqueous waste fraction. Small-scale ion exchange testing with AZ-102 tank waste conducted at the Savannah River Technology Center demonstrated poor Cs removal using the SL-644 (Hassan et al. 2001). One reason proposed for the demonstrated poor Cs ion exchange performance was that the Na concentration in this tank waste was low (2.77 M). The SL-644 is supposed to operate best with high ionic strength solution and typical tank waste Na concentrations of 5 M.

Battelle Pacific Northwest Division (PNWD) was tasked with the testing of concentrated AZ-102 on small-scale SL-644 ion exchange columns per 241-AZ-101 and 241-AZ-102 Ion Exchange Test Specification 24590-PTF-TSP-RT-01-002, Rev.1, J. Toth, 10/1/01. The AZ-102 tank waste had to be concentrated to nominally 5 M Na. This report describes the analytical testing of the AZ-102 as-received sample, the concentration process, and the AZ-102 concentrate and solids byproduct analyses and compositions. Other processing aspects of the test plan (ion exchange, batch contacts, effluent and eluate analyses) are reported separately.

The objectives of this work were to:

- composite the AZ-102 samples received from 222-S
- perform limited characterization of the inorganic anion and metals content of AZ-102
- concentrate the AZ-102 to nominally 5 M Na
- perform limited characterization of the AZ-102 concentrate
- provide concentrated AZ-102 to the Cs ion exchange task.

2.0 Sample Receiving

Tank AZ-102 was sampled from June 23, 1999, through September 23, 1999, from Core 261 and Core 262. Various sub-samples from different segments along the core were composited at the 222-S laboratory into ten nominally 400-mL samples. The composite samples were received under chain of custody (Appendix A) in the Radiochemical Processing Laboratory (RPL) Shielded Analytical Laboratory (SAL) hot cells on October 9, 2001. Each sample was assigned an RPL identification number.

The samples were weighed and observations of their physical appearances recorded. The measured gross composite sample masses agreed well with the gross masses reported by 222-S prior to sample transfer. All samples contained a small amount of solids; the solids' appearance was recorded for each of these samples and is given in Table 2.1. The solids' color may have been distorted through the yellow hot cell windows. There was no evidence of a separate organic phase in any of the samples.

Table 2.1. Observations from As-Received AZ-102 Samples

Bottle ID	RPL ID	Reported gross mass, g	Measured gross mass, g	Solids present	Solids color	Estimated solids volume	Solids Appearance
18819	02-0226	782.1	782.04	Yes	White	1 mL	White crystalline, some large, ~2 mm long
18990	02-0227	757.6	757.80	Yes	White with slight gray	0.5 mL	Flocculent, white
18988	02-0228	767.5	764.15	Yes	White	2 mL	Crystalline
18989	02-0229	776.5	776.99	Yes	White	3 mL	White crystalline, small + one large piece ~5 mm
18996	02-0230	746.2	746.70	Yes	Grey	1 mL	Small particles, silty appearance
18992	02-0231	772.9	773.34	Yes	White	4 mL	Flocculent
18993	02-0232	737.7	738.14	Yes	White	2 mL	Flocculent
18998	02-0233	739.0	739.40	Yes	White	<1 mL	Mostly small with some large pieces ~2mm
18994	02-0234	771.8	772.27	Yes	Dark gray	2 mL	Silty
18986	02-0235	772.4	772.63	Yes	Brown	4 mL	Silty

3.0 AZ-102 Sample Processing

The AZ-102 samples were processed according to Test Specification (TS) 24590-PTF-TSP-RT-01-002 [a] and Test Plan TP-RPP-WTP-111 (Appendix B). Raw data were recorded in Test Instruction TI-RPP-WTP-127 (Appendix C), and are maintained in the Project 42365 file.

3.1 Filtration and Compositing

The contents of the as-received AZ-102 bottles were passed sequentially through a 0.45-µm nylon filter, and the filtrates were combined in a 6-L stainless steel evaporating beaker. The combined filtrates were then stirred thoroughly and sub-sampled for various tests including characterization. The compositing and sub-sampling are summarized in Figure 3.1. There was a 25-g mass loss attributed primarily to evaporation during hot cell processing activities. The residual solids from the filter were retained for possible additional characterization. The supernatant density was determined in duplicate and averaged 1.143 ± 0.002 g/mL (T = 28°C).

3.2 Sample Splitting

The filtered composite sample was split into sub-samples for mixing process heels testing activities (not addressed in this report), large archive sub-samples, and archive analytical sub-samples. All sub-samples were stored in glass bottles. The various fractions were given the sample identifications shown in Figure 3.1. The analytical sub-samples were assigned a new RPL ID of 02-366 and analyzed according to Analytical Services Request (ASR) 6265 and, as amended, 6265.01. The remaining AZ-102 bulk sample remained in the stainless steel beaker for subsequent evaporation.

3.3 Evaporation

The AZ-102 filtrate was heated and evaporated at a controlled temperature of 50 ± 2°C under an argon cover gas with continuous stirring from a stainless steel impeller. Evaporation continued from 10/31/01 15:15 to 11/3/01 12:00 (2.9 days) to nominally half the original volume. The concentrated filtrate was cooled and then passed through a 0.45-µm nylon filter. Solids formation was evident; most solids settled to the bottom of the beaker, but a small fraction floated. The settled solids remained in the bottom of the beaker during the supernatant decant for filtration. The wet solids (hereafter identified as "AZ102C solids") weighed 56.4 g (52.8 g in beaker and 3.6 g captured in the filter). The solids were allowed to air-dry in the beaker to constant mass at ambient temperature. The total air-dried solids mass remaining in the beaker was measured at 35.5 g. The loss of mass (17 g) is attributed to free water. Most of this water source was from residual concentrated AZ-102 solution remaining with the solids. The filtered concentrated AZ-102 density was determined to be 1.271 ± 0.004 g/mL (T = 25°C).

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[a] Test Specification 24590-PTF-TSP-RT-01-002, Rev. 1, *Tank 241-AZ-101 and 241-AZ-102 Ion Exchange Test Specification*, James Toth, October 1, 2001.

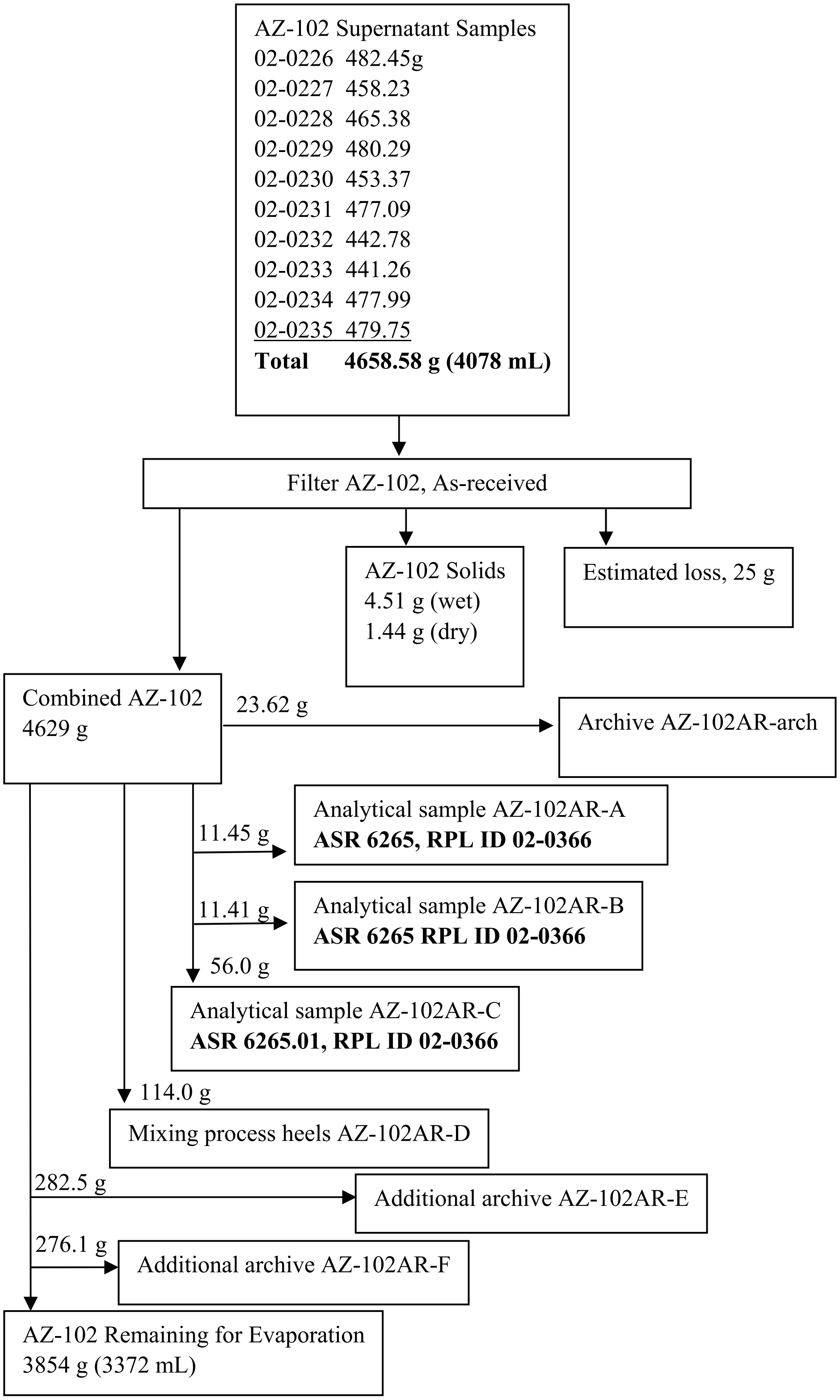

Figure 3.1. AZ-102 Sample Compositing and Splitting

The dried solids mass remaining in the beaker was a combination of the precipitated solids and the dissolved solids (DS) from the residual supernatant phase. The actual precipitated solids mass (M_P) from evaporative concentration can be calculated by subtracting the mass of residual supernatant solids (M_{DS}) from the total solids mass (M_T) according to Equation 1.

$$M_P = M_T - M_{DS} \tag{1}$$

The mass of residual supernatant dissolved solids (M_{DS}) can be estimated from the mass loss on drying of the total solids. By assuming that the weight loss on drying is water, M_{DS} can be estimated by the density of the residual liquid (ρ_L), density of water (ρ_W), and the water mass loss (M_W) according to Equation 2.

$$M_{DS} = \left(\rho_L * \frac{M_W}{\rho_W} \right) - M_W \tag{2}$$

where ρ_L = 1.271 g/mL
ρ_W = 1.000 g/mL
M_W = 17 g

Based on Equation 2, the estimated M_{DS} is 4.6 g or 13 wt% (i.e., 100 * [4.6 g / 35.5 g]) of the total dry solids. Applying Equation 1, the mass of solids precipitated from solution as a result of evaporative concentration was *estimated* to be:

$$M_P = 35.5\,g - 4.6\,g = 30.9\,g$$

The dry-mass precipitated solids (30.9 g in beaker plus 3.6 g on filter) represented 0.89 wt% of the starting AZ-102 as-received supernatant mass (3854 g) and 1.7 wt% of the concentrated AZ-102 mass (2057 g).[a] Because the solids were not dried to 100°C, the total air-dried mass could include residual water. Thus the calculated wt% solids should be considered an upper bound.

The solids were transferred to glass bottles for storage. The dried solids were assigned RPL ID 02-1299 and submitted for characterization under ASR 6344.

The AZ-102 concentrate density of 1.271 g/mL was considered to be too high for subsequent processing through the Cs ion exchange SL-644 resin beds. A 200-mL aliquot of 0.01M NaOH was added back to the filtered AZ-102 concentrate to reduce the total density. The density of the slightly diluted AZ-102 concentrate was determined in duplicate to be 1.246 ± 0.003 g/mL (T = 26°C), satisfactory for subsequent Cs ion exchange processing. This concentrate, labeled AZ-102C, was the AZ-102 feed solution for Cs ion exchange testing. Analytical sub-samples were taken and assigned an RPL ID of 02-0751 and submitted for characterization under ASR 6280. Figure 3.2 summarizes the entire sequence of evaporation, filtration, dilution, and analytical sub-sampling.

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[a] Most, if not all, supernatant was removed from the 3.6 g solids on the filter, however the solids were not necessarily dry. The wt% solids can be considered and upper bound.

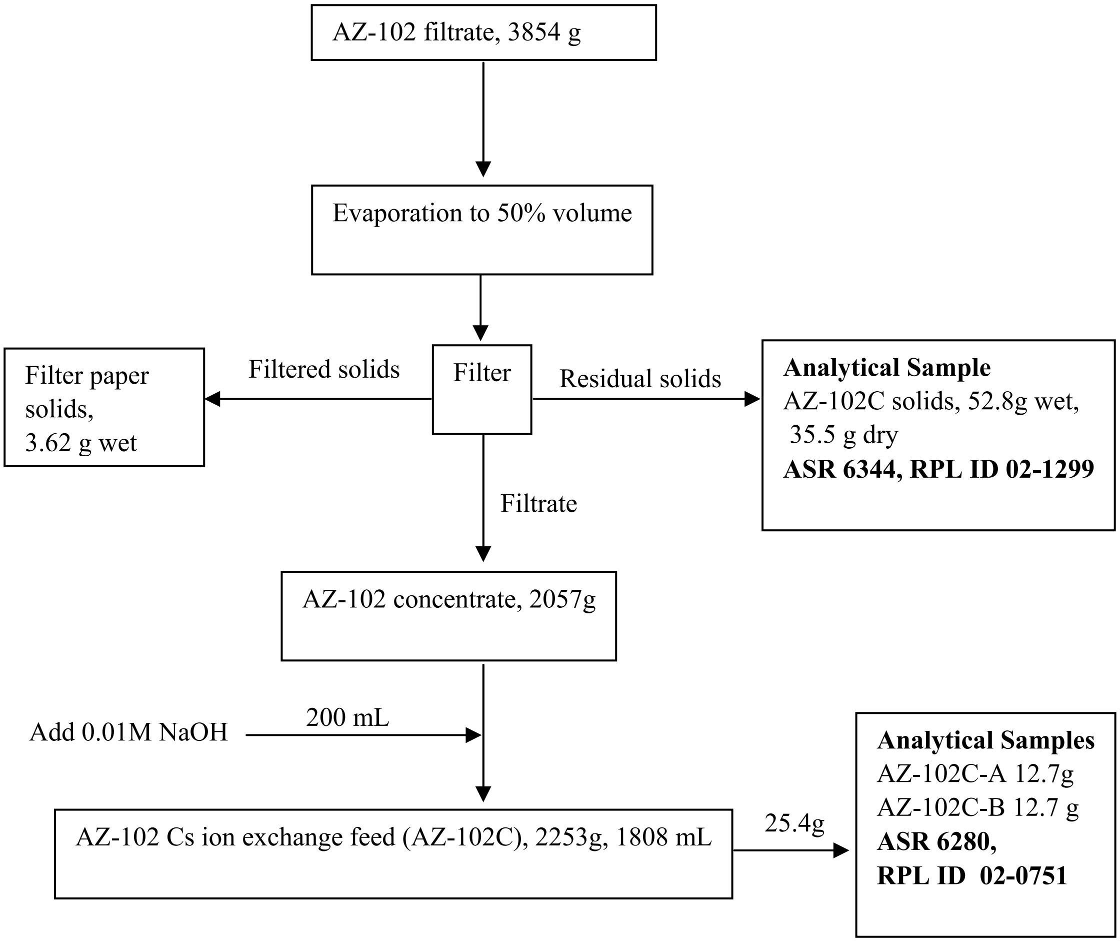
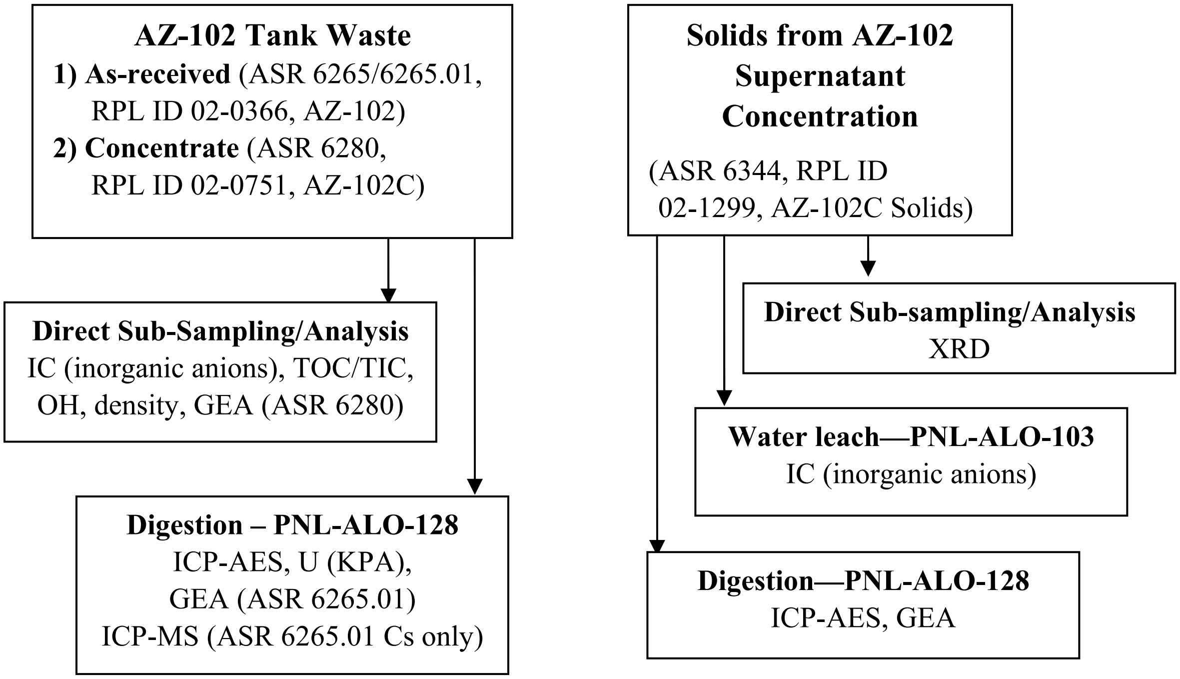


Figure 3.2. AZ-102 Composite Concentration and Subsequent Processing

4.0 Analytical Sample Processing

The analytical processing and distribution of the AZ-102 as-received composite (AZ-102), concentrate (AZ-102C), and solids from the concentration of the as-received composite (AZ-102C solids) are detailed in Figure 4.1. The ASRs and assigned RPL IDs are shown with each sample.



IC = ion chromatography

GEA = gamma energy analysis

ICP-AES = inductively coupled plasma-atomic emission spectrometry

KPA = kinetic phosphorescence analysis

ICP-MS = inductively coupled plasma-mass spectrometry

OH = hydroxide

TIC = total inorganic carbon

TOC = total organic carbon

U = uranium

XRD = x-ray diffraction

Figure 4.1. Flow Diagram for Analytical Processing of AZ-102, AZ-102C, and AZ-102C Solids Sub-samples

4.1 Density

Density was determined in the SAL hot cells using 10-mL Class A volumetric flasks. All density determinations were performed in duplicate by measuring the net mass in the volumetric flask.

4.2 Direct Sub-Sampling/Analysis

Sub-samples of the AZ-102 and AZ-102C filtrates were taken in the SAL hot cells and then delivered to the RPL analytical workstations for various measurements including anions, hydroxide, TOC, and TIC. Preparation blanks (PBs) or diluent blanks were prepared with the samples, as appropriate. The analytical workstation was responsible for assuring that the appropriate batch and analytical QC samples were analyzed, as well as providing any additional processing to the sub-samples that might be required. That is, no lab control samples/blank spikes (LCS/BS), process blanks (PB), or matrix spikes (MSs) were prepared in the SAL. Aliquots of AZ-102C filtrate were also submitted for direct gamma energy analysis (GEA).

4.3 Acid Digestion

Aliquots of the AZ-102 as-received filtrate were acid digested in the SAL hot cells according to procedure PNL-ALO-128, *HNO_3-HCl Acid Extraction of Liquids for Metals Analysis Using a Dry-Block Heater*. The SAL processed 1-mL aliquots of the AZ-102 filtrates in duplicate. The acid-extracted solutions were brought to a nominal 25-mL volume, absolute volumes were determined based on final solution weights and densities. The final digestion solution appeared to be clear and contain no precipitated solids. Along with a sample and duplicate, the SAL processed duplicate digestion PBs, two blank spikes (BSs) (one for ICP-AES and one for ICP-MS), and two MSs (one for ICP-AES and one for ICP-MS). Aliquots of the BS, MS, and PBs were provided with aliquots of the duplicate samples for ICP-AES and ICP-MS analyses. For AZ-102 (as-received) GEA, only the two PBs were provided with aliquots of the duplicate samples for analysis. Aliquots of the digested solutions were delivered to the 329 Facility for ICP-MS and to various RPL analytical workstations for ICP-AES, total U by KPA, and for gamma emitters by GEA, as appropriate. Aliquots of the filtered AZ-102C (concentrate) were processed identically but at a different time, and the digested solution distributed for all analyses except ICP-MS and GEA. The AZ-102C was analyzed directly (no acid digestion) by GEA.

Portions of AZ-102C solids were processed in the SAL hot cells according to PNL-ALO-129, *HNO_3-HCl Acid Extraction of Solids for Metals Analysis Using a Dry-Block Heater*. The SAL processed 0.2-g aliquots of AZ-102C solids in duplicate. The acid-extracted solutions were brought to a nominal 25-mL volume, absolute volumes were determined based on final solution weights and densities. Along with the sample and duplicate, the SAL processed one PB, one BS, and one MS. The solids samples appeared to be completely dissolved by the acid-extraction process. The sample, duplicate, and all QC samples were submitted for ICP-AES analysis; only the sample, duplicate, and PB were submitted for GEA.

4.4 Water Leach

Aliquots of AZ-102C solids were water leached according to PNL-ALO-103, *Water Leach of Sludges, Soils and Other Solid Samples* in the SAL hot cells. Nominally 0.2-g aliquots of solids were contacted with nominally 11 g of deionized (DI) water. The actual water volume was determined gravimetrically. The solid samples completely dissolved in the DI water based on visual examination. A PB, BS, and MS were processed in the SAL with the samples. Sample aliquots were submitted to the inorganic anion analysis workstation.

4.5 X-Ray Diffraction

Aliquots of the AZ-102C solids were analyzed by XRD according to PNNL-RPG-268, *Solids Analysis: X-ray Diffraction Analysis*. Corundum was added as an internal standard to precisely calibrate the x-ray diffractometer. Sample duplicates were run with a 45-kV accelerating potential and 40 ma current to the XRD tube. The step size was 0.02 degrees 2-theta.

4.6 Cs Isotopic Distribution

The Cs isotopic distribution (^{133}Cs, ^{135}Cs, and ^{137}Cs) was determined on the AZ-102 as-received supernatant according to PNL-SC-01, *Inductively Coupled Plasma Mass Spectrometric (ICP-MS) Analysis*. The Cs was separated from isobaric interferences using high-performance ion chromatography (HPIC), and the eluate was fed directly to the ICP-MS.

5.0 Analytical Results

5.1 Introduction

Tables 5.1 through 5.3 summarize the analytical results for the composited AZ-102 (as-received supernatant) tank waste. Tables 5.4 through 5.6 summarize the analytical results for the AZ-102 concentrated supernatant (AZ-102C). Tables 5.7 through 5.9 summarize the analytical results for solids that formed upon evaporation of the AZ-102 as-received supernatant (AZ-102C solids). Results are reported in μg/mL or μCi/mL (or μg/g or μCi/g), as appropriate. For some analyses, the nominal propagated uncertainties are also provided (as 1-σ, unless otherwise noted). However, for most analyses, no uncertainties are included in the tables. For these analyses, the estimated uncertainty is 10 to 15% for results above the estimated quantitation limit (EQL). Besides the duplicate sample results, the results obtained on the PBs are also reported, as appropriate.

The analytical results in Tables 5.1 through 5.9 and the quality control (QC) results in Tables 6.1 through 6.9 include a Data Flag column (i.e., a "Data Qualifier Code"), and the analyte concentrations or averages are flagged, as appropriate. The codes utilized are taken from the QA Plan and are defined below, as they relate to this report:

U Undetected: Analyte was analyzed, but not detected (e.g., no measurable instrument response) or response was less than the MDL. (Note: For some analyses, no results are reported below an EQL established by the lowest calibration standard adjusted for processing and analysis dilutions. In these cases, results less than EQL are flagged with a U. Footnotes in the tables identify which analyses use the lowest calibration standard as the reporting level.)

J Estimated value: The value reported is below the EQL and above the MDL. For radiochemical data, the J flag identifies results that have a propagated error of >10%, indicating that the results are typically within 10 times the minimum detectable activity (MDA).

B Analyte found in associated laboratory PB above the QA plan acceptance criteria (i.e., analyte concentration in the blank is greater than the EQL, or exceeds 5% of sample concentration).

X A QC deficiency is associated with the reported result. For this report, the X flag is used for the following: a) batch LCS or BS fails, b) both the MS *and* the post spike fail, c) serial dilution test (if required) fails for analytes with concentration greater than 0.1%.

The term MDL used in this report is an estimated MDL. That is, the MDLs have not been determined on the AZ-102 waste matrix per SW-846 [a] protocol. For the inorganic methods, the estimated MDLs are based on an instrument detection limit (IDL) established from using reagents and/or low-concentration high-purity standards as samples and evaluating instrument response near background levels. For radiochemical methods, the MDA is calculated per the QA Plan and is based on the background counting statistics.

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[a] U.S. Environmental Protection Agency (EPA). 1998. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,* SW-846, Third Edition Update IIIA, Office of Solid Waste and Emergency Response. Washington, D.C.

The EQL is typically set at 10 times the estimated MDL, which is adjusted for dilution factors resulting from digestion or leaching processing. No estimated MDL is determined for the IC analysis. The IC analysis EQL is based on the lowest calibration standard adjusted for sample dilution; no results are reported below the EQL for this method. For radiochemical methods, no EQL is established; however, results are flagged with a "J" when the uncertainty exceeds 10%.

The test specification TS 24590-PTF-TSP-RT-01-002[a] was used as the basis to define the target analyte list, minimum reportable quantities (MRQ), and QC performance criteria for these analyses. The TOC and TIC were measured to help define the fractional recoveries of major species (organics and carbonate). Specific QC and QA discussions are given in Section 6.0.

5.2 Analyte List Modifications

- Analyte concentrations in addition to those required by the TSs are provided. These additional analytes were measured as part of the method and are provided for additional information only.
- Total Cs was calculated from the AZ-102 (as-received) ICP-MS ^{133}Cs result and the Cs isotopic ratios: ^{133}Cs (52.9 wt%), ^{135}Cs (15.0 wt%), and ^{137}Cs (32.2 wt%). The isotopic ratio does not change as a function of the processing conditions; thus the same isotopic ratio was used for the AZ-102C and AZ-102C solids, where total Cs was calculated based on ^{137}Cs determined by GEA.

5.3 Data Limitations and General Observations

- The F results have significant technical deficiencies. The reported F results represent the summation of F, acetate, and formate concentrations, as these are not readily resolved on the anion analysis IC system. The F results are most likely an overestimate of the actual F present in the AZ-102 samples.
- Total Cs concentrations in the AZ-102C and AZ-102C solids were calculated based on the ^{137}Cs in the solids and concentrated supernatant measured by GEA, and the Cs atomic mass ratio measured in the as-received AZ-102 supernatant.
- The TIC and TOC results from the two analysis methods (i.e., hot persulfate oxidation and furnace oxidation) are significantly different for both the AZ-102 and AZ-102C samples, with the TIC from the hot persulfate method being very similar in concentration to the TOC from the furnace method. Since it is unlikely that the TIC from the hot persulfate method is in error, the high TOC from the furnace method is considered to be questionable and should not be used.
- The anion and cation composition of the as-received AZ-102 generally agreed well with previously reported data from the Savannah River Technology Center (Hay and Bronikowski 2000).
- Good agreement for ^{137}Cs concentration in the AZ-102 as-received supernatant was obtained between the calculated concentration from ICP-MS-measured ^{133}Cs and applied isotopic mass ratios, and the independently-measured ^{137}Cs by GEA (see Table 5.3).

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[a] Tank 241-AZ-101 and 241-AZ-102 Ion Exchange Test Specification 24590-PTF-TSP-RT-01-002, Rev. 1, J. Toth, 10/1/01

Table 5.1. AZ-102 As-Received Supernatant Metals Analysis by ICP-AES

Analyte	Process Blank 1			Process Blank 2			Sample			Duplicate		
	MDL	02-366 PB1	Data Flag	MDL	02-366 PB2	Data Flag	MDL	02-366	Data Flag	MDL	02-366D	Data Flag
	µg/mL$^{(a)}$			µg/mL$^{(a)}$			µg/mL$^{(a)}$			µg/mL$^{(a)}$		
ICP-AES Test Specification Analytes												
Al	1.6	1.6	U	1.6	1.6	U	7.9	**513**		8.0	**524**	
Ca	6.6	6.6	U	6.7	6.7	U	33	33	U	33	33	U
Cr	0.52	0.52	U	0.54	0.54	U	2.6	**846**		2.7	**867**	
Li	0.79	0.79	U	0.81	0.81	U	3.9	3.9	U	4.0	4.0	U
K	52	52	U	54	54	U	262	**3,310**		267	**3,380**	
Na	3.9	**[17]**	J	4.0	**[14]**	J	**19.7**	**63,700**		**20.0**	**65,000**	
U	52	52	U	54	54	U	262	260	U	267	270	U
Other Analytes Measured												
Ag	0.66	0.66	U	0.67	0.67	U	3.3	3.3	U	3.3	3.3	U
As	6.6	6.6	U	6.7	6.7	U	33	33	U	33	33	U
B	1.3	**[12]**	J	1.3	**[12]**	J	**6.6**	**97.5**	B	6.7	**86.8**	B
Ba	0.26	0.26	U	0.27	0.27	U	1.3	1.3	U	1.3	1.3	U
Be	0.26	0.26	U	0.27	0.27	U	1.3	1.3	U	1.3	1.3	U
Bi	2.6	2.6	U	2.7	2.7	U	13	13	U	13	13	U
Cd	0.39	0.39	U	0.40	0.40	U	2.0	2.0	U	2.0	2.0	U
Ce	5.2	5.2	U	5.4	5.4	U	26	26	U	27	27	U
Co	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.7	6.7	U
Cu	0.66	0.66	U	0.67	0.67	U	3.3	3.3	U	3.3	3.3	U
Dy	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.7	6.7	U
Eu	2.6	2.6	U	2.7	2.7	U	13	13	U	13	13	U
Fe	0.66	0.66	U	0.67	0.67	U	3.3	3.3	U	3.3	3.3	U
La	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.7	6.7	U
Mg	2.6	2.6	U	2.7	2.7	U	13	13	U	13	13	U
Mn	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.7	6.7	U
Mo	1.3	1.3	U	1.3	1.3	U	6.6	**[59]**	J	6.7	**[61]**	J
Nd	2.6	2.6	U	2.7	2.7	U	13	13	U	13	13	U
Ni	0.79	**[3.3]**	J	0.81	**[3.2]**	J	3.9	**[13]**	JB	4.0	**[10]**	JB
P	2.6	2.6	U	2.7	2.7	U	13	**147**		13	**153**	
Pb	2.6	2.6	U	2.7	2.7	U	13	13	U	13	13	U
Pd	20	20	U	20	20	U	98	98	U	100	100	U
Rh	7.9	7.9	U	8.1	8.1	U	39	39	U	40	40	U
Ru	29	29	U	30	30	U	144	140	U	147	150	U
Sb	13	13.1	U	13	13.5	U	66	66	U	67	67	U
Se	6.6	6.6	U	6.7	6.7	U	33	33	U	33	33	U
Si	13	**[26]**	J	13	**[25]**	J	66	**[280]**	JB	**67**	**[270]**	JB
Sn	39	39	U	40	40	U	197	200	U	200	200	U
Sr	0.4	0.4	U	0.4	0.4	U	2.0	2.0	U	2.0	2.0	U
Te	39	39	U	40	40	U	200	200	U	200	200	U
Th	26	26	U	27	27	U	131	131	U	130	130	U
Ti	0.66	0.7	U	0.67	0.7	U	3.3	3.3	U	3.3	3.3	U
Tl	13	13	U	13	14	U	66	66	U	67	67	U

Table 5.1 (Contd)

Analyte	Process Blank 1			Process Blank 2			Sample			Duplicate		
	MDL	02-366 PB1	Data Flag	MDL	02-366 PB2	Data Flag	MDL	02-366	Data Flag	MDL	02-366D	Data Flag
	µg/mL[(a)]			µg/mL[(a)]			µg/mL[(a)]			µg/mL[(a)]		
V	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.7	6.7	U
W	52	52	U	54	54	U	260	260	U	270	270	U
Y	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.7	6.7	U
Zn	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.7	6.7	U
Zr	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.7	6.7	U

Analytes detected by ICP-AES are bolded for clarity and better readability.

U signifies undetected analyte; the concentration provided represents the IDL multiplied by the sample dilution factors.
B signifies that the associated preparative blank concentration resulted in 5% or more of the sample concentration.
X signifies that a QC parameter (e.g., precision, blank spike recovery, etc.) was exceeded.
J signifies an estimated concentration; the concentration is >MDL but <EQL.

(a) The overall error for bolded values without brackets is estimated to be within ±15% (analytes greater than 10-times the MDL). Bracketed values identify sample concentrations that are <10-times the MDL, and errors likely exceed 15%.

Table 5.2. AZ-102 As-Received Supernatant Anion and TOC/TIC Analysis

Analyte	Process Blank				Sample				Duplicate			
	EQL[(a)]	MDL [(a)]	02-366 PB	Data	EQL[(a)]	MDL [(a)]	02-366	Data	EQL[(a)]	MDL [(a)]	02-366D	Data
	µg/mL			Flag	µg/mL			Flag	µg/mL			Flag
Test Specification Analytes												
F [(b)]	0.13	NA	0.13	U	140	NA	**1,100**		140	NA	**1,000**	
Cl	0.13	NA	0.13	U	140	NA	140	U	140	NA	140	U
NO_2	0.25	NA	0.25	U	2,800	NA	**38,100**		2,800	NA	**36,900**	
NO_3	0.25	NA	0.25	U	280	NA	**19,900**		280	NA	**19,200**	
OH	NA	NA	[(d)]	U	NA	NA	**10,000**		NA	NA	**10,300**	
Other Analytes Measured												
TOC/F [(c)]	NA	NA	NM[(e)]		NA	1,400	**11,300**[(f)]		NA	1,400	**9000**	
TOC/P [(c)]	NA	NA	NM[(e)]		NA	1,000	1,000	U	NA	1,000	1,000	U
TIC/F [(c)]	NA	NA	NM[(e)]		NA	1,400	1,400	U	NA	1,400	1,400	U
TIC/P [(c)]	NA	NA	NM[(e)]		NA	380	**6,380**	X	NA	380	**8,300**	X
Br	0.13	NA	0.13	U	140	NA	140	U	140	NA	140	U
C_2O_4	0.25	NA	0.25	U	280	NA	**3,150**	X	280	NA	**3,170**	X
PO_4	0.25	NA	0.25	U	280	NA	**850**		280	NA	**800**	
SO_4	0.25	NA	0.25	U	280	NA	**20,000**		280	NA	**19,900**	

Analytes detected are bolded for clarity and better readability.

U signifies undetected analyte; the concentration provided represents the IDL multiplied by the sample dilution factors.

X signifies that a QC parameter (e.g., precision, blank spike recovery, etc.) was exceeded.

NA = not applicable; NM = not measured

(a) F, Cl, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Br, and $C_2O_4^{2-}$ report only results above the EQL; therefore, the EQL is presented in this column. For all other analytes, the MDL is presented.

(b) Fluoride results should be considered the upper-bound concentration. Significant peak distortion of the F peak suggests the presence of co-eluting anion(s), possibly formate or acetate.

(c) For TOC and TIC: P = by hot persulfate method; F = by furnace method where TIC was determined by difference of two subsamples (TIC = total carbon [TC]-TOC); system blanks are subtracted from all sample results per procedure and are not reported (i.e., not applicable, NA).

(d) For the OH^- blank, no inflection point was detected.

(e) The sample was diluted before analysis; a diluent blank was not analyzed.

(f) Result is significantly higher than sample and duplicate TC results (9,400 µg/mL and 9,200 µg/mL, respectively), suggesting result may be higher than the actual TOC concentration. Note footnote (c).

Table 5.3. AZ-102 As-Received Supernatant Uranium, Cs, and ^{125}Sb Analysis

	Process Blank 1				Process Blank 2				Sample				Duplicate			
Analytes	MDL	02-366 PB1	± 1SD	Data Flag	MDL	02-366 PB2	± 1SD	Data Flag	MDL	02-366	± 1SD	Data Flag	MDL	02-366	± 1SD	Data Flag
	µg/mL				µg/mL				µg/mL				µg/mL			
U(KPA)(a)	0.01	**0.048**	17%	J	0.01	**0.078**	11%	J	0.06	**10.3**	2%		0.06	**9.88**	2%	
^{133}Cs	0.04	0.04		U	0.06	0.06		U	0.03	**20.1**	5%		0.02	**18.6**	1%	
^{135}Cs (b)	NA	NA			NA	NA			NA	**5.70**	5%		NA	**5.28**	1%	
^{137}Cs (b)	NA	NA			NA	NA			NA	**12.2**	5%		NA	**11.3**	1%	
Total Cs (b)	0.04	0.04		U	0.06	0.06		U	0.03	**38.0**	5%		0.02	**35.2**	1%	
	µCi/mL				µCi/mL				µCi/mL				µCi/mL			
^{137}Cs(c)	nr	**0.00036**	9%		nr	**0.00037**	13%	J	nr	**942**(d)	4%		nr	**949**(d)	4%	
^{125}Sb	0.0003	0.0003		U	0.0003	0.0003		U	4	4		U	4	4		U

Analytes detected are bolded for clarity and better readability.
Standard deviation (SD) in report in percent.
NA = not applicable; nr = not reported

U signifies undetected analyte; the concentration provided represents the IDL multiplied by the sample dilution factors.
J signifies an estimated concentration; the analyte concentration is >MDL but <EQL. For radiochemical analyses, the uncertainty is >10%.

(a) Uranium results by KPA
(b) Total Cs, ^{135}Cs, and ^{137}Cs were calculated from the ICP-MS ^{133}Cs results, and independent Cs atomic mass ratios determined by ICP-MS: ^{133}Cs 52.9%, ^{135}Cs 15.0%, ^{137}Cs 32.2%. MDL is set to ^{133}Cs MDL.
(c) Decay correction reference date is nominally March 2002.
(d) The ^{137}Cs concentration is calculated to be 10.8 and 10.9 µg/mL based on the specific activity of ^{137}Cs (87 µCi/µg).

Table 5.4. AZ-102 Filtered Concentrate (AZ-102C) Metals Analysis by ICP-AES

	Process Blank 1			**Process Blank 2**			**Sample**			**Duplicate**		
	MDL	**02-751 PB1**	**Data**	**MDL**	**02-751 PB2**	**Data**	**MDL**	**02-751**	**Data**	**MDL**	**02-751D**	**Data**
Analyte	**μg/mL(a)**		**Flag**	**μg/mL(a)**		**Flag**	**μg/mL(a)**		**Flag**	**μg/mL(a)**		**Flag**
ICP-AES Test Specification Analytes												
Al	1.6	**[2.0]**	J	1.6	1.6	U	7.9	**917**		8.2	**941**	
Ca	6.7	6.7	U	6.7	6.7	U	33	33	U	34	34	U
Cr	0.54	0.54	U	0.53	0.53	U	2.6	**1,490**		2.7	**1,530**	
Li	0.81	0.81	U	0.80	0.80	U	4.0	4.0	U	4.1	4.1	U
K	54	54	U	53	53	U	264	**6,560**		273	**6,750**	
Na	4.0	**[19]**	J	4.0	**[14]**	J	20	**104,000**		20	**108,000**	
U	54	54	U	53	53	U	260	260	U	270	270	U
Other Analytes Measured												
Ag	0.67	0.67	U	0.67	0.67	U	3.3	3.3	U	3.4	3.4	U
As	6.7	6.7	U	6.7	6.7	U	33	33	U	34	34	U
B	1.34	**[13]**	XJ	1.3	**[12]**	XJ	6.6	**69**	BX	6.8	**85**	BX
Ba	0.27	0.27	U	0.27	0.27	U	1.3	1.3	U	1.4	1.4	U
Be	0.27	0.27	U	0.27	0.27	U	1.3	1.3	U	1.4	1.4	U
Bi	2.7	2.7	U	2.7	2.7	U	13	13	U	14	14	U
Cd	0.40	0.40	U	0.40	0.40	U	2.0	2.0	U	2.0	2.0	U
Ce	5.4	5.4	U	5.3	5.3	U	26	26	U	27	27	U
Co	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.8	6.8	U
Cu	0.67	0.67	U	0.67	0.67	U	3.3	3.3	U	3.4	3.4	U
Dy	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.8	6.8	U
Eu	2.7	2.7	U	2.7	2.7	U	13	13	U	14	14	U
Fe	0.67	0.67	U	0.67	0.67	U	3.3	3.3	U	3.4	3.4	U
La	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.8	6.8	U
Mg	2.7	2.7	U	2.7	2.7	U	13	13	U	14	14	U
Mn	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.8	6.8	U
Mo	1.3	1.3	U	1.3	1.3	U	6.6	**108**		6.8	**111**	
Nd	2.7	2.7	U	2.7	2.7	U	13	13	U	14	14	U
Ni	0.81	**[0.88]**	J	0.80	0.80	U	4.0	4.0	U	4.1	4.1	U
P	2.7	2.7	U	2.7	2.7	U	13	**283**		14	**290**	
Pb	2.7	2.7	U	2.7	2.7	U	13	13	U	14	14	U
Pd	20	20	U	20	20	U	99	99	U	100	100	U
Rh	8.1	8.1	U	8.0	8.0	U	40	40	U	41	41	U
Ru	30	30	U	29	29	U	145	145	U	150	150	U
Sb	13	13	U	13	13	U	66	66	U	68	68	U
Se	6.7	6.7	U	6.7	6.7	U	33	33	U	34	34	U
Si	13	**[33]**	J	13	**[25]**	J	66	**[220]**	BJ	68	**[290]**	BJ
Sn	40	40	U	40	40	U	200	200	U	200	200	U
Sr	0.40	0.40	U	0.40	0.40	U	2.0	2.0	U	2.0	2.0	U
Te	40	40	U	40	40	U	200	200	U	200	200	U
Th	27	27	U	27	27	U	130	130	U	140	140	U
Ti	0.67	0.67	U	0.67	0.67	U	3.3	3.3	U	3.4	3.4	U
Tl	13	13	U	13	13	U	66	66	U	68	68	U
V	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.8	6.8	U

Table 5.4 (Contd)

Analyte	Process Blank 1			Process Blank 2			Sample			Duplicate		
	MDL	02-751 PB1	Data	MDL	02-751 PB2	Data	MDL	02-751	Data	MDL	02-751D	Data
	µg/mL[(a)]		Flag	µg/mL[(a)]		Flag	µg/mL[(a)]		Flag	µg/mL[(a)]		Flag
W	54	54	U	53	53	U	260	260	U	270	270	U
Y	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.8	6.8	U
Zn	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.8	6.8	U
Zr	1.3	1.3	U	1.3	1.3	U	6.6	6.6	U	6.8	6.8	U

Analytes detected by ICP-AES are bolded for clarity and better readability.

U signifies undetected analyte; the concentration provided represents the IDL multiplied by the sample dilution factors.
B signifies that the associated preparative blank concentration resulted in 5% or more of the sample concentration.
X signifies that a QC parameter (e.g., precision, blank spike recovery, etc.) was exceeded.
J signifies an estimated concentration; the concentration is >MDL but <EQL.

(a) The overall error for bolded values without brackets is estimated to be within ±15% (analytes greater than 10 times the MDL). Bracketed values identify sample concentrations that are <10 times the MDL, and errors likely exceed 15%.

Table 5.5. AZ-102 Filtered Concentrate (AZ-102C) Anion and TIC/TOC Analysis

Analyte	Process Blank				Sample				Duplicate			
	EQL[(a)]	MDL[(a)]	02-751 PB	Data	EQL[(a)]	MDL[(a)]	02-751 PB	Data	EQL[(a)]	MDL[(a)]	02-751 PB	Data
	µg/mL			Flag	µg/mL			Flag	µg/mL			Flag
Test Specification Analytes												
F [(b)]	1.4	NA	1.4	U	140	NA	**1,840**		140	NA	**1,690**	
Cl	1.4	NA	1.4	U	140	NA	140	U	140	NA	140	U
NO_2	2.8	NA	2.8	U	1,400	NA	**81,800**		1,400	NA	**74,100**	
NO_3	2.8	NA	2.8	U	1,400	NA	**39,400**		1,400	NA	**36,000**	
OH		NA	[(d)]	U	NA	NA	**17,400**			NA	**20,100**	
Other Analytes Measured												
TOC/F [(c)]	NA	NA	NM[(e)]		NA	1,000	**14,500**		NA	1,000	**13,300**	
TOC/P [(c)]	NA	NA	NM[(e)]		NA	500	500	U	NA	500	**1,000**	
TIC/F[(c)]	NA	NA	NM[(e)]		NA	1,000	1,000	U	NA	1,400	1,400	U
TIC/P [(c)]	NA	NA	NM[(e)]		NA	190	**15,000**		NA	190	**14,100**	
Br	1.4	NA	1.4	U	140	NA	140	U	140	NA	140	U
C_2O_4	2.8	NA	2.8	U	280	NA	**1,900**	X	280	NA	**1,450**	X
PO_4	2.8	NA	2.8	U	280	NA	**1,380**		280	NA	**1,310**	
SO_4	2.8	NA	2.8	U	1,400	NA	**37,100**		1,400	NA	**33,600**	

Analytes detected are bolded for clarity and better readability.

NA = not applicable; NM = not measured

U signifies undetected analyte; the concentration provided represents the IDL multiplied by the sample dilution factors.

X signifies that a QC parameter (e.g., precision, blank spike recovery, etc.) was exceeded.

(a) F, Cl, NO_2, NO_3, PO_4, SO_4, Br, and C_2O_4 report only results above the EQL; therefore, the EQL is presented in this column. For all other analytes, the MDL is presented.

(b) Fluoride results should be considered the upper bound concentration. Significant peak distortion of the F peak suggests the presence of co-eluting anion(s), possibly formate or acetate.

(c) For TOC and TIC: P=by hot persulfate method; F=by furnace method/TIC by difference (TIC = total carbon [TC]-TOC); system blanks are subtracted from all sample results per procedure and are not reported (i.e., not applicable, NA).

(d) For the OH blank, no inflection point was detected.

(e) The sample was diluted before analysis; a diluent blank was not analyzed.

Table 5.6. AZ-102 Filtered Concentrate (AZ-102C) U, Cs, and GEA

Analytes	Process Blank 1				Sample				Duplicate			
	MDL	02-751 PB1	± 1 RSD	Data Flag	MDL	02-751	± 1 RSD	Data Flag	MDL	02-751D	± 1 RSD	Data Flag
	µg/mL				µg/mL				µg/mL			
U(KPA)$^{(a)}$	0.03	0.032	64%	J	0.03	**14.9**	4%		0.03	**15.4**	4%	
^{133}Cs$^{(b)}$		NA			NA	**38.3**			NA	**37.4**		
^{135}Cs$^{b)}$		NA			NA	**10.9**			NA	**10.6**		
^{137}Cs$^{(b)}$		NA			NA	**23.3**			NA	**22.8**		
Total Cs$^{(b)}$		NA			NA	**72.5**			NA	**70.7**		
	µCi/mL				µCi/mL$^{(c)}$				µCi/mL$^{(c)}$			
^{137}Cs		$^{(d)}$			nr	**2,030**	3%		nr	**1,980**	3%	
^{125}Sb		$^{(d)}$			4	4		U	4	4		U
Other Analytes measured by GEA												
	µCi/mL				µCi/mL$^{(c)}$				µCi/mL$^{(c)}$			
^{134}Cs		$^{(d)}$			nr	**1.32**	6%		nr	**1.19**	7%	
^{60}Co		$^{(d)}$			0.03	0.03		U	0.05	0.05		U
^{106}Ru/Rh		$^{(d)}$			6	6		U	6	6		U
^{126}Sn/Sb		$^{(d)}$			0.02	0.02		U	0.02	0.02		U
^{154}Eu		$^{(d)}$			0.1	0.1		U	0.1	0.1		U

Analytes detected are bolded for clarity and better readability.
Relative standard deviation (RSD) in report in percent.
NA = not applicable; nr = not reported

U signifies undetected analyte; the concentration provided represents the IDL multiplied by the sample dilution factors.
J signifies an estimated concentration; the analyte concentration is >MDL but <EQL. For radiochemical analyses, the uncertainty is >10%.

(a) Uranium results by KPA
(b) Total Cs, ^{133}Cs, and ^{135}Cs are calculated from the ^{137}Cs GEA results, and independent Cs atomic mass ratios are determined by ICP-MS for the as-received sample (RPL ID 02-0366): ^{133}Cs 52.9%, ^{135}Cs 15.0%, ^{137}Cs 32.2%.
(c) Decay-correction reference date is nominally December 2001.
(d) Not required; GEA measured on direct sample aliquot.

Table 5.7. AZ-102C Precipitated Solids Metals Analysis

Analyte	Process Blank 1			Sample			Duplicate		
	MDL	02-1299 PB1	Data Flag	MDL	02-1299	Data Flag	MDL	02-1299D	Data Flag
	µg/g$^{(a)}$			µg/g$^{(a)}$			µg/g$^{(a)}$		
ICP-AES Test Specification Analytes									
Al	7.2	**[31]**	J	7.3	**1,040**		6.9	**1,110**	
Ca	30	30	U	30	**[260]**	J	29	**[260]**	J
Cr	2.4	2.4	U	2.4	**1,260**		2.3	**1,160**	
Li	3.6	3.6	U	3.6	3.6	U	3.5	3.5	U
K	240	240	U	243	**5,660**	X	231	**5,250**	X
Na	18	**272**	X	91	**367,000**	X	87	**362,000**	X
U	240	240	U	240	240	U	230	230	U
Other Analytes Measured									
Ag	3.0	3.0	U	3.0	3.0	U	2.9	2.9	U
As	30	30	U	30	30	U	29	29	U
B	6.0	**212**		6.1	**1,500**	XB	5.8	**1,460**	XB
Ba	1.2	1.2	U	1.2	**[7.2]**	J	1.2	**[6.5]**	J
Be	1.2	1.2	U	1.2	1.2	U	1.2	1.2	U
Bi	12	12	U	12	12	U	12	12	U
Cd	1.8	1.8	U	1.8	**[4.0]**	J	1.7	**[4.1]**	J
Ce	24	24	U	24	24	U	23	23	U
Co	6.0	6.0	U	6.1	6.1	U	5.8	5.8	U
Cu	3.0	3.0	U	3.0	3.0	U	2.9	2.9	U
Dy	6.0	6.0	U	6.1	6.1	U	5.8	5.8	U
Eu	12	12	U	12	12	U	12	12	U
Fe	3.0	**[6.0]**	J	3.0	**[19]**	JB	2.9	**[21]**	JB
La	6.0	6.0	U	6.1	**[6.5]**	J	5.8	**[6.3]**	J
Mg	12	12	U	12	12	U	12	12	U
Mn	6.0	6.0	U	6.1	6.1	U	5.8	5.8	U
Mo	6.0	6.0	U	6.1	**95**		5.8	**87**	
Nd	12	12	U	12	**[15]**	J	12	**[15]**	J
Ni	3.6	3.6	U	3.6	3.6	U	3.5	3.5	U
P	12	12	U	12	**235**		12	**222**	
Pb	12	12	U	12	12	U	12	12	U
Pd	90	90	U	91	91	U	87	87	U
Rh	36	36	U	36	36	U	35	35	U
Ru	130	130	U	130	130	U	130	130	U
Sb	60	60	U	61	61	U	58	58	U
Se	30	30	U	30	30	U	29	29	U
Si	60	**[600]**	J	61	**7230**	XB	58	**4870**	XB
Sn	180	180	U	180	180	U	170	170	U
Sr	2	1.8	U	1.8	**[2.8]**	J	1.7	**[2.6]**	J
Te	180	180	U	180	180	U	170	170	U
Th	120	120	U	120	120	U	120	120	U
Ti	3.0	3.0	U	3.0	**[5.2]**	J	2.9	**[5.5]**	J
Tl	60	60	U	61	61	U	58	58	U

Table 5.7 (Contd)

Analyte	**Process Blank 1**			**Sample**			**Duplicate**		
	MDL	**02-1299 PB1**	**Data Flag**	**MDL**	**02-1299**	**Data Flag**	**MDL**	**02-1299D**	**Data Flag**
	µg/g^(a)^			**µg/g^(a)^**			**µg/g^(a)^**		
V	6	6.0	U	6.1	6.1	U	5.8	5.8	U
W	240	240	U	240	240	U	230	230	U
Y	6	6.0	U	6.1	6.1	U	5.8	5.8	U
Zn	6.0	6.0	U	6.1	6.1	U	5.8	5.8	U
Zr	6.0	6.0	U	6.1	**[16]**	J	5.8	**[16]**	J

Analytes detected by ICP-AES are bolded for clarity and better readability.

U signifies undetected analyte; the concentration provided represents the IDL multiplied by the sample dilution factors.
B signifies that the associated preparative blank concentration resulted in 5% or more of the sample concentration.
X signifies that a QC parameter (e.g., precision, blank spike recovery, etc.) was exceeded.
J signifies an estimated concentration; the concentration is >MDL but <EQL.

(a) The overall error for bolded values without brackets is estimated to be within ±15% (analytes greater than 10-times the MDL). Bracketed values identify sample concentrations that are <10 times the MDL, and errors likely exceed 15%.

Table 5.8. AZ-102C Precipitated Solids Anion Analysis

	Process Blank			**Sample**			**Duplicate**		
Analyte	**EQL$^{(a)}$**	**02-1299 PB**	**Data Flag**	**EQL$^{(a)}$**	**02-1299**	**Data Flag**	**EQL$^{(a)}$**	**02-1299D**	**Data Flag**
	µg/g			**µg/g**			**µg/g**		
Test Specification Analytes									
F$^{(b)}$	8	8	U	1,400	**40,400**		1,500	**39,900**	
Cl	8	8	U	71	71	U	73	73	U
NO_2	16	16	U	2,800	**49,900**		2,900	**44,000**	
NO_3	16	16	U	2,800	**27,200**		2,900	**24,400**	
PO_4	16	16	U	140	**600**		150	**590**	
SO_4	16	16	U	2,800	**225,000**		2,900	**213,000**	
Other Analytes Measured									
Br	8	8	U	71	71	U	73	73	U
C_2O_4	16	16	U	2,800	**217,000**		2,900	**225,000**	

Analytes detected are bolded for clarity and better readability.

U signifies undetected analyte; the concentration provided represents the IDL multiplied by the sample dilution factors.

(a) F, Cl, NO_2, NO_3, PO_4, SO_4, Br, and C_2O_4 report only results above the EQL.
(b) Fluoride results should be considered the upper bound concentration. The F is not resolved from formate or acetate.

Table 5.9. AZ-102C Precipitated Solids Gamma Analysis

	Process Blank 1				Sample				Duplicate			
	MDL	**02-1299 PB**	**± 1SD**	**Data**	**MDL**	**02-1299**	**± 1SD**	**Data**	**MDL**	**02-1299D**	**± 1SD**	**Data**
Analytes	**µCi/g(a)**			**Flag**	**µCi/g(a)**			**Flag**	**µCi/g(a)**			**Flag**
Test Specification Analytes												
^{137}Cs	nr	**0.021**	5%		nr	**1,390**	4%		nr	**1,300**	4%	
^{125}Sb	0.002	0.002		U	4	4		U	4	4		U
	µg/g				**µg/g**				**µg/g**			
^{137}Cs	nr	**0.0003**			nr	**16.0**	4%		nr	**14.9**	4%	
Cs (total)	NA	(b)			NA	**49.6(c)**	4%		NA	**46.4(c)**	4%	
Other Analytes Measured												
	µCi/g(a)				**µCi/g(a)**				**µCi/g(a)**			
^{241}Am	nr	**0.001**	23%	J	20	20		U	20	20		U

Analytes detected are bolded for clarity and better readability.
Standard deviation (SD) in report in percent.
NA = not applicable; nr = not reported

U signifies undetected analyte; the concentration provided represents the IDL multiplied by the sample dilution factors.
J signifies an estimated concentration; the analyte concentration is >MDL but <EQL. For radiochemical analyses, the uncertainty is >10%.

(a) Decay correction reference date is nominally February 2002.
(b) Total Cs cannot be determined since isotopic ratio of the blank is not known.
(c) Total Cs and ^{137}Cs in µg/g are calculated from the GEA ^{137}Cs concentration, specific activity of ^{137}Cs (87 µCi/µg), and the isotopic ratio of AZ-102 as-received supernatant (RPL ID 02-0366) where ^{137}Cs = 32.2 wt%.

5.4 X-Ray Diffraction Analysis of Solids

The duplicate sample analyses resulted in virtually identical XRD spectra. An XRD spectrum with the stick diagrams of identified components is given in Figure 5.1. The major phases found in the solids were sodium fluorosulfate (Na_3FSO_4, Kogarkoite) and sodium oxalate ($Na_2C_2O_4$, natroxalate). The dominant materials found by destructive analysis support the Na_3FSO_4 and $Na_2C_2O_4$ compositions where 36-wt% Na, 4-wt% F, 22-wt% SO_4, and 22-wt% C_2O_4 were found. A small amount of sodium nitrite ($NaNO_2$) was present and is supported by the measured 4.7-wt% NO_2. Very small amounts of phases matching zinc nitrate hydroxide hydrate [$Zn_5(NO_3)_2(OH)_8{\bullet}2H_2O$] and potassium hydrogen acetate ($C_6H_{11}KO_6$) patterns were present. Potassium was detected by ICP-AES analysis in the AZ-102C solids at 0.5 wt%; however, zinc was not detected. A breakdown of the estimated solids composition based on the anion, metals, and XRD results is provided in Table 5.10. The presence of $NaNO_3$ is estimated based on the anion and cation composition, but was not detected by XRD.

Table 5.10. Estimated Solids Composition from AZ-102 Evaporation

Compound	Formula	Weight percent
Sodium fluorosulfate	Na_3FSO_4	57
Sodium oxalate	$Na_2C_2O_4$	28
Sodium nitrite	$NaNO_2$	7
Sodium nitrate[(a)]	$NaNO_3$	4
Minor constituents	Various	4

(a) The presence of $NaNO_3$ is assumed based on ICP-AES and IC analyses; its presence is not supported by the XRD analysis.

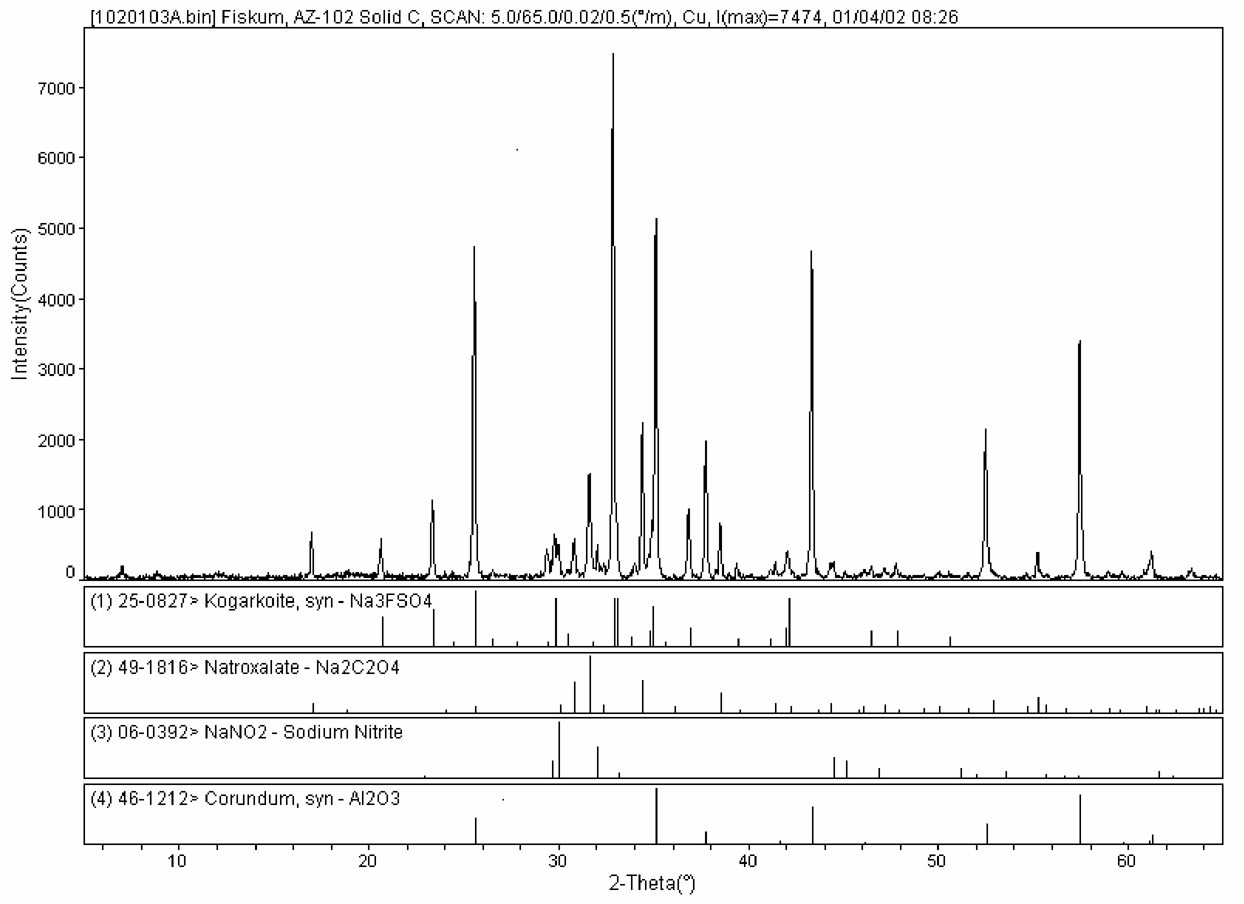

Figure 5.1. XRD Pattern for Precipitated AZ-102C Solids with Matching Stick Diagrams of Identified Components

The major phases (Na_3FSO_4 and $Na_2C_2O_4$) certainly precipitated from solution as part of the AZ-102 concentration process. A small fraction (~4.6 g) of the total solids mass (35.5 g) was contributed from total dissolved solids of residual AZ-102C (Section 3.3). It is possible that the observed $NaNO_2$ and predicted $NaNO_3$ are from the dried, residual AZ-102 concentrate fraction.

5.5 Fractional Analyte Recovery

Within analytical uncertainty, generally 100% of the anions and metals present in the AZ-102 as-received sample were recovered in the combined AZ-102 concentrate filtrate plus solids. Most of the analytes in the AZ-102 as-received material were recovered in the AZ-102 concentrate filtrate. Losses from the aqueous phase to the solid phase were found for SO_4, F, C_2O_4, and some Na. Analyte concentrations, masses, and fractionations are summarized in Table 5.11. Despite the presence of SO_4 in the solids, the final SO_4 concentration in the aqueous phase was a factor of 1.8 more concentrated than the initial sulfate concentration and equivalent to the average concentration factors of other analytes. Oxalate concentration, however, dropped with the aqueous phase volume reduction from an initial 0.036 M to a final 0.019 M. Silicon showed mass loss; however, the aqueous compositions had high uncertainties for Si, and thus initial and final Si masses in the aqueous fractions may be higher or lower than shown.

Table 5.11. Mass Balance of Various Analytes

	AZ-102 As-Received		AZ-102 Concentrate				AZ-102 Precipitated Solids			
Analyte	**Average M**	**Total mg**	**Average M**	**Total mg**	**% recovered**	**Conc. factor**	**Average µg/g**	**Total mg**	**% recovered**	**% accounted for**
Metals										
Al	1.90E-2	1.73E+3	3.44E-2	1.68E+3	97	1.8	1.08E+3	3.82E+1	2.2	99.2
Cr	1.65E-2	2.89E+3	2.90E-2	2.73E+3	94.5	1.8	1.21E+3	4.30E+1	1.5	96
K	8.56E-2	1.13E+4	1.70E-1	1.20E+4	107	2.0	5.46E+3	1.94E+2	1.7	108
Na	2.80E+0	2.17E+5	4.61E+0	1.92E+5	88.3	1.6	3.65E+5	1.29E+4	6	94.3
U (KPA)	4.24E-5	3.40E+1	6.37E-5	2.70E+1	80.5	1.5	NM	NA	NA	80.5
Mo	[6.25E-4]	[2.02E+2]	1.14E-3	1.98E+2	97.9	1.8	9.07E+1	3.22E+0	[1.6]	99.5
P	4.84E-3	5.06E+2	9.25E-3	5.18E+2	102	1.9	2.29E+2	8.11E+0	1.6	104
Si	[9.79E-3]	[9.27E+2]	[9.08E-3]	[4.61E+2]	49.7	0.93	6.05E+03	2.15E+2	[23.2]	72.9
Anions										
F[a]	5.53E-2	3.54E+3	9.29E-2	3.19E+3	90.1	1.7	4.02E+4	1.43E+3	40.3	130
NO_2	8.15E-1	1.26E+5	1.69E+0	1.41E+5	112	2.1	4.70E+4	1.67E+3	1.3	113
NO_3	3.15E-1	6.59E+4	6.08E-1	6.82E+4	103	1.9	2.58E+4	9.16E+2	1.4	105
PO_4	8.69E-3	2.78E+3	1.42E-2	2.43E+3	87.4	1.6	5.95E+2	2.10E+1	0.8	88.2
SO_4	2.08E-1	6.73E+4	3.68E-1	6.39E+4	95	1.8	2.19E+5	7.78E+3	11.6	107
C_2O_4	3.59E-2	1.07E+4	1.90E-2	3.03E+3	28.4	0.53	2.21E+5	7.85E+3	73.6	102
OH	5.98E-1	3.43E+4	1.11E+0	3.40E+4	99.2	1.8	NM	NA	NA	99.2
TIC[b]	6.12E-1	2.48E+4	1.21E+0	2.63E+4	106	2.0	NM	NA	NA	106
Radioisotope	**Average µCi/mL**	**Total µCi**	**Average µCi/mL**	**Total µCi**	**% recovered**	**Conc. factor**	**Average µCi/g**	**Total µCi**	**% recovered**	**% accounted for**
^{137}Cs	9.46E+2	3.19E+6	2.01E+3	3.63E+6	114	2.1	1.34E+3	4.77E+4	1.5	115

NM = not measured; NA = not applicable

The overall error for bolded values without brackets is estimated to be within ±15% (analytes greater than 10-times the MDL). Bracketed values identify sample concentrations that are <10-times the MDL, and errors likely exceed 15%.

(a) Fluoride results should be considered the upper-bound concentration. Significant peak distortion of the F peak suggests the presence of co-eluting anion(s), possibly formate or acetate.

(b) TIC, or carbonate, is reported as mg C and is based on the hot persulfate results.

6.0 Procedures, Quality Control, and Data Evaluation

A discussion of procedures, data quality, and QC is provided below for each analytical method. Analytical instrument calibration and calibration verification were performed in accordance with the QA Program's plan *Conducting Analytical Work in Support of Regulatory Programs*, which is in compliance with the Hanford Analytical Services QA Requirements Document (HASQARD)[a]. Raw data, including bench sheets, instrument printouts, data reduction, and calibration files, are maintained or cross-referenced in the Project 42365 file.

The sample averages, MRQs, quality data flags, QC parameters, and QC acceptance criteria are summarized in Tables 6.1 through 6.7. In some cases, one sample value was reported as less than the MDL/MDA (i.e., U flagged) and the duplicate reported with a value (i.e., either J flagged or a value measured above the EQL). The reported average was conservatively estimated as the single reported value above the MDL/MDA.

The QC and results evaluations provided in the following sections are limited to the analytes of interest defined by the TSs (See Section 5.1). Analytes other than those specified by the TSs are considered "opportunistic" and are provided for information only. Some of these "opportunistic" analytes have been measured per the requirements stated in the governing QA Plan or TS; however, the data have not been fully evaluated against the acceptance criteria. The QC performance of "opportunistic" analytes is not discussed.

6.1 Inductively Coupled Plasma-Atomic Emission Spectroscopy

Tables 5.1, 5.4, 5.7, 6.1, 6.2, and 6.3

The AZ-102 and AZ-102C acid-digested (PNL-ALO-128) samples and the AZ-102C solids acid-digested (PNL-ALO-129) samples were analyzed according to PNL-ALO-211, *Determination of Elements by Inductively Coupled Argon Plasma Atomic Emission Spectrometry*. The detected analytes at or above the EQL (equivalent to ten times the MDL) were reported with an uncertainty of ±15% (2-σ). As the MDL was approached, uncertainty increased to 100%. The samples (i.e., AZ-102, AZ-102C, and AZ-102C solids) were processed and analyzed at separate times; thus, each had a different set of QC samples for evaluating system performance. Quality control for the ICP-AES analysis consisted of sample duplicates, PBs, MSs, LCS/BSs, post spikes, calibration verification check standards, instrument blanks, interference check standards, and linear range check standards.

<u>AZ-102 as-received:</u> All QC acceptance criteria were met. The ICP-AES MS for this analysis did not contain U; however, the U concentration was <MDL, and the U concentration was measured by KPA, which had a MS. The MSs and post spikes for Na and Cr did not show adequate recovery since the spikes were less than 20% of the analyte concentration; serial dilution was used to assess matrix interferences for these analytes.

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[a] Hanford Analytical Services Quality Assurance Requirements Document; Volume 4: Laboratory Technical Requirements. DOE/RL-96-68, Rev. 2, September 1998.

AZ-102C concentrate: Except for the Na RPD, all QC acceptance criteria were met. However, Na RPD only slightly exceeded the acceptance criterion (i.e., 3.7% versus criterion of 3.5%) and was not considered a significant failure. The ICP-AES MS for this analysis did not contain U; however, the U concentration was <MDL and the U concentration was measured by KPA, which had a MS. The MSs and post spikes for Na and Cr could not be recovered since the spikes were less than 20% of the analyte concentration; serial dilution was used to assess matrix interferences for these analytes.

AZ-102C solids: Although QC acceptance criteria were not specifically addressed in the TSs, the AZ-102C solids analysis was evaluated to the same criteria as the supernatant analysis. Except for the K and Na LCS/BS and the K MS, all QC acceptance criteria were met. The Na LCS/BS over-recovery was assumed to be from contamination during processing; the PB exhibited Na contamination well above the EQL. The K MS under-recovery was attributed to incorrect K concentration being assigned to the matrix spiking standard (see Appendix E for discussion).[a] The K post spike, which used a different spiking standard, exhibited excellent recovery, and thus the failure of the K MS was not considered significant.

6.2 Inductively Coupled Plasma/Mass Spectrometry

Tables 5.2 and 6.1

Only the AZ-102 as-received supernatant samples (acid digested per PNL-ALO-128) were analyzed by ICP-MS for ^{133}Cs and Cs isotopic analysis according to procedure PNL-ALO-280, *Inductively Coupled Plasma-Mass Spectrometer Analysis*. Except for the MS and LCS/BS, the acid-digested samples were from the same processed solutions as were analyzed by ICP-AES analysis.

Quality control for the ICP-MS analysis consisted of sample duplicates, PBs, MS, LCS/BS, calibration verification check standards, and instrument blanks. All QC met the acceptance criteria. The duplicate analyses met the QC criterion of <15% RPD. The Cs MS (i.e., ^{133}Cs) recovery was within the acceptance criteria of 70% to 130%. No Cs was measured in the PBs above the acceptance criteria (i.e., <EQL or <5% of sample concentration).

6.3 U Analysis by KPA

Tables 5.3, 5.6, 6.1, and 6.2

Aliquots from the acid digestion (PNL-ALO-128) of the AZ-102 as-received supernatant and AZ-102C concentrate samples were further processed for U analysis. The aliquots were treated with concentrated HNO_3, evaporated to dryness, and then re-dissolved in dilute HNO_3 for U analysis. Total U was measured according to procedure RPG-CMC-4014, *Uranium by Kinetic Phosphorescence Analysis*. The AZ-102C solids were not analyzed for U by KPA. The aliquots from the AZ-102 as-received and AZ-102C concentrate samples were processed at different times and analyzed in separate analytical batches. Each processing batch for U(KPA) analysis consisted of a sample, duplicate, PB, MS, and BS. Calibration verification standards and instrument blanks were analyzed to verify system performance.

The U concentration for both the AZ-102 as-received supernatant and AZ-102C concentrate were well below the MRQ value of 780 µg/mL. For both samples, all QC criteria were met with the exception of one MS. The duplicate analysis RPDs (4% and 3%) easily met the QC criterion of <15%. The BS

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[a] The K concentration in the spiking standard was lower than the certificate value.

recoveries (95% and 91%) met the acceptance criteria of 80% to 120%. The MS recovery for the AZ-102 as-received supernatant met the QC criteria of 75% to 125%, but the MS recovery for the AZ-102C was low at 66%; the reason was unknown. Uranium was present in the SAL hot cell PBs, but at a concentration <<1% of any sample U concentration.

Table 6.1. ICP-AES, ICP-MS, and KPA QC Results for AZ-102

Analyte	**MRQ µg/mL$^{(a)}$**	**MDL µg/mL**	**02-366 Average µg/mL$^{(b)}$**	**Data Flag**	**RPD %$^{(c)}$**	**Target RPD %**	**Lab Control (LCS/BS) % Rec.**	**Matrix Spike (MS) %Rec.**	**Post Matrix Spike (PS-A) %Rec.**	**Post Matrix Spike (PS-B) % Rec.**	**Serial Dilution %D**
Acceptance Criteria							*80% - 120%*	*75% - 125%*	*75% - 125%*	*75% - 125%*	< ±*10%*
Test Specification Analytes											
Al	75	7.9	**518**		2.2	<15	99	99	97		0.2
Ca	150	33	33	U		<15	101	104	101		
Cr	15	2.6	**856**		2.5	<15	99	n/r	n/r		3.4
^{133}Cs$^{(d)}$	1.5	0.0003	**19.4**		7.1	<15	99	99			
Li	4	3.9	3.9	U		<15	101	99	98		
K	75	260	**3,340**		2.1	<15	100	106	93		
Na	75	20	**64,400**		2.1	<3.5	103	n/r	n/r		3.0
U	600	260	**260**	U		<15	95	$^{(e)}$			
U (KPA)	780	0.06	**10.1**		4	<15	95	97			
Other Analytes Measured											
Ag		3.3	3.3	U							
As		33	33	U							
B		6.6	**92**	B	11.7		113	77	100		
Ba		1.3	1.3	U			97	98	96		
Be		1.3	1.3	U							
Bi		13	13	U					98		
Cd		2.0	2.0	U			101	101	99		
Ce		26	26	U							
Co		6.6	6.6	U			99				
Cu		3.3	3.3	U			98	93	95		
Dy		6.6	6.6	U						95	
Eu		13	13	U							
Fe		3.3	3.3	U			99	103	100		
La		6.6	6.6	U							
Mg		13	13	U			102	108	105		
Mn		6.6	6.6	U			102				
Mo		6.6	**[60]**	J					97		
Nd		13	13	U							
Ni		3.9	**[12]**	JB			99	102	105		
P		13	**150**		4		101	106	98		
Pb		13	13	U			100	98	95		

Table 6.1 (Contd)

Analyte	MRQ µg/mL[(a)]	MDL µg/mL	02-366 Average µg/mL[(b)]	Data Flag	RPD %[(c)]	Target RPD %	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS) %Rec.	Post Matrix Spike (PS-A) %Rec.	Post Matrix Spike (PS-B) % Rec.	Serial Dilution %D
Pd		98	98	U							
Rh		39	39	U							
Ru		140	140	U							
Sb		66	66	U							
Se		33	33	U							
Si		66	**[280]**	JB					106		
Sn		200	200	U							
Sr		2.0	2.0	U			98	99	98		
Te		200	200	U							
Th		130	130	U						99	
Ti		3.3	3.3	U					93		
Tl		66	66	U							
V		6.6	6.6	U							
W		260	260	U							
Y		6.6	6.6	U							
Zn		6.6	6.6	U			100	103	102		
Zr		6.6	6.6	U					97		

Analytes detected by ICP-AES are bolded for clarity and better readability.
Blank areas indicate that QC results were not evaluated, or QC analyses were not performed, for opportunistic (other) analytes.
n/r = not recovered; spike concentration <20% of sample concentration.

U signifies undetected analyte; the concentration provided represents the IDL multiplied by the sample dilution factors.
B signifies that the associated preparative blank concentration resulted in 5% or more of the sample concentration.
J signifies an estimated concentration; the concentration is >MDL but <EQL.

(a) MRQs from 24590-WTP-TSP-RT-01-002, Tables A.1, B.2, and D.1.
(b) The overall error for bolded values without brackets is estimated to be within ±15% (analytes greater than 10-times the MDL). Bracketed values identify sample concentrations that are <10-times the MDL, and errors likely exceed 15%.
(c) RPD only calculated when both the sample and duplicate results are greater than the EQL.
(d) Cs concentration and QC are based on ^{133}Cs analysis by ICP-MS.
(e) U was not present in the MS spike solution.

Table 6.2. ICP-AES and KPA QC Results for Filtered AZ-102 Concentrate (AZ-102C)

Analyte	MRQ µg/mL[a]	MDL µg/mL	02-751 Average µg/mL[b]	Data Flag	RPD %[c]	Target RPD %	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS)[d] %Rec.	Post Matrix Spike (PS-A) %Rec.	Post Matrix Spike (PS-B) % Rec.	Serial Dilution %D
Acceptance Criteria							*80% - 120%*	*75% - 125%*	*75% - 125%*	*75% - 125%*	*< ±10%*
Test Specification Analytes											
Al	75	7.9	**929**		2.6	<15	98	95	99		1.6
Ca	150	33	34	U		<15	98	99	101		
Cr	15	2.6	**1,510**		2.6	<15	96	n/r	n/r		1.5
Li	4	4.0	4.0	U		<15	99	94	100		
K	75	260	**6,660**		2.8	<15	99	94	102		
Na	75	20	**106,000**		**3.7**	<3.5	99	n/r	n/r		5.7
U	600	270	270	U		<15	99	[e]		103	
U (KPA)	780	0.03	**15.2**	X	3	<15	91	**66**			
Other Analytes Measured											
Ag		3.3	3.3	U					101		
As		33	33	U					105		
B		6.6	**77.2**	B	21		108	102	100		
Ba		1.3	1.3	U			95	94	96		
Be		1.3	1.3	U					102		
Bi		13	13	U					99		
Cd		2.0	2.0	U			99	99	103		
Ce		26	27	U						99	
Co		6.6	6.6	U			96		102		
Cu		3.3	3.3	U			97	86	94		
Dy		6.6	6.6	U						100	
Eu		13	13	U						99	
Fe		3.3	3.3	U			98	100	101		
La		6.6	6.6	U						98	
Mg		13	13	U			98	103	105		
Mn		6.6	6.6	U			100		103		
Mo		6.6	**110**		2.6				99		
Nd		13	13	U						100	
Ni		4.0	4.0	U			97	100	103		
P		13	**286**		2.5		99	100	101		
Pb		13	13	U			107	111	111		
Pd		100	100	U						114	
Rh		40	40	U						96	
Ru		150	150	U							

Table 6.2 (Contd)

Analyte	MRQ µg/mL(a)	MDL µg/mL	02-751 Average µg/mL(b)	Data Flag	RPD %(c)	Target RPD %	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS)(d) %Rec.	Post Matrix Spike (PS-A) %Rec.	Post Matrix Spike (PS-B) % Rec.	Serial Dilution %D
Sb		66	66	U					102		
Se		33	33	U					103		
Si		66	**[255]**	JB					111		
Sn		200	200	U						101	
Sr		2.0	2.0	U			96	94	97		
Te		200	200	U						102	
Th		130	130	U						98	
Ti		3.3	3.3	U					93		
Tl		66	66	U					100		
V		6.6	6.6	U					100		
W		270	270	U							
Y		6.6	6.6	U					101		
Zn		6.6	6.6	U			98		101		
Zr		6.6	6.6	U					97		

Analytes detected by ICP-AES are bolded for clarity and better readability.
Blank areas indicate that QC results were not evaluated, or QC analyses were not performed, for opportunistic (other) analytes.
Shaded/bolded results highlight non-compliances with QC acceptance criteria; see report for discussion.
n/r = not recovered; spike concentration <20% of sample concentration.

U signifies undetected analyte; the concentration provided represents the IDL multiplied by the sample dilution factors.
B signifies that the associated preparative blank concentration resulted in 5% or more of the sample concentration.
X signifies that a QC parameter (e.g., precision, blank spike recovery, etc.) was exceeded.
J signifies an estimated concentration; the concentration is >MDL but <EQL.

(a) MRQs from 24590-WTP-TSP-RT-01-002 Table A.1 and B.2.
(b) The overall error for bolded values without brackets is estimated to be within ±15% (analytes greater than 10 times the MDL). Bracketed values identify sample concentrations that are <10-times the MDL, and errors likely exceed 15%.
(c) RPD only calculated when both the sample and duplicate results are greater than the EQL.
(d) The process batch matrix spike was prepared from another sample of similar matrix (02-0752, AZ-102C Cs ion exchange effluent) and run with this sample.
(e) U was not present in the MS spike solution.

Table 6.3. ICP-AES QC Results for AZ-102C Solids

Analyte	MRQ µg/g(a)	MDL µg/g	02-1299 Average µg/g(b)	Data Flag	RPD %(c)	Target RPD %	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS) %Rec.	Post Matrix Spike (PS-A) %Rec.	Post Matrix Spike (PS-B) % Rec.	Serial Dilution %D
Acceptance Criteria							*80% - 120%*	*75% - 125%*	*75% - 125%*	*75% - 125%*	*< ±10%*
Test Specification Analytes											
Al	NA	6.9	**1,080**		6.3	<15	105	101	101		3.2
Ca	NA	29	**[260]**	J		<15	103	97	103		
Cr	NA	2.3	**1,210**		8.4	<15	106	n/r	103		5.0
Li	NA	3.5	3.5	U		<15	106	99	103		
K	NA	231	**5,460**	X	7.5	<15	**35(e)**	**24(e)**	98		-1.6
Na	NA	87	**364,500**	X	1.5(d)	<3.5	**144**	n/r	109		-0.1(d)
U	NA	240	240	U		<15	107	99		102	
Other Analytes Measured											
Ag		2.9	2.9	U					101		
As		29	29	U					105		
B		5.8	**1,480**	BX	2.4		**169**	**136**	103		**3.3**
Ba		1.2	**[6.9]**	J			105	92	102		
Be		1.2	1.2	U			100	98	103		
Bi		12	12	U			108	106	103		
Cd		1.7	**[4.1]**	J			103	100	105		
Ce		23	23	U			105	97		98	
Co		5.8	5.8	U					106		
Cu		2.9	2.9	U			111	91	103		
Dy		5.8	5.8	U						101	
Eu		12	12	U						102	
Fe		2.9	**[20]**	JB			109	107	106		
La		5.8	**[6.4]**	J			103	96		101	
Mg		12	12	U			104	100	109		
Mn		5.8	5.8	U			105	99	105		
Mo		5.8	**91**		8.4		106	97	104		3.5
Nd		12	**[15]**	J			103	96		99	
Ni		3.5	3.5	U			106	102	106		
P		12	**229**		5.6		103	100	103		0.4
Pb		12	12	U			117	113	117		
Pd		87	87	U							
Rh		35	35	U						94	
Ru		130	130	U							
Sb		58	58	U					101		

Table 6.3 (Contd)

Analyte	MRQ µg/g[(a)]	MDL µg/g	02-1299 Average µg/g[(b)]	Data Flag	RPD %[(c)]	Target RPD %	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS) %Rec.	Post Matrix Spike (PS-A) %Rec.	Post Matrix Spike (PS-B) % Rec.	Serial Dilution %D
Se		29	29	U					105		
Si		58	**6050**	BX	**39**		107	75	111		
Sn		180	180	U						83	
Sr		1.7	**[2.7]**	J			106	99	106		
Te		180	180	U						104	
Th		120	120	U			101	97		101	
Ti		2.9	**[5.4]**	J			103	97	101		
Tl		58	58	U					103		
V		5.8	5.8	U			98	93	99		
W		240	240	U			100	92			
Y		5.8	5.8	U					100		
Zn		5.8	5.8	U			111	107	109		
Zr		5.8	**[16]**	J			105	101	105		

Analytes detected by ICP-AES are bolded for clarity and better readability.
Blank areas indicate that QC results were not evaluated, or QC analyses were not performed, for opportunistic (other) analytes.
Shaded/bolded results highlight non-compliances with QC acceptance criteria; see report for discussion.
n/r = not recovered; spike concentration <20% of sample concentration.

U signifies undetected analyte; the concentration provided represents the IDL multiplied by the sample dilution factors.
B signifies that the associated preparative blank concentration resulted in 5% or more of the sample concentration.
X signifies that a QC parameter (e.g., precision, blank spike recovery, etc.) was exceeded.
J signifies an estimated concentration; the concentration is >MDL but <EQL.

(a) The TS provides no MRQs for solids.
(b) The overall error for bolded values without brackets is estimated to be within ±15% (analytes greater than 10 times the MDL). Bracketed values identify sample concentrations that are <10-times the MDL, and errors likely exceed 15%.
(c) RPD only calculated when both the sample and duplicate results are greater than the EQL.
(d) RPD calculated from samples after an additional 5x dilution; %D calculated from results after additional 5x and 25x dilutions.
(e) The K LCS/BS and MS failures were attributed to instability of K in the multi-element spiking standard. The K concentration at the time of spiking was much lower than the original certified value (see Appendix E for discussion).

6.4 Gamma Spectrometry

Tables 5.3, 5.6, 5.9, and 6.4

Diluted aqueous sample aliquots were directly counted for gamma emitters according to procedure PNL-ALO-450, *Gamma Energy Analysis and Low-Energy Photon Spectrometry*. For the GEA analyses performed on acid-digested aliquots (i.e., RPL ID 02-366 and 02-1299), only sample, duplicate, and PBs were analyzed for gamma emitters; LCS/BS and MS were not prepared, nor required, for this analysis since the measurement is a direct reading of the gamma energy and is not subject to matrix interferences. The AZ-102C concentrate (i.e., RPL ID 02-751) was analyzed without digestion processing, and no PB was prepared. Before any analysis, reference standard and background counts were performed to verify GEA system performance. Only ^{137}Cs and ^{125}Sb determinations were required.

All ^{137}Cs sample results were well above the MRQ. All SAL hot cell PBs show the presence of ^{137}Cs, but the activities in the PBs are negligible with respect to the sample activities. The sample duplicates showed excellent repeatability for ^{137}Cs with RPD values well within the acceptance criterion of <15%. No ^{125}Sb was detected above the MDA of 4 µCi/mL for the supernatants or 4 µCi/g for the solids.

Table 6.4. GEA QC Results for ^{137}Cs

RPL ID	Sample ID	MRQ µCi/mL[(a)]	Average ^{137}Cs µCi/mL[(b)]	±1SD	Data Flag	RPD %	Target RPD%
02-366	AZ102 As-received Filtrate	0.01	**946**	4%		1	<15
02-751	AZ102C Concentrate	0.01	**2,010**	3%		3	<15
02-1299	AZ102C Solids	NA	**1,350**[(c)]	4%		6.7	<15

Analytes detected are bolded for clarity and better readability.
Standard deviation (SD) in report in percent.
NA = not applicable

(a) MRQ from TS 24590-PTF-TSP-RT-01-002.
(b) GEA decay correction reference dates: 02-366 Feb 4, 2002; 02-751 Dec 3, 2001; 02-1299 Feb 20, 2002.
(c) AZ102C Solids reported as µCi/g.

6.5 Anions

Tables 5.2, 5.5, 5.8, 6.5, 6.6, and 6.7

Anion analyses were conducted according to method PNL-ALO-212, *Determination of Inorganic Anions by Ion Chromatography*. The IC method was used to evaluate the anions of interest on unprocessed aqueous sub-samples and on the water leach solutions (PNL-ALO-103) of the solids sample. Aliquots of the aqueous sub-samples and water leach solutions were prepared for IC anion analysis by dilution (100x to 5000x for aqueous samples and 10x to 200x for the water leach solutions) to assure that the anions were measured within the calibration range. The samples (i.e., AZ-102, AZ-102C, and AZ-102C solids) were processed and analyzed at separate times; thus, each has a different set of QC samples for evaluating system performance. Quality control for the anion analyses consisted of sample duplicates, PBs, MSs, BSs, calibration verification check standards, and instrument blanks.

For the AZ-102, AZ-102C, and AZ-102C solids, all QC samples analyzed meet acceptance criteria, and no further discussion of the QC performance is necessary. Only those anions detected above the lowest calibration standard concentration adjusted for sample dilution factors (i.e., above the EQL) are reported. The EQL was less than the required MRQ for all anions, except F for the AZ-102C solids and Cl for all samples. The high total anion concentration for all samples required significant sample dilution to prevent column overloading during the IC analysis; this dilution made it impossible to meet the very low MRQ (10 µg/mL) for Cl.

6.6 Hydroxide Titration

Tables 5.2, 5.5, 6.5, and 6.6

The AZ-102 and AZ-102C samples were analyzed in duplicate for the hydroxide content following procedure PNL-ALO-228, *Determination of Hydroxyl and Alkalinity of Aqueous Solutions, Leachates & Supernates*. Sample aliquots were diluted in the SAL hot cells. These diluted aliquots were analyzed using a Brinkman 636 Auto-Titrator. A 0.1186 N NaOH solution was prepared for use as a verification standard and the matrix spiking solution, and a 0.2040 M HCl solution was prepared as the titrant. The first inflection point was defined as the hydroxide equivalency. The RPDs were within the acceptance criterion of <15%. The BS recoveries were within the acceptance criterion of 80% to 120%; an acceptance criterion for the MS was not specified. No hydroxide was detected in the reagent blanks.

6.7 TOC/TIC by Hot Persulfate and Furnace

Tables 5.2, 5.5, 6.5, and 6.6

The AZ-102 and AZ-102C samples were analyzed for TOC and TIC by two different procedures: PNL-ALO-381, *Direct Determination of TC, TOC, and TIC in Radioactive Sludges and Liquids by Hot Persulfate Method*, and PNL-ALO-380, *Determination of Carbon in Solids Using the Coulometric Carbon Dioxide Coulometer*. The AZ-102 and AZ-102C samples were analyzed in separate batches; thus, each has a different set of QC samples for evaluating system performance. The AZ-102C solids were not analyzed for TOC or TIC. The TIC and TOC analyses were not required by the test specification. The quality control discussions refer to QA criteria delineated in the QA Plan *Conducting Analytical Work in Support of Regulatory Programs*.

6.7.1 Hot Persulfate Method (PNL-ALO-381)

The hot-persulfate wet oxidation method uses acid decomposition to measure TIC and acidic potassium persulfate oxidation at 92 to 95°C for measurement of TOC, with both the TIC and TOC being obtained from the same sample. The TC is defined as the sum of the TIC and TOC. All sample results were corrected for average percent recovery of instrument calibration check standards and were also corrected for contribution from the instrument blanks, as per procedure PNL-ALO-381 calculations. The QC for the method uses sample duplicates, LCS (or BS), and a MS.

The LCS/BS recoveries and MS recoveries for both the AZ-102 (as-received) and AZ-102C (concentrate) samples met the QC criteria (i.e., 80% to 120% for LCS/BS and 75% to 125% for MS) for both the TIC and TOC analysis. The RPD for the AZ-102C TIC analysis met the QC criterion of <20%.

However, the RPD for the AZ-102 TIC analyses was 26% and exceeded the QC criterion; the reason for the poor reproducibility is unknown. The RPDs for the AZ-102 or AZ-102C TOC analyses could not be determined since the TOC results were <5x MDL.

6.7.2 Furnace Oxidation Method (PNL-ALO-380)

The furnace oxidation method determined TOC by combusting an aliquot of sample in oxygen at 700°C for 10 to 20 minutes. The TC was determined on another aliquot of sample by combusting at 1000°C for 10 minutes, and the TIC was obtained by difference between the TC and TOC. All sample results were corrected for average percent recovery of instrument calibration check standards and were also corrected for contribution from the instrument blanks, as per procedure PNL-ALO-380 calculations. The QC for the method uses sample duplicates, LCS (or BS), and a MS.

The LCS/BS recoveries and MS recoveries for both the AZ-102 (as-received) and AZ-102C (concentrate) samples met the QC criteria (i.e., 80% to 120% for LCS/BS and 75% to 125% for MS) for both the TOC and TC analysis. The RPD for AZ-102 and AZ-102C TC analysis and the AZ-102C concentrate TOC analysis met the acceptance criterion of <20%. However, the RPD for the AZ-102 TOC analyses was 23%, and slightly exceeded the QC criterion.

6.7.3 Comparison of TIC/TOC by Hot Persulfate and Furnace Oxidation Methods

The TIC results from the furnace oxidation method were obtained by difference (TC-TOC), with the analysis being performed on two independent sample aliquots (one for TOC and one for TC). The TC for the hot-persulfate method was the summation of the TIC and TOC, with the analyses for both TOC and TIC being performed on a single aliquot under different oxidation conditions.

The average AZ-102 TC result from the hot-persulfate method (7300 μg C/mL) was lower than the average TC result from the furnace method (9300 μg C/mL), whereas the average AZ-102C TC results from the two methods were in excellent agreement (i.e., both 14,700 μg/mL). However, there were significant differences between the TOC and TIC results between the methods for both the AZ-102 and AZ-102C samples. Oxidation efficiency has been shown to vary between the methods as a function of the carbon-bearing compound (Baldwin et al. 1994). Volatile components may be removed by initial sparging during the hot-persulfate method. TIC determination and certain metal carbonates may fully or partially oxidize at the 700°C temperature used for the furnace method TOC determination. Thus, the reported results from the two methods may vary. Typically, the furnace method produces the most accurate TC results (i.e., results from single measurements and not a summation from two measurements) and the hot persulfate method provides the most accurate TIC results.

Table 6.5. Anion and TOC/TIC QC Results for AZ-102 As-Received

Analyte	MRQ µg/mL	EQL(a) µg/mL	02-366 Average µg/mL	Data Flag	(c) RPD %	Target RPD %	Lab Control (LCS/BS) % Rec.	Matrix Spike (MS) % Rec.	Matrix Spike Duplicate (MSD) % Rec.
Acceptance Criteria							*80% - 120%*	*75% - 125%*	*75% - 125%*
Test Specification Analytes									
F(b)	150	140	**1,050**		5	<15	94	95	91
Cl	300	140	140	U		<15	95	98	96
NO_2	3,000	2,800	**37,500**		3	<15	98	99	108
NO_3	3,000	280	**19,600**		4	<15	92	94	100
OH	17	–	**10,200**		3	<15	94	91(f)	
Other Measured Analytes									
TOC/F (d)		1,400(a)	**10,200(g)**		23		102	81	
TIC/F (d)		1,400(a)	1,400	U	2(e)		103(e)	104(e)	
TOC/P (d)		1000(a)	1,000	U			105	105	
TIC/P (d)		380(a)	**7,340**		26		103	98	
Br		140	140	U			97	98	95
C_2O_4		280	**3,160**	X	1		100	101	**0**
PO_4		280	**820**		6		95	94	92
SO_4		280	**20,000**		1		94	95	103

Analytes detected are bolded for clarity and better readability.

Blank areas indicate that QC results were not evaluated, or QC analyses were not performed, for opportunistic (other) analytes.

Shaded/bolded results highlight non-compliances with QC acceptance criteria; see report for discussion.

MSD = matrix spike duplicate

U signifies undetected analyte; the concentration provided represents the IDL multiplied by the sample dilution factors.

X signifies that a QC parameter (e.g., precision, blank spike recovery, etc.) was exceeded.

(a) F, Cl, NO_2, NO_3, PO_4, SO_4, Br, and C_2O_4 report only results above the EQL; therefore, the EQL is presented in this column. For all other analytes, the MDL is presented.

(b) Fluoride results should be considered the upper-bound concentration. Significant peak distortion of the F peak suggests the presence of co-eluting anion(s), possibly formate or acetate.

(c) RPD only calculated when both the sample and duplicate results are greater than the EQL.

(d) For TOC and TIC: P=by hot persulfate method; F=by furnace method/TIC by difference (TIC = TC-TOC).

(e) The LCS and MS recovery represents the recovery for the TC analysis. RPD represents the RPF for the TC analysis (9,400 µg/mL and 9,200 µg/mL).

(f) No MS criteria for OH specified in TS.

(g) One of the two TOC results (11,300 µg/mL) was significantly higher than sample and duplicate TC result (9,400 µg/mL and 9,200 µg/mL, respectively), suggesting that the average result may be higher than the actual TOC concentration.

Table 6.6. Anion and TOC/TIC QC Results for Filtered AZ-102 Concentrate (AZ-102C)

Analyte	MRQ µg/mL[g]	EQL[a] µg/mL	02-751 Average µg/mL	Data Flag	[c] RPD %	Target RPD %	Lab Control (LCS/BS) % Rec.	Lab Control Duplicate (LCS/BS) % Rec.	Matrix Spike (MS) % Rec.
Acceptance Criteria							*80% - 120%*	*80% - 120%*	*75% - 125%*
Test Specification Analytes									
F [b]	150	140	**1,760**		9	<15	104	104	104
Cl	10	140	140	U		<15	97	96	101
NO_2	3,000	1,400	**78,000**		10	<15	102	103	105
NO_3	3,000	1,400	**37,700**		9	<15	94	96	97
OH	17		**18,800**		14	<15	93	100[f]	89
Other Analytes									
TOC-F [d]		1,000[a]	**13,900**		9		97		112
TIC-F [d]		1,000[a]	1,000	U	6[e]		103[e]		108[e]
TOC-P [d]		500[a]	1000				95		100
TIC-P [d]		220[a]	**14,600**		6		102		101
Br		140	140	U			98	103	104
C_2O_4		280	**1,680**		27		107	107	105
PO_4		280	**1,340**		5		103	103	103
SO_4		1,400	**35,400**		10		102	102	103

Analytes detected are bolded for clarity and better readability.
Blank areas indicate that QC results were not evaluated, or QC analyses were not performed, for opportunistic (other) analytes.
Shaded/bolded results highlight non-compliances with QC acceptance criteria; see report for discussion.

U signifies undetected analyte; the concentration provided represents the IDL multiplied by the sample dilution factors.
X signifies that a QC parameter (e.g., precision, blank spike recovery, etc.) was exceeded.

(a) F, Cl, NO_2, NO_3, PO_4, SO_4, Br, and C_2O_4 report only results above the EQL; therefore, the EQL is presented in this column. For TOC and TIC analytes, the MDL is presented.
(b) Fluoride results should be considered the upper-bound concentration. Significant peak distortion of the F peak suggests the presence of co-eluting anion(s), possibly formate or acetate.
(c) RPD only calculated when both the sample and duplicate results are greater than the EQL.
(d) For TOC and TIC: P=by hot persulfate method; F=by furnace method/TIC by difference (TIC = TC-TOC).
(e) The LCS and MS recovery represents the recovery for the TC analysis. The RPD represents the RPD for the TC analysis (15,300 µg/mL and 14,500 µg/mL).
(f) No MS criteria for OH specified in TS.
(g) MRQs from Test Specification 24590-WTP-TSP-RT-01-002.

Table 6.7. Anion QC Results for AZ-102C Solids

Analyte	MRQ µg/mL[e]	EQL[a] µg/g	02-1299 Average µg/g	Data Flag	[b] RPD %	Target RPD %	Lab Control Spike (LSC/BS) % Rec.	Post Matrix Spike% Rec.[c]
Acceptance Criteria							*80% - 120%*	75% - 125%
Test Specification Analytes								
F [d]		1,400	**40,200**		1	<15	90	112
Cl		71	71	U		<15	93	106
NO_2		2,800	**47,000**		13	<15	97	110
NO_3		2,800	**25,800**		11	<15	92	102
PO_4		140	**600**		2	<15	92	104
SO_4		2,800	**219,000**		5	<15	92	118
Other Analytes								
Br		71	71	U			94	105
C_2O_4		2,800	**221,000**		3		96	119

Analytes detected are bolded for clarity and better readability.
Blank areas indicate that QC results were not evaluated, or QC analyses were not performed, for opportunistic (other) analytes.

U signifies undetected analyte; the concentration provided represents the IDL multiplied by the sample dilution factors.

(a) F, Cl, NO_2, NO_3, PO_4, SO_4, Br, and C_2O_4 report only results above the EQL.
(b) RPD only calculated when both the sample and duplicate results are greater than the EQL.
(c) The matrix spike was not recoverable. The diluted MS sample (leached) resulted in all anion concentrations <EQL or <<20% of the sample concentration. A post-matrix spike was performed instead.
(d) Fluoride results should be considered the upper-bound concentration. The F co-elutes with formate and acetate.
(e) No MRQs for solids were defined.

7.0 Conclusions

The Hanford tank waste AZ-102 samples received from 222-S were composited and characterized for metals (ICP-AES), inorganic anions, TOC/TIC, and ^{137}Cs. The AZ-102 composite was evaporated to nominally 50% volume, resulting in nominally 1-wt% precipitate formation. The precipitate consisted primarily of Na_3FSO_4 (57%) and $Na_2C_2O_4$ (28%). Characterization of the AZ-102 concentrate showed good total mass recovery of most measured analytes (e.g., Na, Al, K, Cr, Mo, P, NO_3, NO_2, PO_4, SO_4, OH, and ^{137}Cs), with the notable exception of oxalate. The AZ-102 concentrate was forwarded to the Cs ion exchange task for ion exchange processing.

8.0 References

Baldwin DL, RW Stromatt, and WI Winters. 1994. *Comparative Study of Total Organic Carbon (TOC) Methods for High-Level Mixed Waste*, PNL-SA-23718, Battelle Pacific Northwest Laboratory, Richland, WA.

Hassan NM, WD King, DJ McCabe, and ML Crowder. 2001. *Small-Scale Ion Exchange Removal of Cesium and Technetium form Envelope B Hanford Tank 241-AZ-102*, WSRC-TR-2000-00419, SRT-RPP-2000-000036, Savannah River Technology Center, Aiken, SC.

Hay MS, and MG Bronikowski. 2000. *Chemical Characterization of an Envelope B/D Sample from Hanford Tank 241-AZ-102*, BNF-003-98-0249, Savannah River Technology Center, Aiken, SC.

Appendix A

Chains of Custody

Appendix A: Chains of Custody

CHAIN OF CUSTODY/SAMPLE ANALYSIS REQUEST

C.O.C. No. shipment A6004

Page 1 of 1

Collector Rice, Andrew D.	Contact/Requestor Myers, Ronald L.	Telephone No. 372-1323 · MSIN P7-28 · FAX 376-7127
SAF No.	Sample Origin Tank 241-AZ-102	Purchase Order/Charge Code 116198/EF21
Project Title Packaging and Shipping for Tank 241-AZ-102	Logbook No. n/a	Ice Chest No. n/a · Temp. n/a
Shipped To (Lab) PNNL 325 Bld. SAL Hot Cell (west end of bld.)	Method of Shipment TWRS CPO Sample Truck	Bill of Lading/Air Bill No.
Protocol n/a	Data Turnaround n/a	Offsite Property No. n/a

Sample No.	Lab ID	*	Date	Time	No./Type Container	Sample Analysis	Preservative
						TS 10-25-01	
AZ-102 COMP9	S01T001856	L			500 mL glass	i.a.w. ICD-23 requirements JAR 18994 overpak" WT-OP-6004 D	none
AZ-102COMP10	S01T001857	L			500 mL glass	i.a.w. ICD-23 requirements JAR 18986 overpak# WT-OP-6004 ~~B~~ A 10-25-01 TS	none

POSSIBLE SAMPLE HAZARDS/REMARKS (List all known wastes) MSDS ☐ Yes ☒ No

See DST Part A in DOE-RL88-21 for listed waste codes.

SPECIAL INSTRUCTIONS

Contact Rudy Thornhill upon arrival, 376-6769.

Hold Time n/a

Relinquished By	Print	Sign	Date/Time	Received By	Print	Sign	Date/Time
R T Steele	RHSteel		10/25/01 1440	James Sickels		James Sickels	10-25-01 1440
Relinquished By			Date/Time	Francisko Steen		F Steen	10/25/01 2100
Relinquished By			Date/Time	Received By			Date/Time
Relinquished By			Date/Time	Received By			Date/Time

Matrix*

S = Soil		DS = Drum Solids	
SE = Sediment		DL = Drum Liquids	
SO = Solid		T = Tissue	
SL = Sludge		WI = Wipe	
W = Water		L = Liquid	
O = Oil		V = Vegetation	
A = Air		X = Other	

FINAL SAMPLE DISPOSITION

Disposal Method (e.g., Return to customer, per lab procedure, used in process): per lab procedure

Disposed By

Date/Time

All samples containing hazardous materials shall be picked up by requestor and returned to parent container or site of origin.

DISTRIBUTION: White - Remain with Samples Color - Customer

CHAIN OF CUSTODY/SAMPLE ANALYSIS REQUEST

C.O.C. No. shipment A6000

Page 1 of 1

Collector Rice, Andrew D.	Contact/Requestor Myers, Ronald L.	Telephone No. 372-1323 MSIN P7-28 FAX 376-7127
SAF No.	Sample Origin Tank 241-AZ-102	Purchase Order/Charge Code 116198/EF21
Project Title Packaging and Shipping for Tank 241-AZ-102	Logbook No. n/a	Ice Chest No. n/a Temp. n/a
Shipped To (Lab) PNNL 325 Bld. SAL Hot Cell (west end of bld.)	Method of Shipment TWRS CPO Sample Truck	Bill of Lading/Air Bill No.
Protocol n/a	Data Turnaround n/a	Offsite Property No. n/a

Sample No.	Lab ID	*	Date	Time	No./Type Container	Sample Analysis	Preservative
AZ-102 COMP1	S01T001848	L			500 mL glass	i.a.w. ICD-23 requirements JAR 18819 ✓ Pig 460.23	none
AZ-102 COMP2	S01T001849	L			500 mL glass	i.a.w. ICD-23 requirements JAR 18990 ✓ Pig 460.26	none

POSSIBLE SAMPLE HAZARDS/REMARKS (List all known wastes) MSDS ☐ Yes ☒ No

See DST Part A in DOE-RL88-21 for listed waste codes.

SPECIAL INSTRUCTIONS

Contact Rudy Thornhill upon arrival, 376-6769.

Hold Time

n/a

Relinquished By Print	Sign	Date/Time	Received By Print	Sign	Date/Time
RL Chambers	RL Chambers	1400 10-24-01	Louie Aguilar		10/24/01 1420
Louie Aguilar		1920 10-24-01	F Steen	F. Steen	10/24/01 1920

Matrix*

S = Soil		DS = Drum Solids	
SE = Sediment		DL = Drum Liquids	
SO = Solid		T = Tissue	
SL = Sludge		WI = Wipe	
W = Water		L = Liquid	
O = Oil		V = Vegetation	
A = Air		X = Other	

FINAL SAMPLE DISPOSITION

Disposal Method (e.g., Return to customer, per lab procedure, used in process)
per lab procedure

Disposed By

Date/Time

All samples containing hazardous materials shall be picked up by requestor and returned to parent container or site of origin.

DISTRIBUTION: White - Remain with Samples Color - Customer

BC-6000-828 (04/98)

CHAIN OF CUSTODY/SAMPLE ANALYSIS REQUEST

C.O.C. No. shipment A6001

Page 1 of 1

Collector Rice, Andrew D.	Contact/Requestor Myers, Ronald L.	Telephone No. 372-1323 MSIN P7-28 FAX 376-7127
SAF No.	Sample Origin Tank 241-AZ-102	Purchase Order/Charge Code 116198/EF21
Project Title Packaging and Shipping for Tank 241-AZ-102	Logbook No. n/a	Ice Chest No. n/a Temp. n/a
Shipped To (Lab) PNNL 325 Bld. SAL Hot Cell (west end of bld.)	Method of Shipment TWRS CPO Sample Truck	Bill of Lading/Air Bill No.
Protocol n/a	Data Turnaround n/a	Offsite Property No. n/a

Sample No.	Lab ID	*	Date	Time	No./Type Container	Sample Analysis	Preservative
AZ-102 COMP3	S01T001850	L			500 mL glass	i.a.w. ICD-23 requirements JAR 18988 pig # 460-22	none
AZ-102 COMP4	S01T001851	L			500 mL glass	i.a.w. ICD-23 requirements JAR 18989 pig # 460-3	none

POSSIBLE SAMPLE HAZARDS/REMARKS (List all known wastes) MSDS ☐ Yes ☒ No

See DST Part A in DOE-RL88-21 for listed waste codes.

SPECIAL INSTRUCTIONS

Contact Rudy Thornhill upon arrival, 376-6769.

Hold Time n/a

Relinquished By (Print / Sign)	Date/Time	Received By (Print / Sign)	Date/Time
RL Chambers	1430 10-24-01	V. Matthews / V. MATTHEWS	1430 10-24-01
V. Matthews / V. Matthews	1930 10-24-01		1935 10/24/01

Matrix*

S = Soil		DS = Drum Solids	
SE = Sediment		DL = Drum Liquids	
SO = Solid		T = Tissue	
SL = Sludge		WI = Wipe	
W = Water		L = Liquid	
O = Oil		V = Vegetation	
A = Air		X = Other	

FINAL SAMPLE DISPOSITION — Disposal Method (e.g., Return to customer, per lab procedure, used in process): per lab procedure — Disposed By — Date/Time

All samples containing hazardous materials shall be picked up by requestor and returned to parent container or site of origin.

DISTRIBUTION: White - Remain with Samples Color - Customer

CHAIN OF CUSTODY/SAMPLE ANALYSIS REQUEST

C.O.C. No. shipment A6002

Page 1 of 1

Collector Rice, Andrew D.	Contact/Requestor Myers, Ronald L.	Telephone No. 372-1323 MSIN P7-28 FAX 376-7127
SAF No.	Sample Origin Tank 241-AZ-102	Purchase Order/Charge Code 116198/FF21
Project Title Packaging and Shipping for Tank 241-AZ-102	Logbook No. n/a	Ice Chest No. n/a Temp. n/a
Shipped To (Lab) PNNL 325 Bld. SAL Hot Cell (west end of bld.)	Method of Shipment TWRS CPO Sample Truck	Bill of Lading/Air Bill No.
Protocol n/a	Data Turnaround n/a	Offsite Property No. n/a

Sample No.	Lab ID	*	Date	Time	No./Type Container	Sample Analysis	Preservative
AZ-102 COMP5	S01T001852	L			500 mL glass	i.a.w. ICD-23 requirements JAR 18996 ✓ PiG# 460.4	none
AZ-102 COMP6	S01T001853	L			500 mL glass	i.a.w. ICD-23 requirements JAR 18992 ✓ PiG# 460.11	none

POSSIBLE SAMPLE HAZARDS/REMARKS (List all known wastes) MSDS ☐ Yes ☒ No

See DST Part A in DOE-RL88-21 for listed waste codes.

SPECIAL INSTRUCTIONS

Contact Rudy Thornhill upon arrival, 376-6769.

Hold Time

n/a

Relinquished By (Print / Sign)	Date/Time	Received By (Print / Sign)	Date/Time
RL Chambers / RL Chambers	2059 10-24-01	Louie Aguila / Louie Aguila	2059 10-24-01
Louie Aguilar / Louie Aguilar	22.20 10-24-01	F. Steen / F. Steen	2210 10/24/01

Matrix*

S	= Soil	DS	= Drum Solids
SE	= Sediment	DL	= Drum Liquids
SO	= Solid	T	= Tissue
SL	= Sludge	WI	= Wipe
W	= Water	L	= Liquid
O	= Oil	V	= Vegetation
A	= Air	X	= Other

FINAL SAMPLE DISPOSITION

Disposal Method (e.g., Return to customer, per lab procedure, used in process)
per lab procedure

Disposed By

Date/Time

All samples containing hazardous materials shall be picked up by requestor and returned to parent container or site of origin.

DISTRIBUTION: White - Remain with Samples Color - Customer

CHAIN OF CUSTODY/SAMPLE ANALYSIS REQUEST

C.O.C. No. shipment A6003

Page 1 of 1

Collector Rice, Andrew D.	Contact/Requestor Myers, Ronald L.	Telephone No. 372-1323 MSIN P7-28 FAX 376-7127
SAF No.	Sample Origin Tank 241-AZ-102	Purchase Order/Charge Code 116198/BF21
Project Title Packaging and Shipping for Tank 241-AZ-102	Logbook No. n/a	Ice Chest No. n/a Temp. n/a
Shipped To (Lab) PNNL 325 Bld. SAL Hot Cell (west end of bld.)	Method of Shipment TWRS CPO Sample Truck	Bill of Lading/Air Bill No.
Protocol n/a	Data Turnaround n/a	Offsite Property No. n/a

Sample No.	Lab ID	*	Date	Time	No./Type Container	Sample Analysis	Preservative
AZ-102 COMP7	S01T001854	L			500 mL glass	i.a.w. ICD-23 requirements JAR 18993 ✓ Pig # 460.15	none
AZ-102 COMP8	S01T001855	L			500 mL glass	i.a.w. ICD-23 requirements JAR 18998 ✓ Pig # 460.16	none

POSSIBLE SAMPLE HAZARDS/REMARKS (List all known wastes) MSDS ☐ Yes ☒ No

See DST Part A in DOE-RL88-21 for listed waste codes.

SPECIAL INSTRUCTIONS

Contact Rudy Thornhill upon arrival, 376-6769.

Hold Time

n/a

Relinquished By Print	Sign	Date/Time	Received By Print	Sign	Date/Time
RLChambers	RLChambers	2110 10-24-01	V. MATTHEWS	V. Matthews	2110 10-24-01
V. MATTHEWS	V. Matthews	2222 10-24-01	J Steen	J Steen	2225 10/24/01
Relinquished By		Date/Time	Received By		Date/Time
Relinquished By		Date/Time	Received By		Date/Time

Matrix*

S = Soil		DS = Drum Solids	
SE = Sediment		DL = Drum Liquids	
SO = Solid		T = Tissue	
SL = Sludge		WI = Wipe	
W = Water		L = Liquid	
O = Oil		V = Vegetation	
A = Air		X = Other	

FINAL SAMPLE DISPOSITION

Disposal Method (e.g., Return to customer, per lab procedure, used in process)
per lab procedure

Disposed By

Date/Time

All samples containing hazardous materials shall be picked up by requestor and returned to parent container or site of origin.

DISTRIBUTION: White - Remain with Samples Color - Customer

Appendix B

Test Plan TP-RPP-WTP-111
“Tank 241-AZ-101 and 241-AZ-102 Waste Sample Ion Exchange Testing”

Appendix B: Test Plan TP-RPP-WTP-111 "Tank 241-AZ-101 and 241-AZ-102 Waste Sample Ion Exchange Testing"

Battelle Test Plan

Document No.: TP-RPP-WTP-111
Rev. No.: 0

Title: Tank 241-AZ-101 and 241-AZ-102 Waste Sample Ion Exchange Testing

Work Location: RPL/ Various

Page 1 of 29

Author: D.L. Blanchard Jr.

Effective Date: On final signature
Supersedes Date: New

Identified Hazards:
___Radiological
___Hazardous Materials
___Physical Hazards
___Hazardous Environment
___Other:

Required Reviewers:
_X_ Author
_X_ Technical Reviewer
_X_ Quality Engineer
_X_ Project Manager
_X_ Client

Approval	**Signature**	**Date**
Author		11/5/01
Technical Reviewer	Sandra K. Fisk	11/5/01
Quality Engineer	T Almeida	11/5/01
Project Manager	D E Kurath	11/5/01
Client		11/5/01

Applicability

This test plan applies to the testing of solid phase extractant materials (organic and inorganic ion exchange materials) with samples from Hanford tanks 241-AZ-101 and 241-AZ-102. (The "241" prefix will be hereafter omitted in this document.) Both of these tank wastes belong to the RPP-WTP (River Protection Project-Waste Treatment Plant) tank waste classification Envelope B. The testing includes contacting the tank wastes with ion exchange material (i.e. batch contacts), and passing the tank wastes through small column (5-30 mL) packed with the ion exchange material in flow tests. The materials to be tested include Superlig® 644 (SL-644, for cesium removal), and Superlig® 639 (SL-639, for technetium removal). The testing may be conducted in hot cells in the HLRF (High Level Radiation Facility) and its supporting analytical laboratories, and in labs 410, 507, 510, and 511. This test plan also applies to the use of a prototype instrument being developed under a separate task to monitor technetium during testing.

Justification

The tests described herein will be conducted for the River Protection Project Waste Treatment Plant Project (RPP-WTP) to demonstrate contract cesium (Cs) and technetium (Tc) decontamination, operating and throughput requirements with Envelope B waste samples, and to demonstrate a prototype instrument suitable for monitoring Tc-99 in the Envelope B samples at the contract Tc removal decontamination, operating and throughput requirements.

The RPP-WTP is conducting batch contacts with ion exchange materials and simulated and radioactive candidate LAW solutions to determine ion selectivity. Small-scale ion exchange column tests are being conducted with simulated and radioactive candidate LAW feed solutions to provide breakthrough curves for modeling and to prepare LAW solutions for subsequent LAW vitrification testing. The information from this series of ion exchange material tests will be used to validate ion exchange models(1),(2) prepared by SRTC personnel. These models will enable personnel to verify design and predict performance of the full-scale ion exchange systems within the waste treatment plant.

SRTC personnel have evaluated the ability of the SL-644 resin to remove cesium from an Envelope B waste sample from tank AZ-102(3). The cesium ion exchange column performance was unexpectedly poor. However, the test was conducted on as-received decanted tank waste supernate at 2.65 M sodium with a density of 1.15 g/mL. The reference process for the treatment of LAW solutions includes dilution or evaporation, as necessary, to provide a feed at 5 M sodium concentration, not 2.65 M as used in prior tests. Column and batch contact tests with Envelope B wastes AZ-101 and AZ-102 need to be repeated under reference process conditions, using the proper ionic strength of the feed. The resulting data will be used validate ion exchange models for AZ-101 and AZ-102 supernate pretreatment design verification (Envelope B). Sufficient samples will be taken from both AZ-101 and AZ-102 to determine the extent, if any, of precipitation that occurs during the ion-exchange of these materials. It is essential that this precipitation data be obtained to provide insight into the limitations of performing the ion exchange

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(1) BNF-003-98-0220, *Preliminary Ion Exchange Modeling for Removal of Cesium from Hanford Waste using SuperLig® 644 Resin,* June 16, 2000, L. L. Hamm et al, Westinghouse Savannah River Company, Aiken South Carolina.

(2) SRT-RPP-2000-00011 November 2000, *Preliminary Ion Exchange Modeling for Removal of Technetium from Hanford Waste using SuperLig® 639 Resin,* June 16, 2000, L. L. Hamm et al, Westinghouse Savannah River Company, Aiken South Carolina.

(3) WSRC-TR-2000-00419, *Small Scale Ion Exchange Removal of Cesium and Technetium from Envelope B Hanford Tank 241-AZ-102,* N.M. Hassan, Savannah River Technology Center, January 17, 2001, Aiken, South Carolina.

process at the baseline 5 M sodium concentration. In addition, sufficient sample exists from Tank AZ-102 to perform an additional Cs IX test if necessary.

On-line monitoring of the Tc removal process in the Waste Treatment Plant will be required for continuous operation. On-line monitoring will simplify operations and allow on-line process control. A separate Tc monitor task is underway because no on-line Tc monitors are currently commercially available. The work described in this test plan includes tasks to demonstrate the operation of a prototype on-line Tc monitor using the Envelope B waste samples. Successful demonstration of the prototype will enable design and assembly of an on-line Tc monitor for the Waste Treatment Plant.

Test Objectives

The objectives of this test are to:

- Measure and report equilibrium Cs and Tc batch distribution coefficients (i.e. K_d's) for AZ-101 supernate using SL-644 (Cs) and SL-639 (Tc) ion exchange resin.
- Measure and report equilibrium Cs batch distribution coefficients (i.e. K_d's) of AZ-102 supernate using SL-644 (Cs) ion exchange resin.
- Develop loading and elution breakthrough profiles for columns of SL-644 (Cs) and SL-639 (Tc) ion exchange materials using samples of candidate LAW feed solutions from Tank AZ-101 supernate.
- Develop loading and elution breakthrough profiles for columns of SL-644 (Cs) resin ion exchange material using samples of candidate LAW feed solutions from Tank AZ-102.
- Pretreat the AZ-101 filtrate sample to reduce the concentrations of ^{137}Cs and ^{99}Tc to meet LAW pretreatment requirements.
- Pretreat the AZ-102 supernate sample to reduce the concentration of ^{137}Cs to meet LAW pretreatment requirements.
- Measure the concentration of Tc in the AZ-102 sample over a range of values from the concentration in the feed down to an estimated detection limit (EDL) of 1.8E-06 Ci/L using the prototype Tc monitor.

Test Success Criteria

The batch contact data will provide a practical description of the projected resin performance of envelope B wastes AZ-101 and AZ-102 in the form of an equilibrium distribution coefficient (K_d). The column tests will provide performance measures including column distribution ratio (the product of K_d and the resin bed density), composite decontamination factors, and maximum decontamination factors.

The Cs and Tc concentration in the column loading effluent must be accurately determined to quantify the exchange capacity of each ion exchange resin. Therefore, the Estimated Quantitation Levels (EQL) for ^{137}Cs and ^{99}Tc should be at least 10 to 100 times lower than the LAW vitrification criteria. The EQL for ^{137}Cs must be 1E-05 Ci/L (or less) and the EQL for ^{99}Tc must be 3E-06 Ci/L (or less) to accurately determine the loading profiles. The EQL is defined as the lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions.

For analytes that are detected above the estimated quantitation level (EQL), the relative percentage difference between duplicate analyses should be less than 20%. For laboratory analyses where matrix spikes, blank spikes, post-spikes, process blanks, and serial dilutions are used the following criteria should be met.

Criteria for Laboratory Analyses

Quality Control Method	Tolerance Limit
Matrix spikes recoveries	75% to 125%
Blank spikes recoveries	80% to 120%
Post spikes recoveries	75% to 125%
Process blanks analyses	Analytes of interest below the EQL or less than 5% of the sample concentration
Serial Dilutions	± 10% of the sample analysis, where the analyte concentration exceeds the EQL

Laboratory control standards (LCSs) shall be traceable to the National Institute of Standards and Technology (NIST), and all analytes above the EQL should exhibit recoveries within acceptance criteria. The acceptance criteria for calibration verification check standards are ± 10% of true value.

The use of the Tc monitor to analyze AZ-101 samples will be considered successfully completed when the prototype monitor has accurately determined at least four different Tc concentrations in the waste during continuous operation with sampling rates of at least two samples per hour. The concentrations will be considered accurately determined if the values are within 20% of those determined for the same samples by ICP-MS, with an estimated detection limit (EDL) for Tc-99 of 1.8E-06 Ci/L for a 5 M sodium waste solution. In addition, statistical methods will be used to show that results of the two methods are statistically equivalent.

Background

The RPP-WTP has identified reference processes for the treatment of low activity waste (LAW) solutions and high-level waste (HLW) slurries[4]. The reference process for separating cesium and technetium from LAW solutions is ion exchange using SL-644 and SL-639 resins, respectively. The RPP-WTP has conducted tests with these resins using simulated and radioactive LAW solutions. SL-644 resin is a proprietary ion exchange resin comprised of a polymer ligand that selectively separates cesium from alkaline solutions. SL-639 resin is also a proprietary material that consists of a ligand attached to a polystyrene substrate. SuperLig 639 resin separates pertechnetate (or perrhenate) as a salt-pair from acidic or basic solutions. Both resins are elutable. IBC Advanced Technologies Inc. in American Fork, Utah developed and manufactures both SL-644 and SL-639.

The LAW glass-equivalent production rate requirement is at least 30 MT LAW glass per day with envelope B waste. The LAW facility must average 1100 units of waste throughput per year, in accordance with Specification 7.2.3. For envelope B feed, an average processing rate of 1100 units of waste annually corresponds to processing 423.1 MT of sodium (Na) annually. The average flowrate through the 1.05 m^3 column is about 0.4 resin bed volumes per hour (BV/hr) at 100% attainment. Assuming 60% process attainment, the required flowrate through the ion exchange column must be only 0.67 BV/hr. An

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[4] (4) Waste Treatment Plant Request for Proposals Solicitation No. DE-RP27-00RV14136, August 31, 2000, section C.7, FACILITY SPECIFICATION, item (d)(iii) and (d)(iv), U. S. Department of Energy Office of River Protection, Richland, Washington.

important objective of this test is demonstration of the required Cs and Tc decontamination at the required throughput.

A method must be demonstrated to detect ^{99}Tc in the effluent from the technetium removal columns at the concentration required to comply with the immobilized LAW product specification[5] for process control. A prototype instrument for this purpose is currently under development and testing[6]. Part of the planned testing of the instrument is the analysis of the samples from one of the small column actual waste Tc removal tests in a continuous test. More background may be found in test plan TP-PNNL-WTP-045.

Equipment and Materials Descriptions

The test equipment required for the batch distribution tests are as follows:

- Aqueous test solutions - prepared as required in accordance with test instructions.
- Ion Exchange Materials – obtained from the RPP-WTP client or from a vendor as required.
- Appropriate tracers (^{99}Tc, ^{99m}Tc, ^{95m}Tc, ^{137}Cs) - the radiotracers may be obtained either through commercial sources (i.e., New England Nuclear, Boston, MA; or Amersham, Arlington, IL) or from stock solutions already in the laboratory. Technical data sheets accompanying the commercial shipments should list the assay of the isotope (i.e., chemical form, purity, assay date, specific activity, concentration, and volume).
- Counting Equipment - gamma counting is performed by the use of a multichannel analyzer and a suitable detector, such as a high purity germanium detector. Additionally a liquid scintillation counter may be used for ^{99}Tc determination. The equipment is user calibrated to determine that the equipment is working properly. Known standards of each tracer are counted along with the samples.
- Shaker/Temperature Control Systems - A variety of shaker systems are used, such as those made by Eberbach, Ann Arbor, MI. The shaker table will include a test chamber that holds the sample container.
- Filters, 0.2 um pore size disposable Gelman #4192 or equivalent (man-made material).
- Syringe, 5 mL, plastic, Luer-Loc or equivalent.
- Vials, 20 mL glass scintillation.
- Bottles, 20 to 2000 mL polyethylene, Nalgene #2003-0001 or equivalent.
- Pipets, adjustable, 100 to 10,000 uL maximum capacity, Gilson Pipetman or equivalent.
- The vessel material of construction selected for the evaporation shall not leach metals nor silicon into the waste feed.

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[5] WTP Contract No. DE-AC27-01RV14136, December 2000, Specification 2.2.2.8 Radionuclide Concentration Limitations.

[6] Battelle Test Plan TP-PNNL-WTP-045, "On-Line Tc Monitor Development and Testing"

For the Ion Exchange column tests, the following additional equipment is required:

- An analytical balance.
- Pump.
- Ion exchange columns (< 30mL volume).
- Gamma counting equipment.
- Liquid scintillation counter.
- Prototype Tc Monitoring Equipment[7]
- Recirculating heater/chiller.

The experimental apparatuses for the SL-644 and SL-639 column flow tests have already been assembled and used for testing AP-101 and AN-102/C-104 waste samples[8]. Each apparatus consists primarily of two ion exchange columns, (a lead and a lag column), feed storage bottles, pump, valves, and effluent collection and storage bottles. A recirculating heater/chiller is also used with the SL-639 apparatus to heat the column during elution. The SL-644 resin beds are nominally 10 mL in 0.25 M NaOH; 1.5 cm in diameter by 6 cm in height. The SL-639 resin beds are nominally 5 mL in 0.25 M NaOH; 1.5 cm in diameter by 3 cm in height. The columns of the SL-644 system may be run independently or connected in series; similarly for the SL-639 system. The SL-639 columns employ plungers to restrict the volume available for the resin bed. A plug of quartz wool at the top of each column is used to provide some space for liquid above the bed but prevent the resin from floating

All solutions to the columns are normally fed downflow through pumps from feed tanks. The feed pump is used to control the flow rate. A valve located at the bottom of each column permits sampling of each column's effluent during testing. The effluent from the final column is routed to the weighing bottle. The bed volumes (BV's) of the effluent processed are determined by the effluent weight divided by the specific gravity of the feed. The systems include a pressure relief valve between the pump and the first column. The valve insures that no solution is lost in case of overpressurization and reduces the likelihood of a contamination incident in that event. The columns are generally operated 24 hours, 7-days per week until the objective of a test is met, although testing may be halted overnight or over a weekend if the system can be placed in a safe state without significantly interrupting the test. Such an interruption may occur between feed displacement rinse and elution, for example. A process step (i.e., loading, feed displacement, elution, etc.) would generally not be interrupted unless there was a safety concern, or continuation of the process step was deemed fruitless in consultation with the WTP pretreatment technical contact. Additional equipment that may be used, for indication only, includes gamma-counting equipment, a ruler and a clock.

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[7] The prototype Tc monitor instrumentation is described in Test Plan TP-PNNL-WTP-045, "On-Line Tc Monitor Development and Testing"

[8] Battelle Test Plan TP-RPP-WTP-013, "AP-101 and AN-102/C-104 Actual Waste Ion Exchange Testing."

Test Description

AZ-101 Feed

A sample of the candidate LAW feed solution from tank AZ-101 is being used to verify the combined LAW and HLW pretreatment process flowsheet and prepare LAW solutions for subsequent LAW vitrification. As part of a separate test specification, Battelle will characterize the AZ-101 sample to determine compliance with the LAW and HLW feed specifications(9). The test specification for the AZ-101 HLW filtration using the CUF is described elsewhere. The permeate solution from the ultrafiltration process test will be used for the cesium and technetium ion exchange tests described in this test plan. The allowable ion exchange feed concentration range of sodium in the AZ-101 supernate feed for this test is 5.0 ±0.2 M sodium. If evaporation of the AZ-101 supernate sample is necessary to achieve this sodium concentration range, the directions for AZ-102 evaporation below will be used, on notification and concurrence of the RPP-WTP pretreatment technical contact. If dilution is necessary, the feed will be diluted with 0.01 M NaOH to reach the required range, on notification and concurrence of the RPP-WTP pretreatment technical contact. A sample of the AZ-101 feed will be archived for six months following completion of the AZ-101 Cs IX test. If evaporation or dilution is necessary, a sample of the AZ-101 feed will be collected beforehand and archived for the same duration.

AZ-102 Feed

A sample of the candidate LAW feed solution from tank AZ-102 will be used primarily to verify cesium ion exchange process parameters for this waste. The allowable ion exchange feed concentration range of sodium in the AZ-102 supernate feed for this test is 5.0 ±0.2 M sodium.
Data from the TWINS[10] database indicates that the samples will have an average sodium concentration of 2.43 M. Therefore the AZ-102 feed will be prepared as follows:

1. The hot cell temperature will be recorded periodically during the feed preparation.

2. A material balance for the AZ-102 sample will be maintained throughout the process steps. Items to be recorded (whenever possible) include sample bottle identification number, the mass (or volume) of sample received in each bottle, loss of sample due to residual sample left in each bottle, mass (or volume) of combined AZ-102 sample, mass and volume of chemical additions, mass of samples removed for analysis, mass of solids removed by filtering, mass of sample transferred to process testing, and any other significant activities that add or remove mass from the AZ-102 sample.

3. The material present in each of the AZ-102 sample bottles will be transferred into a clean mixing vessel. If solids are evident (opaque solution or visible solids) it will be filtered first. Concurrence of the BNI pretreatment technical contact will be obtained prior to recovery and analysis of the solids. The vessel used to combine the samples may be the evaporation vessel, if the evaporation step is imminent. Filter the material after the evaporation step to prevent any introduction of solids into the Ion Exchange system.

4. The combined supernatant will be mixed with a mechanical stirrer.

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(9) TSP-W375-01-00031, Tank 241-AZ-101 Sample Composite, Homogeneity, and Analysis. E. Lee, Characterization, R&T, BNI/WGI, May 1, 2001.

[10] http://twins.pnl.gov/twins3/twins.htm

5. Two subsamples will be collected from the supernate after mixing. The first will be immediately prepared and submitted for (sodium) Na analysis by ICP (Inductively Coupled Plasma). The second sample (approximately 20 mL in a glass vial) will be archived for six months after completion of the Cs IX test in case future characterization of the initial (non-concentrated) supernatant is needed. The density and volume of the combined supernate sample will be determined.

6. Data from the TWINS database indicates that the samples will have an average sodium concentration of 2.43 M. The volume reduction required to reach a target of 5.0 M sodium will be calculated based on this sodium concentration and the measured volume of the combined supernate sample.

7. The AZ-102 sample will be concentrated by evaporation at 50 (+/-5) °C. An inert gas such as argon (Ar) or nitrogen (N_2) will be used to cover the surface of the sample to minimize reaction with atmospheric oxygen. The sample will be stirred as needed during evaporation.

8. The evaporation will proceed until the target volume calculated in (6) is reached. As soon as the Na analysis from step 5 is available, the evaporation will be continued 0.01 M NaOH will be added as necessary to reach 5.0 ± 0.2 M Na.

9. Once the target volume is obtained, the feed will be filtered in preparation for Cs IX. Any solids present will be recovered, and appropriate analyses will be determined in consultation with the BNI (Bechtel National Incorporated) pretreatment technical contact. Analyses of the solids will be covered outside of this test plan.

10. A sample of the evaporated, filtered feed will be collected and analyzed for the analytes listed in Table 1. Submission may wait for the AZ-102 effluent and eluate composite samples. A sample of the evaporated, filtered feed will also be collected and archived in a glass vial or bottle for six months after completion of the Cs IX test.

Batch Contacts

1. The lot number, date of receipt of the resin, any treatment of the resin, and general storage conditions prior to use in the batch contact tests will be recorded and reported.

2. The solution temperatures will be recorded to ±1°C for the batch contact test, and each contact will be conducted in duplicate.

3. The AZ-101 feed will be analyzed to determine the concentrations of Na, potassium (K), total Cs, free hydroxide, total inorganic carbon (TIC), total organic carbon (TOC), nitrate, chloride, Cs^{137}, pertechnetate, total ^{99}Tc and the density. The AZ-102 is to be analyzed for the same analytes, except pertechnetate and total ^{99}Tc. The minimum reportable quantity (MRQ) for each analyte is provided in Table 1. SuperLig 644 and 639 resins have exhibited exchange affinity for these analytes. Additional analytes will be reported on an opportunistic basis.

Table 1. Analyte Minimum Reportable Quantity

Analyte	**MRQ (μg/mL)**
Na, K	7.5E+01
Cs	1.0 E+01
Free Hydroxide	1.7E+01
TIC	1.5E+02
TOC	1.5E+03
Nitrate	3.0E+03
Nitrite	3.0E+03
Fluoride	3.0E+02
Chloride	3.0E+02
Radionuclide	**MRQ (μCi/mL)**
Cs^{137}	1.0E-02
Pertechnetate	3.0E-03
Total Tc^{99}	3.0E-03

4. The SL-639 resin will be pre-conditioned by contacting with an NaOH solution, then rinsing with de-ionized (or demineralized) water.
    a. The SL-639 will be contacted with 1 M NaOH (volume in milliliters equal to 10 times the mass of the resin in grams) for a minimum of 2 hours with gentle agitation. Most of the solution will then be separated from the resin by decanting and discarded as waste.
    b. The SL-639 will be contacted with de-ionized (or demineralized) water (volume in milliliters equal to 10 times the mass of the resin in grams). The contact will be agitated gently for 1 hour. Most of the rinse water will then be separated from the resin by decanting and discarded as waste.
    c. The water rinse will be repeated twice more for a total of 3 water rinses.
    d. The resin will be dried in air and stored until use.

5. The SL-644 will be converted to the H^+ form for the batch contacts, due to the presence of a large amount of potassium (K) in the as-received SL-644 that may alter the composition of the contacting solution and resulting equilibrium.
    a. The SL-644 resin will be soaked for a minimum of 4 hours in deionized water (volume in milliliters equal to 10 times the mass of the resin in grams). Most of the water will then be separated from the resin by decanting.
    b. The resin will then be contacted with 0.5 M HNO_3 (volume in milliliters equal to10 times the mass of resin in grams). Most of the 0.5 M HNO_3 will be separated from the resin by decanting.
    c. Step (b) will be repeated twice more.
    d. The resin will then be contacted with deionized water (volume in milliliters equal to 10 times the mass of the resin in grams). Most of the water will then be separated from the resin by decanting.

   e. Step (d) will be repeated twice more.
   f. The resin will be allowed to air dry until the mass changes no more than 5% between measurements taken at least 3 hours apart.

6. The SL-644 and SL-639 resins will be contacted with the solutions shown in Table 2. A 10±0.1-mL of each solution will be contacted with 0.1±0.01-g samples of the appropriate resin. The batch contacts will be conducted for a minimum of 48 hours.

Table 2. Cs Batch Contacts

Solution	Additive
SuperLig 644 Resin Batch Contacts	
AZ-101 solution	None
AZ-101 solution	Increase total Cs concentration to ~1E-03M
AZ-101 solution	Increase total Cs concentration to ~4E-03M
AZ-101 solution	Increase total Cs concentration to ~7E-03M
AZ-102 solution	None
AZ-102 solution	Increase total Cs concentration to ~1E-03M
AZ-102 solution	Increase total Cs concentration to ~4E-03M
AZ-102 solution	Increase total Cs concentration to ~7E-03M
SuperLig 639Resin Batch Contacts	
AZ-101 solution	None
AZ-101 solution	Increase ^{99}Tc concentration to ~1E-03 Ci/L
AZ-101 solution	Increase ^{99}Tc concentration to ~4E-03 Ci/L
AZ-101 solution	Increase ^{99}Tc concentration to ~7E-03 Ci/L

7. The batch contacts of AZ-101 and AZ-102 conducted with SuperLig 644 resin will be analyzed to determine the concentrations of Na, K, and Cs^{137} or total cesium. The batch contacts of AZ-101 conducted with SuperLig 639 resin will be analyzed to determine the concentrations of nitrate, fluoride, chloride, nitrite, and ^{99}Tc. The MRQ for each analyte is provided in Table 1.

8. The F factors for the SL-644 and SL-639 resins will be determined. The subsamples for the F factor determinations will be weighed out at the same time and from the same samples of resin used for the batch contacts. Since these samples are already preconditioned, the subsamples only need to be dried.
   a. Two approximately 0.5 g samples of the resin will be weighed out. The masses will be measured and recorded to the nearest ± 0.01 g.
   b. The samples will be dried at 50 ± 5°C under house vacuum (approx. 20in Hg).
   c. The sample masses will be measured periodically to +/- 0.01 g. The samples will be sealed in vials during weighing to prevent water absorption.
   d. The samples will be considered dry and the final weight will be recorded when the mass of a sample has not changed by more than ±0.01g over one 24 hour period or three consecutive measurements taken at intervals of at least two hours.

Cs Ion Exchange Column Tests

The AZ-101 and AZ-102 supernate solutions will be processed through the SL-644 ion exchange columns. All solutions will be passed downflow at ambient hot cell temperature through the two columns in series, except as noted below. Note that the AZ-102 tank will be processed first. The lead column will then be eluted and regenerated prior to proceeding with the next test. If significant loading of the lag column is experience, it will also be eluted and regenerated prior to the next test. This decision will be made in consultation with the WTP representative.

1. The AZ-101 feed will be analyzed to determine the concentrations of Na, K, total Cs, free hydroxide, TIC, TOC, nitrate, chloride, Cs^{137}, pertechnetate, total ^{99}Tc and the density. The AZ-102 is to be analyzed for the same analytes, except pertechnetate and total ^{99}Tc. The minimum reportable quantity (MRQ) for each analyte is provided in Table 1 above. SuperLig 644 and 639 resins have exhibited exchange affinity for these analytes. Additional analytes will be reported on an opportunistic basis.

2. The actual volume of waste solution and reagents used during the ion exchange column tests will be recorded. The temperature in the cell where the Cs ion exchange testing is being conducted will be recorded periodically.

3. The lead and lag column positions will be switched from those of the previous run (AN-102/C-104 sample). The lead column was eluted at the end of the previous test. No significant loading of the lag column was observed during the prior test.

4. In each test the waste solution will be transferred into the lead column at a flow-rate of 1.5 BV/hr.

5. Single small samples (approx. 2 mL) of the effluent will be collected from the lead column during the loading cycle at 10-BV increments, and from the lag column during the loading cycle at 20-BV increments. These samples will be analyzed to determine the concentration of ^{137}Cs.

6. The AZ-101 sample will be processed through the columns until reaching ~50% cesium breakthrough on the first column. The lag column effluent will be collected in 10 BV fractions. The Ci Cs^{137}/mole Na ratio for each fraction will be evaluated. The fractions will be combined, in the order collected, until addition of the next fraction would result in a composite that exceeds the target level of 1.75E-05 Ci ^{137}Cs/mole Na. This composite sample will be analyzed for the analytes listed in Table 1. Additional analytes will be reported on an opportunistic basis. This effluent composite will be used for Tc removal testing.

7. The AZ-102 sample will be processed through the columns until reaching ~50% cesium breakthrough on the first column. The composite effluent sample will be analyzed for the analytes listed in Table 1. Additional analytes will be reported on an opportunistic basis.

8. Residual feed solution will be displaced from the columns following the load cycle.
    a. A minimum of two total apparatus volumes of 0.1 molar sodium hydroxide will be transferred at 3 BV/hr through the lead column into the lag column.
    b. Feed displacement using 0.1 M sodium hydroxide solution will continue until the ^{137}Cs concentration in the effluent from the lag column decreases to less 0.01 times the ^{137}Cs concentration of the waste sample (i.e., $C/C_O < 0.01$).
    c. The 0.1 M sodium hydroxide solution will be collected in 1-BV increments in separate containers, and analyzed to determine the concentrations of ^{137}Cs. MRQ is given in Table 1.

9. The 0.1 M sodium hydroxide solution will be displaced from both columns with de-ionized or de-mineralized water.

   a. A minimum of two total apparatus volumes of de-ionized (or de-mineralized) water will be transferred through the columns at 3 BV/hr.

   b. The water displacement solution will be collected in 1-BV increments in separate containers.

   c. Each water displacement sample will be analyzed for the concentration of ^{137}Cs.

10. The lead column will be eluted. If more than 5% of the ^{137}Cs removed from the feed is present on the second column, it may also be eluted, based on Battelle's recommendation and concurrence of the WTP contractor.

    a. The column(s) will be eluted at 1 BV/hr using at least 15 BV of 0.5 M nitric acid solution. The elution will be continued, if necessary, until the ^{137}Cs concentration decreases to less than 1% of the initial ^{137}Cs feed concentration ($C/Co < 0.01$). The eluate will be collected in fractions of 2 BV or less. The fractions will be analyzed for the concentration of ^{137}Cs.

    b. The eluted column(s) will be rinsed with 2 total apparatus volumes of de-ionized (or de-mineralized) water to displace acid from the resin bed. Excess liquid will be drained from atop the lead column and collected.

    c. The AZ-102 cesium eluate fractions will be combined and analyzed for the analytes listed in Table 3. Additional analytes will be reported on an opportunistic basis. Chloride in the AZ-102 eluate composite will be measured to a 10 mg/L MRQ. This will require methods development outside the current scope of this task, and is contingent on approval of funding. Analytical requirements for the AZ-102 tests are different than for the AZ-101 tests.

Table 3. Analytical Requirements for AZ-102 Cs Eluate Composite

Analyte	**MRQ (μg/mL)**
K, Na	7.5E+01
TOC	1.5+E03
Cl	1.0 E+01
Nitrate	3.0E+03
Total and free OH	1.7E+01
Total Cs	1.0E+01
Radionuclide	**MRQ (μCi/mL)**
Cs^{137}	1.0E-02

    d. The AZ-101 cesium eluate fractions will be combined and analyzed for the analytes listed in Table 4. Quality control parameters are given in Table 6. The table includes analytes requested for the vitrification activity. Chloride in the AZ-101 will be measured to a 10 mg/L MRQ. This will require methods development outside the current scope of this task, and is contingent on approval of funding.

    e. The WTP contractor will review the TOC result for the AZ-101 ^{137}Cs eluate composite and then decide and direct Battelle either to deliver 50 mL of sample for organic analysis or to skip organic analysis and deliver the IX pretreated feed to vitrification. Organic analysis requires significant sample and is beyond the scope of this test specification.

f. The cesium eluate solutions from both tests will be archived for 6 months following the completion of the tests. The AZ-101 cesium eluate will be combined with HLW sludge for vitrification tests.

11. The eluted column(s) will be regenerated and rinsed.
    a. Two total apparatus volumes of 0.25M sodium hydroxide solution will be transferred at 1 BV/hr through the eluted column(s).
    b. The excess liquid will be drained from atop the column, leaving approximately 1-BV of sodium hydroxide solution atop the resin bed. The regeneration solution will be composited and analyzed to determine the concentrations of ^{137}Cs, sodium, and hydroxide. The MRQ's are given in Table 1. The residual concentration of cesium on the columns after elution and regeneration will be calculated based on the Cs mass balance.
    c. The solution from regeneration of the column will be archived for six months after completion of testing.
    d. The 0.25 M NaOH regenerant solution will be displaced from the column with 2 AV of de-ionized or demineralized water. No analysis of this displacement solution will be performed and it will be disposed as waste.
12. The positions of the lead and lag columns will be switched between processing of the two waste samples.
13. Unless otherwise noted, all solutions used in the testing will be archived until analytical data is returned and analysis indicates no problems. A portion of the AZ-102 sample will be used for testing of the Tc monitor. Other solutions will be disposed, archived, or used for additional testing based on Battelle's recommendation and the WTP contractor's concurrence.

Technetium Removal Column Tests

The pretreated AZ-101 LAW solution from the cesium ion exchange column test will be used as feed to the SL-639 technetium removal columns. If more feed is deemed necessary for the Tc removal test, additional feed may be processed to remove Cs, based on Battelle's recommendation and the WTP contractor's concurrence, and contingent on receipt of funding for this additional scope. The processing would follow the Cesium Ion Exchange Test description, but with greatly reduced sampling and analysis.

1. The actual volume of waste solution and reagents used during the ion exchange column tests will be recorded.
2. All solutions for the SL-639 test will be passed downflow at 25±2°C through the two columns in series, except as noted below.
3. If not already analyzed as part of previous testing, the feed to the technetium ion exchange columns will be analyzed to determine the concentrations of pertechnetate, total ^{99}Tc, hydroxide, and nitrate. The MRQ's for these analytes are listed in Table 1. Other analytes will be reported on an opportunistic basis.

4. A Tc-95m pertechnetate tracer will be added to the AZ-101 feed to follow the progress of the various processing steps and to indicate the pertechnetate behavior in the waste.
5. The waste solution will be transferred downflow into the lead technetium column at a flow rate of 3 BV/hr.
6. Single samples of the effluent from the lead technetium column will be collected during the loading cycle at ~20-BV increments and from the lag technetium column at ~40-BV increments.
    a. The effluent samples from the lead and lag columns will be analyzed to determine the concentration of ^{99}Tc.
    b. The loading effluent from the column run will be composited and analyzed for ^{99}Tc.
    c. After reaching ~50% pertechnetate breakthrough in the lead column, the waste flow will be stopped. Excess liquid, if present, will be drained from atop the lead column into the lag column.
7. Residual feed solution will be displaced from the columns following the load cycle.
    a. Two total apparatus volumes of 0.1 M sodium hydroxide will be transferred at 3 BV/hr through the columns.
    b. Feed displacement will continue until the concentration of technetium in the lead column effluent is less than 1% of the feed concentration ($C/Co < 0.01$).
    c. The 0.1 M sodium hydroxide solution will be collected in 1-BV increments in separate containers.
    d. The 1-BV increments of 0.1 M sodium hydroxide solution will be analyzed to determine the concentrations of ^{99}Tc.
8. The 0.1 M sodium hydroxide solution will be displaced from the lead column as follows.
    a. One-half (0.5) of a total apparatus volume of de-ionized (or de-mineralized) water at 3 BV/hr will be transferred through the lead column.
    b. The displaced solution will be collected in 1-BV increments in separate containers. Excess liquid, if present, will be drained from atop the column in preparation for elution.
    c. The 1-BV increments of water displacement solution will be analyzed to determine the concentrations of ^{99}Tc.
9. The lead technetium column will be eluted. If more than 5% of the Tc removed from the feed is present on the second column, it may also be eluted, based on Battelle's recommendation and concurrence of the WTP contractor.
    a. The temperature of the resin bed, now containing water, will be raised to 65 ± 5°C.
    b. The column will be eluted at 1 BV/hr using de-mineralized water at 65 ± 5°C. Elution will continue until the ^{99}Tc concentration in the column effluent is less than 1% of the original lead

column feed concentration. Excess liquid, if present, will be drained from atop the lead column and collected.

c. The technetium eluate will be collected in no more than 2-BV increments, which will be analyzed to determine the concentration of ^{99}Tc.

d. The technetium eluate fractions will be combined and analyzed for the analytes listed in Table 4. Quality control parameters are given in Table 6. The table includes analytes requested for the vitrification activity. Chloride will be measured to a 10 mg/L MRQ. This will require methods development outside the current scope of this task, and is contingent on approval of funding.

e. The technetium eluate solution will be saved for combination with HLW sludge for vitrification tests.

10. Prior to subsequent tests, the eluted column(s) will be regenerated.

    a. Two total apparatus volumes of 0.25M sodium hydroxide solution will be transferred at 1 BV/hr through the eluted column(s).

    b. The excess liquid, if present, will be drained from atop the column. The regeneration solution will be composited and analyzed to determine the concentrations of ^{99}Tc, sodium, and hydroxide. The MRQ's are given in Table 1. The residual concentration of Tc on the columns after elution and regeneration will be calculated based on the Tc mass balance.

    c. The solution from regeneration of the column will be archived for six months after completion of testing.

8. Unless otherwise noted, all solutions used in the testing will be archived until analytical data is returned and analysis indicates no problems. The solutions will then be disposed, archived, or used for additional testing based on Battelle's recommendation and the WTP contractor's concurrence.

Quality Assurance

Battelle implements the RPP-WTP quality requirements in a quality assurance project plan (QAPjP) as approved by the RPP-WTP QA organization. This work is to be conducted to the quality requirements in NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, subpart 2.7 as instituted through Battelle's Nuclear Quality Assurance Requirements and Description Manual (NQARD).

A listing of applicable NQARD implementing procedures is shown in Table 7 below.

The Tc monitor system will be calibrated using spiked simulants and actual waste samples spiked with ^{99}Tc. Monitor calibration will be performed prior to analysis of the sample batch. During operation, automated standard addition measurements will be implemented with at least every fourth sample to verify instrument calibration.

The following tables give the analytical requirements for the Cs and Tc eluates (Table 4) and the pretreated LAW analyses (Table 5), and quality control parameters (Table 6).

Table 4. Analytical Requirements for Cs and Tc Ion Exchange Eluates (3)

Analyte	Minimum Reportable Quantity (1)	Analysis Method/ Driver
	mg/L	
Al	7.50E+01	
Ba	2.30E+00	
Ca	1.50E+02	
Cd	7.50E+00	
Co	3.00E+01	
Cr	1.50E+01	
Cu	1.70E+01	
Fe	1.50E+02	
K	7.50E+01	ICP-AES (4)
La	3.50E+01	(Pretreatment Specification)
Mg	3.00E+02	
Mn	1.50E+02	
Mo	1.50E+02	
Na	7.50E+01	
Ni	3.00E+01	
Pb	3.00E+02	
Si	1.70E+02	
Sn	1.50E+03	
Ti	1.70E+01	
U	6.00E+02	
Zn	1.65E+01	
Ag	--	
As	--	
B	--	
Be	--	
Bi	--	
Cs	1.0E+01	

Table 4. Analytical Requirements for Cs and Tc Ion Exchange Eluates (3)

Analyte	Minimum Reportable Quantity (1)	Analysis Method/ Driver
Ce	--	ICP-AES (4) (Vitrification Request)
Dy	--	
Eu	--	
Li	--	
Nd	--	
P	--	
Sb	--	
Se	--	
Sr	--	
Te	--	
Th	--	
V	--	
Y	--	
Zr	--	
Pd	--	ICP-MS (Vitrification Specification)
Pr	--	
Pt	--	
Rh	--	
Ru	--	
Ta	--	
TOC	1.50E+03	Silver catalyze persulfate method
TIC	1.50E+02	Silver catalyze persulfate method
Cl	1.00E+01	IC Anions
Br	--	
F	1.50E+02	
NO_2	3.00E+03	
NO_3	3.00E+03	
oxalate	--	
PO_4	2.50E+03	
SO_4	2.30E+03	
Hg	--	Cold Vapor AA
CN	--	Colorimetric
NH_3	--	ISE
total and free OH	1.70E+01	Titration
Radionuclides	**mCi/L**	
^{99}Tc	3.00E-03	ICP-MS (Pretreatment Specification)
^{237}Np	--	
^{239}Pu	--	
^{240}Pu	--	
^{241}Pu / ^{241}Am	--	
^{129}I	--	

Table 4. Analytical Requirements for Cs and Tc Ion Exchange Eluates [3]

Analyte	Minimum Reportable Quantity [1]	Analysis Method/ Driver
^{233}U	--	ICP-MS (Vitrification Request)
^{234}U	--	
^{235}U	--	
^{236}U	--	
^{238}U	--	
^{242}Pu	--	
^{63}Ni	--	Beta Scintillation
^{90}Sr	1.50E-01	Separations / Liquid Scintillation
^{241}Pu	--	
^{3}H	--	Distillation and Liquid Scintillation
^{14}C	--	
^{151}Sm	--	Separation / Beta Scintillation
^{79}Se	--	
^{236}Pu	--	Separations / AEA
^{238}Pu	--	
$^{239/240}$Pu	--	
^{241}Am	3.00E-02	
^{242}Am	--	
^{242}Cm	--	
^{242}Pu	--	
$^{243/244}$Cm	--	
^{51}Cr	--	Extended Counting Time GEA
^{59}Fe	--	
^{60}Co	--	
^{88}Y	--	
^{95}Nb	--	
^{103}Ru	--	
^{106}Ru	--	
^{113}Sn	--	
^{125}Sb	--	
^{126}Sn/Sb	--	
^{134}Cs	--	
^{137}Cs	5.00E-02	
^{144}Ce	--	
^{152}Eu	--	
^{154}Eu	2.00E-03	
^{155}Eu	9.00E-02	

Table 4. Analytical Requirements for Cs and Tc Ion Exchange Eluates (3)

Analyte	Minimum Reportable Quantity (1)	Analysis Method/ Driver
^{232}Th	--	
Total Alpha	2.30E-01	Alpha counting
Total Beta	--	Beta Counting
Sum of Alpha	To be determined	Summation of ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Am, ^{242}Cm $^{243+244}$Cm
Physical Property	**Expected Range**	
Wt% Oven Dried Solids	0.1 to 100 wt%	Gravimetry
Separate Organic Phase	N/A	Visual Observation
Density	0.9 to 1.7 gm/mL	Gravimetry
Wt% Oxides	0.1 to 100 wt%	Gravimetry

(1) Those analytes without a specified MRQ are to be determined as a best effort by the laboratory. The detection limit for each analyte should be reported along with the analytical results. Matrix spikes and laboratory control standards are not required for these analytes, but should be reported when available.

(3) Organic analyses have been dropped from this table. Only if the TOC is greater than 60 mg/L should samples be submitted for organic analysis. In the event that the TOC exceeds the 60 mg/L limit, the organic analytes of interest will be determined.

(4) Report any additional ICP-AES analytes on an opportunistic basis.

Table 5. Analyses and Analytes Requested for Pretreated LAW Vitrification Feed (Tc IX Effluent Composite)

Analyte	Minimum Reportable Quantity (1)	Analysis Method/ Driver
	mg/L	
Al	7.50E+01	ICP-AES (3) (Pretreatment Specification)
Ba	2.30E+00	
Ca	1.50E+02	
Cd	7.50E+00	
Cr	1.50E+01	
Fe	1.50E+02	
K	7.50E+01	
La	3.50E+01	
Mg	3.00E+02	
Na	7.50E+01	
Ni	3.00E+01	
P	6.00E+02	
Pb	3.00E+02	
U	6.00E+02	
Ag	--	ICP-AES (3) (Vitrification Request)
As	--	
B	--	
Be	--	
Bi	--	
Ce	--	
Co	--	
Cu	--	
Dy	--	
Eu	--	
Li	--	
Mn	--	
Mo	--	
Nd	--	
Sb	--	
Se	--	
Si	--	
Sn	--	
Sr	--	
Te	--	
Th	--	
Ti	--	
V	--	
Y	--	
Zn	--	
Zr	--	
Cs	1.50E+01	ICP-MS (Pretreatment Specification)
Rb	1.00E+00	
Pd	--	

Table 5. Analyses and Analytes Requested for Pretreated LAW Vitrification Feed (Tc IX Effluent Composite)

Analyte	Minimum Reportable Quantity (1)	Analysis Method/ Driver
Pr	--	ICP-MS (Vitrification Specification)
Pt	--	
Rh	--	
Ru	--	
Ta	--	
TOC	1.50E+03	Silver catalyze persulfate method
TIC	1.50E+02	Silver catalyze persulfate method
Cl	3.00E+02	IC Anions
Br	--	
F	1.50E+02	
NO_2	3.00E+03	
NO_3	3.00E+03	
oxalate	1.80E+03	
PO_4	2.50E+03	
SO_4	2.30E+03	
Hg (2)	1.50E+00	Cold Vapor AA
CN	--	Colorimetric
NH_3	--	ISE
total and free OH	7.50E+04	Titration
Organic Analytes	**mg/L**	
Acetate	--	IC (Organic Anions)
Citrate	1.50E+03	
Formate	1.50E+03	
Gluconate	1.50E+03	
Gylcolate	1.50E+03	
D2EHPA	1.50E+03	Derivatization/ GC-MS
EDTA	1.50E+03	
HEDTA	1.50E+03	
IDA	1.50E+03	
NTA	1.50E+03	
Radionuclides	**mCi/L**	
^{99}Tc	3.00E-03	ICP-MS (Pretreatment Specification)
^{237}Np	2.70E-02	
^{239}Pu	3.00E-02	
^{240}Pu	1.00E-02	
^{241}Pu / ^{241}Am	5.10E-02	
^{129}I	--	ICP-MS (Vitrification Request)
^{233}U	--	
^{234}U	--	
^{235}U	--	

Table 5. Analyses and Analytes Requested for Pretreated LAW Vitrification Feed (Tc IX Effluent Composite)

Analyte	Minimum Reportable Quantity (1)	Analysis Method/ Driver
^{236}U	--	
^{238}U	--	
^{242}Pu	--	
^{99}Tc	3.00E-03	Separations / Liquid Beta Scintillation without sample oxidation to determine pertechnetate
^{63}Ni	--	Beta Scintillation
^{90}Sr	1.50E-01	Separations / Liquid Scintillation
^{241}Pu	--	
^{3}H	--	Distillation and Liquid Scintillation
^{14}C	--	
^{151}Sm	--	Separation / Beta Scintillation
^{79}Se	--	
^{236}Pu	--	Separations / AEA
^{238}Pu	1.00E-02	
$^{239/240}Pu$	3.00E-02	
^{241}Am	3.00E-02	
^{242}Am	--	
^{242}Cm	1.50E-01	
^{242}Pu	--	
$^{243/244}Cm$	1.50E-02	
^{51}Cr	--	Extended Counting Time GEA
^{59}Fe	--	
^{60}Co	1.00E-02	
^{88}Y	--	
^{95}Nb	--	
^{103}Ru	--	
^{106}Ru	--	
^{113}Sn	--	
^{125}Sb	--	
$^{126}Sn/Sb$	--	
^{134}Cs	--	
^{137}Cs	9.00E+00	
^{144}Ce	--	
^{152}Eu	--	
^{154}Eu	2.00E-03	
^{155}Eu	9.00E-02	
^{232}Th	--	

Table 5. Analyses and Analytes Requested for Pretreated LAW Vitrification Feed (Tc IX Effluent Composite)

Analyte	Minimum Reportable Quantity (1)	Analysis Method/ Driver
Total Alpha	2.30E-01	Alpha counting
Sum of Alpha	To be determined	Summation of ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Am, ^{242}Cm $^{243+244}$Cm
Physical Property	**Expected Range**	
Wt% Oven Dried Solids	0.1 to 100 wt%	Gravimetry
Separate Organic Phase	N/A	Visual Observation
Density	0.9 to 1.7 gm/mL	Gravimetry
Wt% Oxides	0.1 to 100 wt%	Gravimetry

(1) Those analytes without a specified MRQ are to be determined as a best effort by the laboratory. The detection limit for each analyte should be reported along with the analytical results. Matrix spikes and laboratory control standards are not required for these analytes, but should be reported when available.

(3) Report any additional ICP-AES analytes on an opportunistic basis.

Table 6. Quality Control Parameters for Ion Exchange Effluent Composite and Tc and Cs Eluates

Liquid Fraction	Analytical Technique	QC Acceptance Criteria		
		LCS %Recovery[a]	Spike %Recovery[b]	Duplicate RSD[c]
all requested analytes except Na	ICP/AES	80 - 120%	75 - 125%	<15%
Na	ICP/AES	80 - 120%	75 - 125%	<3.5%
All requested analytes except as specified below	ICP/MS	80 - 120%	70 - 130%	<15%
Cs[d], Eu[d]	ICP/MS	N/A	N/A	N/A
^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{237}Np[e], ^{243}Am/Cm	ICP/MS	90 - 110%	75 - 125%	<15%
^{129}I	ICP/MS or Separation/GEA	NP	N/A	<15%
All requested anions	IC	80 - 120%	75 - 125%	<15%
CN^-	Distillation colorimetric	80 - 120%	75 - 125%	<15%
U (total)	Kinetic Phosphorescence	80 - 120%	75 - 125%	<15%
NH_3/NH_4^+	ISE, standard additions	80 - 120%	75 - 125%	<15%
OH^-	Potentiometric titration	80 - 120%	N/A	<15%
TIC/CO_3^-	Persulfate	80 - 120%	75 - 125%	<15%
TOC	Silver catalyzed persulfate	80 - 120%	75 - 125%	<15%
Density		N/A	N/A	N/A
Wt% oven dried solids and wt% oxides	Gravimetric	80 - 120%	N/A	<21%
Radiochemical Analytes/Methods				
^{3}H[e]	Separation/ Liquid Scintillation	80 - 120%	N/A	<15%
^{14}C	Separation/ Liquid Scintillation	80 - 120%	75 - 125%	<15%
All except ^{125}Sb	GEA	NP	N/A[f]	<15%
^{125}Sb	GEA	to be obtained	N/A[f]	TBD
^{79}Se[e]	Liq. scintillation	NP	N/A	<15%
^{90}Sr[e], ^{241}Pu	Isotopic specific separation/beta count	75 - 125%	N/A	<15%
^{99}Tc (pertechnetate)	Separation/beta count	80 - 120%	70 - 130%	<15%
Total Pu	Sum of Isotopes	N/A	N/A	N/A
^{238}Pu[g], ^{239}Pu[g], ^{240}Pu[g], ^{241}Am[g], ^{242}Cm, $^{243+244}$Cm	Separation/AEA	NP	N/A	<15%
Total Alpha[g]	Proportional counter	70 - 130%	70 - 130%	<15%
Total Beta	Beta counting	70 - 130%	70 - 130%	<15%

Acronyms:

AEA	– Alpha Energy Analysis
CVAA	– Cold Vapor Atomic Absorption
GEA	– Gamma Energy Analysis
IC	– Ion Chromatography
ICP/AES	– Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP/MS	– Inductively Coupled Plasma Mass Spectroscopy

LSC – Laboratory Control Standard
N/A – Not applicable
NP – Not performed
RSD – Relative Standard Deviation
Wt% – Weight percent

Footnotes:

(a) LCS = Laboratory Control Standard. This standard is carried through the entire method. The accuracy of a method is usually expressed as the percent recovery of the LCS. The LCS is a matrix with known concentration of analytes processed with each preparation and analyses batch. It is expressed as percent recovery; i.e., the amount measured, divided by the known concentration, times 100.

(b) For some methods, the sample accuracy is expressed as the percent recovery of a matrix spike sample. It is expressed as percent recovery; i.e., the amount measured less the amount in the sample, divided by the spike added, times 100. One matrix spike is performed per analytical batch. Samples are batched with similar matrices. For other analytes, the accuracy is determined based on use of serial dilutions.

(c) RSD = Relative Standard Deviation between the samples. Sample precision is estimated by analyzing replicates taken separately through preparation and analysis. Acceptable sample precision is usually <15% RSD if the sample result is at least 10 times the instrument detection limit. RSD = (standard deviation of the mean/mean) x 100

(d) Total Cs and Eu are sums of all isotopes, therefore spiking and LCS does not apply.

(e) Matrix spike analyses are not required for this method because a tracer is used to correct for analyte loss during sample preparation and analysis. The result generated using the tracer accounts for any inaccuracy of the method on the matrix. The reported results reflect this correction.

(f) The measurement is a direct reading of the energy and the sample matrix does not affect the analysis; therefore, a matrix spike is not required.

(g) The sum of ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Am activities will be used as a measurement of alpha-emitting TRU. The selected isotopes account for greater than 95% of the alpha-emitting TRU activity based on previous analysis of Phase I candidate tank waste (Esch 1997a, 1997b, 1997c). Additional isotopes that are defined as alpha-emitting TRU (e.g., ^{237}Np, ^{242}Pu, ^{242}Cm, ^{243}Am, and $^{243+244}$Cm) are not used to calculate total TRU activity because the MDAs for these isotopes are large in comparison with the envelope limits and it is expected that their concentrations are well below the MDA. Note that ^{241}Pu is a beta-emitting TRU whose analysis, along with ^{242}Cm, is required specifically for class C waste determination.

A listing of applicable NQARD implementing procedures is shown in the following table.

Table 7. Applicable Quality Assurance Procedures

NQA-1	Yes	No	Implementing Procedure Title	Justification for Exclusion
BR 1	X		NQARD Manual Section 1.1, Organization NQARD-101, Communication and Commitment (Interface) Control	
1S-1	X		NQARD Manual Section 1.1, Organization NQARD-1501, Nonconforming Items	
2	X		NQARD Manual Section 2.1, Quality Assurance Program NQARD-205, Quality Assurance Plans NQARD-208, Applying QA Controls (Grading)	
2S-1		X	NQARD Manual Section 2.1, Quality Assurance Program	This work does not require qualified inspection and test personnel.
2S-2		X	NQARD Manual Section 2.1, Quality Assurance Program	NDE is not performed; therefore qualified NDE personnel.
2S-3	X		NQARD Manual Section 18.1, Audits NQARD-1801, Internal Audits	
2S-4	X		NQARD-201, Indoctrination and Training	
BR 3		X	NQARD Manual Section 3.1 NQARD-301, Hand Calculations NQARD-302, Design Control	Design activities will not be performed.
3S-1		X	NQARD-301, Hand Calculations NQARD-302, Design Control	Design activities will not be performed.
BR 4	X		NQARD Manual Section 4.1 NQARD-401, Purchase Requisitions NQARD-404, Procurement of Internal Quality Affecting Services	
4S-1	X		NQARD-401, Purchase Requisitions NQARD-404, Procurement of Internal Quality Affecting Services	
BR 5	X		NQARD Manual Section 5.1 NQARD-501, Preparation, Review and Approval of QA Implementing Procedures	
BR 6	X		NQARD Manual Section 6.1 NQARD-601, Document Control NQARD-602, Document Change Control	
6S-1	X		NQARD-601, Document Control NQARD-602, Document Change Control	
BR 7	X		NQARD Manual Section 7.1 NQARD-401, Purchase Requisitions NQARD-404, Procurement of Internal Quality Affecting Services	
7S-1	X		NQARD-401, Purchase Requisitions	
BR 8	X		NQARD Manual Section 8.1 NQARD-801, Sample Control	
8S-1	X		NQARD-801, Sample Control	
BR 9		X	NQARD Manual Section 9.1 NQARD-902, Control of Special Processes	Work will be controlled in accordance with BR 5 and BR 11.
9S-1		X	NQARD-902, Control of Special Processes	
BR 10		X		Design activities will not be performed.
10S-1		X		Design activities will not be performed.
BR 11	X		NQARD Manual Section 11.1 NQARD-1101, Scientific Investigation	
11S-1	X		NQARD-1101, Scientific Investigation	
11S-2	X		NQARD-1101, Scientific Investigation	
BR 12	X		NQARD Manual Section 12.1 NQARD-1201, Calibration Control System	
12S-1	X		NQARD-1201, Calibration Control System NQARD-1101, Scientific Investigation	
BR 13	X		NQARD Manual Section 13.1 NQARD-1301, Handling, Storage and Shipping	
13S-1	X		NQARD-1301, Handling, Storage and Shipping	
BR 14	X		NQARD Manual Section 14.1 NQARD-1401, Inspection and Test Status and Tagging	
BR 15	X		NQARD Manual Section 15.1 NQARD-1501, Nonconforming Items	
15S-1	X		NQARD-1501, Nonconforming Items	
BR 16	X		NQARD Manual Section 16.1 NQARD-1601, Trend Analysis NQARD-1602, Corrective Action	

BR 17	X		NQARD Manual Section 17.1 NQARD-1701, Records System NQARD-1704, Laboratory Record Books	
17S-1	X		NQARD-1701, Records System NQARD-1704, Laboratory Record Books	
BR 18	X		NQARD Manual Section 18.1 NQARD-1801, Internal Audits	
18S-1	X		NQARD-1801, Internal Audits	

NQA-2a, Part 2.7	**Yes**	**No**	**Implementing Procedure Title**	**Justification for Exclusion**
1.0	X		QA-RPP-WTP-SCP, Software Control (to be issued)	
2.0	X		QA-RPP-WTP-SCP, Software Control (to be issued)	
3.0	X		QA-RPP-WTP-SCP, Software Control (to be issued)	
4.0	X		QA-RPP-WTP-SCP, Software Control (to be issued) NQARD-604, Independent Technical Review	
5.0	X		QA-RPP-WTP-SCP, Software Control (to be issued)	
6.0	X		QA-RPP-WTP-SCP, Software Control (to be issued)	
7.0	X		QA-RPP-WTP-SCP, Software Control (to be issued) NQARD-604, Independent Technical Review	
8.0	X		QA-RPP-WTP-SCP, Software Control (to be issued)	
9.0	X		QA-RPP-WTP-SCP, Software Control (to be issued)	
10.0	X		QA-RPP-WTP-SCP, Software Control (to be issued) NQARD-401, Purchase Requisitions NQARD-404, Procurement of Internal Quality Affecting Services	
11.0	X		QA-RPP-WTP-SCP, Software Control (to be issued) NQARD-1701, Records System	

Reporting

A final report will be prepared to cover the AZ-101 and AZ-102 batch-contact and column tests described in this test plan. A separate report for the technetium monitor results will be submitted. Each report will include a description of the relevant test apparatus, actual test conditions, all raw data and resin material measurements collected, all calculations conducted, error(s) associated with tests and calculations, and interpretation of test results. Each final report will be delivered to the RPP-WTP contractor within 30 calendar days after receiving comments on the draft report.

All process verification and waste-form qualification test results will be reported. All relevant sample-batch QC sample results (blanks, LCS, MS, MSD, etc.) and standard accuracy and precision measurements will be included. A draft report will be delivered to the RPP-WTP contractor for review within 30 calendar days after completing the cesium and technetium ion exchange tests and receiving the analytical results for both supernate batch contact and column tests.

Appendix C

Test Instruction TI-RPP-WTP-127
"Mixing of AZ-102 and Evaporation to Nominally 5 M Na"
and Addendum

Appendix C: Test Instruction TI-RPP-WTP-127 "Mixing of AZ-102 and Evaporation to Nominally 5 M Na" and Addendum

PNNL Test Instruction	**Document No.: TI-RPP-WTP-127** **Rev. No.: 0**
Title: Mixing of AZ-102 and Evaporation to Nominally 5 M Na	
Work Location: RPL SFO HLRF and SAL	**Page** 1 of 12
Author: SK Fiskum	**Effective Date: New** **Supersedes Date: New**
Use Category Identification: Reference	

Identified Hazards:

_x_ Radiological
_x_ Hazardous Materials
__ Physical Hazards
__ Hazardous Environment
__ Other:

Required Reviewers:

_x_ Author
_x_ Technical Reviewer
__RPL Manager
__Project Manager
__RPG Quality Engineer
__CHG

Are One-Time Modifications Allowed to this Procedure? _x_ Yes __ 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? ____ Yes or __x__ No

FOR REVISIONS:

Is retraining to this procedure required? ____Yes __x__ No

Does the OJT package associated with this procedure require revision to reflect procedure changes?
____Yes ____No __x__ N/A

Approval	**Signature**	**Date**
Author	Sandra K. Fiskum Sandra K. Fiskum	10/29/01
Technical Reviewer	Dave L. Blanchard, Jr.	10/29/01

Purpose/Scope

This test instruction is for the consolidation, sampling, and evaporation of AZ-102 tank waste. The work will be conducted according to RPL *Routine Research Operations Procedure*, RPL-OP-001 and *Tank 241-AZ-101 and 241-AZ-102 Waste Sample Ion Exchange Testing*, TP-RPP-WTP-111, Rev. 0. These tests will use the 10 AZ-102 500-g sample materials received from 222-S. The waste mixture will be evaporated in the SAL to approximately 5 M sodium. This material will then be characterized and used as feed for Cs ion exchange and other pretreatment testing activities. Work will be conducted according to NQARD.

Work is to be performed by hot cell technicians under the supervision of a cognizant specialist. The cognizant specialist shall be responsible for implementation and adherence to this test instruction. This instruction is specific to:

- AZ-102 as-received sub-sample mixing
- AZ-102 as-recieved sample aliquoting
- AZ-102 as-received sample evaporation
- AZ-102 concentrate filtration, and
- AZ-102 concentrate sub-sampling

Applicability

Demonstration of pretreatment processes with the AZ-102 Hanford tank waste needs to be conducted to demonstrate decontamination of the supernatant to meet ILAW requirements. This will require demonstration of Cs ion exchange. The AZ-102 mixture is below 5 M in sodium concentration. Testing at SRTC showed poor performance of this waste in Cs IX testing. Concentrating the waste to 5M may improve the Cs IX performance. Results from this active, small-scale evaporation test will support plant flowsheet development.

Quality Control

Method Specific Quality Control (QC) or special calibration requirements are described here. Items that may be included are:

- Analytical QC requirements and acceptance criteria are shown in Table 4
- Calibration requirements and frequency are defined in the method-specific procedures.

Hazard Mitigation

This work will be conducted in cell. Therefore, contact hazards are not at issue. The major hazard associated with this work is loss of sample through spill. Hot cell technicians shall conduct tests in a manner to minimize the impact of a spill. This will include taking all extra steps prudent for material stabilization. In the event of a spill, all practical efforts will be made to recover the test material. Recovered material will be segregated and retained pending a decision by the Cognizant specialist on how to proceed. Contact Sandy Fiskum or the Task Manager for guidance if uncertain on how to proceed.

Feed Description

This test will use the as-received AZ-102 supernatant received in ten 500-mL bottles. (This material will be evaporated to approximately 5 M sodium.) The approximate density of the as-received AZ-102 is 1.15 g/mL; the approximate Na concentration is 2.4 M (note the reported Na concentration by SRTC was 2.65M).

Equipment Description

Evaporation will be conducted in a large stainless steel beaker in the SAL. An overhead mechanical stirrer will provide mixing of the sample. A hot plate with a temperature controller shall be used to heat the sample to approximately 50 °C. An argon line will purge the beaker headspace to facilitate evaporation. Appropriate glass vials (20 mL) will be used to collect samples. Disposable syringes and filters will be used to filter the supernatant.

Responsible Staff

The staff responsible for executing this test plan are as follows.

- Task Manager – Dave Blanchard
- SFO Manager – Randy Thornhill
- Test Specialist/Scientist – Sandy Fiskum
- Hot Cell Technician – list names/location/work performed
- Radiological Control Technician

Materials, Equipment, Supplies and Reagents Needed

Materials Required

6-L stainless steel beaker fitted with clamp handles top and bottom
Hot Plate
Mechanical stirrer and impeller
Argon line/argon bottle
Analytical balance
4.5-kg balance
Thermocouple/hot plate controller
Dipstick, stainless steel rod marked at 1-cm intervals
Ring stand for stabilization of the beaker on the hot plate
10-mL volumetric flasks
Glass LSC vials

Work Instructions

This Test Instruction shall be used to record observations and other testing information as required. Cross-contamination of samples from outside sources must be minimized at each step. Use new supplies and bottles for each sample as much as practical.

1 Calibrate the liquid level dipstick as a function of volume in the stainless steel beaker. Record the volume and dipstick reading data below:

Volume	Dipstick reading	Volume	Dipstick reading
1. L	3.3 cm		
2. L	7.7		
2.5 L	9.5		
3.0. L	11.5		
3.5 L	13.3		
—	—		

1cm = 0.2621 L

not needed. SKF 10/31/03

2 Obtain the following information:

M&TE List: Note Balance Location, HLRF and cell

_____ Hot Cell Analytical Balance

Calib ID 38914 AW Calib Exp Date 2/02

_____ Hot Cell 4.5 Kg Balance

Calib ID 1120100179 Calib Exp Date 8/02

_____ Benchtop Analytical Balance

Calib ID N04143 Calib Exp Date 2/02

_____ Benchtop Large-capacity Balance

Calib ID 3505099 Calib Exp Date 8/21/02

_____ Temperature reading device (thermometer or thermocouple/reader):

Calib ID S/N 15265 Calib Exp Date 4/9/2002

25-125°C tolerance = 2.2°C
Omega teflon-coated type K thermocouple w/ Digisense temperature controller

3 Sample Reciept

3.1 Observe each sample individually, note the solution color, approximate volume, and appearance of any solids (and volume) that may be present. Note any discrepancies between expected and received condidtion. Record observations in Table 1

3.2 Weigh each sample bottle as-received, record masses in Table 1. Note that the expected gross mass is incorporated in the table.

3.3 Record the hot cell temperature 27 °C 10/31/01 10:00

S.K. Fiskum
10/31/01

Table 1. Sample Receipt Log

	Bottle ID Gross mass	RPL ID	Gross mass, g	Solution color	Solution volume	Solids present	Solids color	Solids volume	Comments
✓✓	**18819** 782.1 g	**02-00226**	782.04	colorless		yes	white	1 mm^3	white crystalline, some large ~2mm long
✓✓	**18990** 757.6 g	**02-00227**	757.80	colorless		yes	white w/ slight gray	0.5 cc	flocculent, white
✓✓	**18988** 767.5 g	**02-00228**	764.15	colorless		yes	white	2 mm^3	crystalline
✓✓	**18989** 776.7 g	**02-00229**	776.99	colorless		yes	white	3 mm^3	white crystalline, small + 1 large piece ~5mm
✓✓	**18996** 746.2 g	**02-00230**	746.70	colorless		yes	grey	1 mm^3	small pid, silty appearance
✓	**18992** 772.9 g	**02-00231**	773.34	colorless		yes	white	4cc	flocculent
✓	**18993** 737.7 g	**02-00232**	738.14	colorless		yes	white	2 cc	flocculent
✓✓	**18998** 739.0 g	**02-00233**	739.40	colorless		yes	white	<1 mm^3	mostly small w/ some large pieces ~2mm
✓✓	**18994** 771.8 g	**02-00234**	772.27	colorless		yes	dark grey	2 mm^3	—
✓✓	**18986** 772.4 g	**02-00235**	772.63	colorless		yes	brown	4 mm^3	silty

S.K. Fiskum

4 Compositing

4.1 Label vials with unique sample identification mark before transfer into the hot cells. NOTE: Tare bottle/vials with caps/lids.

4.2 Inventory materials, equipment, and supplies to ensure all required items are available. Modified materials/equipment as needed for remote handling.

4.3 Record the tare mass of the 6-L evaporating beaker 899.5 g (with all handle clamps in place). no lid

4.4 Stablize the stirrer above the beaker, leaving enough room for maneuvering the beaker.

4.5 Stabilize the beaker on the cool hot plate using ring stand and clamps.

4.6 If solids were observed (step 3.1) the samples will need to be initially filtered prior to compositing. If no solids were observed, this step may be skipped.

4.6.1 Prepare filtration apparatus ensuring a vacuum trap is in line between the filter apparatus and the vacuum hookup.

4.6.2 Tare a 1-L filter apparatus.
Upper reservoir 85.891 (no lid); 109.159 (with lid)
Lower reservoir 206.445 (with lid)

4.6.3 Pour each solution through the filter apparatus. Disconnect the upper section from the lower section and pour filtrate into 6-L stainless steel beaker. Maintain the lid with the bottle for later weighing.

4.6.4 After all solutions are filtered and filtrate collected in 6-L beaker, weigh the upper section and lower filter section. 10/31/01 11/1/01 8:55a.m. 11/2/01 #
Upper reservoir 90.401 g (no lid) 87.327 g 87.331
Lower reservoir 208.353 (with lid)

4.6.5 Save solids for later analysis by scraping them into a 20-mL glass LSC vial.

4.7 Mix and pour the waste solutions from each of ten bottles into the 6-L stainless steel beaker. Maintain the lid with the bottle for later weighing.

4.8 Adjust stirrer to low setting. Adjust stir speed to obtain a good mixing rate of the sample (see Cognizant scientist).

4.9 Allow the solution to stir for nominally 15 minutes. Start 1:40 p.m.

4.10 Reweigh each emptied bottle and record the gross mass in Table 2. Calculate total solution mass transferred.

4.11 Determine the solution density in duplicate:

a) Tare a 10-mL vol. Flask 11.1789
Add AZ-102 from the beaker into the vol flask
Measure the gross flask mass 22.6320
Calculate the net mass 11.4531
Determine the solution density 1.1453

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① scraped solids into vial. final mass of filter reservoir: 86.451 g
"AZ102 AR solids" mass transferred 0.8800 g
note: this mass is combined with solids scraped from bottle 18992

Hot cell temperature 28 °C

b) Tare a 10-mL vol. Flask 12.8417 skf 10/31/01
Add AZ-102 from the beaker into the vol flask
Measure the gross flask mass 24.2508
Calculate the net mass 11.4091
Determine the solution density 1.1409
Hot cell temperature 28 °C

4.12 Pour the 10-mL density aliquots into tared glass LSC analytical sample vials labeled "AZ-102AR-A" and "AZ-102AR-B" re-weigh, and fill out an ASR (QARD) for rapid Na analysis.

a) Tare AZ-102AR-A 17.0988
Gross AZ-102AR-A 28 4317
Net mass AZ-102AR-A
Identify RPL sample ID 02-0366 called AZ102AR on ASR

b) Tare AZ-102AR-B 17.1243
Gross AZ-102AR-B 28.3730
Net mass AZ-102AR-B
Identify RPL sample ID 02-0366 called AZ102AR dup on ASR

4.13 Extract a 20-mL sample into a tared glass LSC vial labeled "AZ-102AR-arch,"[1,2] re-weigh, and archive the sample.
Tare AZ-102AR-arch 17.0974
Gross AZ-102AR-arch 40.7141
Net mass AZ-102AR-arch 23.6167

used plastic syringes to make transfer.

4.14 Extract a 50-mL sample into a tared glass bottle labeled "AZ-102AR-C," re-weigh and alert M. Urie as to the sample location. This will be used for characterization activities.
Tare AZ-102AR-C 87.37
Gross AZ-102AR-C 143.4
Net mass AZ-102AR-C 56.0

4.15 Extract a 100-mL sample into a tared glass bottle labeled "AZ-102AR-D," re-weigh and alert Brian Rapko to the sample location. This will be used for mixing of process heel task (Task 2.07).
Tare AZ-102AR-D 133.56
Gross AZ-102AR-D 247.6
Net mass AZ-102AR-D 114.0

4.16 Consult with the Cognizant Scientist whether this step should continue or be modified (depending on actual as-received volume). Extract two 250-mL samples into tared glass bottles labeled "AZ-102AR-E" and "AZ-102AR-F," re-weigh and alert Dean Kurath to the sample location. These will be used for sulfate crystallization studies.

Tare AZ-102AR-E	218.96	Tare AZ-102AR-F	217.98
Gross AZ-102AR-E	501.5	Gross AZ-102AR-F	494.1
Net mass AZ-102AR-E	282.5	Net mass AZ-102AR-F	276.12

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[1] The term "arch" indicates archival sample.
[2] The term "AR" stands for the as-received condition of the waste.

Table 2. AZ-102 Mass Transferred

Bottle ID	RPL ID	Gross mass, g (from Table 1)	Empty bottle mass, g	Net Mass transferred, g	Comments (filter order)
18819	02-00226	782.04	299.591	482.45	(2)
18990	02-00227	757.80	299.568	458.23	(8)
18988	02-00228	764.15	298.767	465.38	(4)
18989	02-00229	776.99	296.704	480.29	(5) combined w/ #6 below (02-234) note loss.
18996	02-00230	746.70	293.334	453.37	(3) combined w/ 02 228 ~1 drop lost
18992	02-00231	773.34	296.250	477.09	(10) solids still remain in bottle ⓐ
18993	02-00232	738.14	295.364	442.78	(9)
18998	02-00233	739.40	298.137	441.26	(1) combined w/ #02-226 1 drop lost
18994	02-00234	772.27	294.284	477.99	(6) ~20 ml lost on transfer to beaker.
18986	02-00235	772.63	292.883	479.75	(7)
Net upper reservoir mass (filtered solids)				4.51	
Net lower reservoir mass (residual filtrate)				1.91	
Total mass transferred			Loss:	22.8	
AZ-102AR-A density mass				11.453	
AZ-102AR-B density mass				11.4091	
AZ-102AR-arch mass				23.6167	
AZ-102AR-C analytical aliquot mass (Urie)				56.0	
AZ-102AR-D mixing process heels mass (Rapko)				114.0	
AZ-102AR-E sulfate crystallization mass (Kurath)				282.5	
AZ-102AR-F sulfate crystallization mass (Kurath)				276.1	
AZ-102 mass remaining in beaker				3834.1	

ⓐ solids were difficult to break up; inverted bottle. re-weigh 11/02/01 3:40pm 293.39g
11/05/01 9:50am 293.37g
scraped solids into vial "AZ102AR Solids" after scraping 292.831
0.549 mass transferred.

5 Evaporation

5.1 Calculate the final volume required for AZ-102 to reach 5.0 M Na.

$$\frac{Total\ mass\ in\ beaker,\ g}{solution\ density,\ \frac{g}{mL}} * \frac{2.4\ M\ Na}{5.0\ M\ Na} = final\ volume,\ mL$$

Enter calculation here:

$$\frac{3854 \quad g}{1.143 \quad \frac{g}{mL}} * \frac{2.4\ M\ Na}{5.0\ M\ Na} = \underline{\quad 1618 \quad}\ mL$$

Note: Reevaluate this equation when the Na concentration is determined by ICP-AES from samples submitted in Step 4.12.

5.2 Adjust the thermocouple in the beaker, ensuring it does not touch the beaker sides and is at least 2 cm away from the beaker floor.

5.3 Adjust the Ar gas flow to nominally 5-15 cc/min. Flush with Ar for about 15 minutes to displace air from top of solution.

5.4 Continue mixing the waste at a moderate rate with the mechanical stirrer. Maintain the argon flow, and begin heating the waste to 50 ± 5 °C until the volume is reduced to the desired level. Record the time the evaporation was started. Periodically, stop the stirrer and determine the liquid level using the stainless steel dipstick. Use this to calculate an estimated time to complete the evaporation. If this requires multiple days record the time the heat and sparge are turned on each day. After the desired volume reduction has been completed, allow the waste to cool for 60 minutes.

Heat time/date on 10/31/01 3:15 p.m	Temperature 28.6
Heat time/date off 10/31/01 1645	Temperature 49.6
Heat time/date on 11/01/01 0629	Temperature 26.9 9:00; 49.5 °C
Heat time/date off see addendum pages	Temperature
Heat time/date on	Temperature
Heat time/date off	Temperature SKF
Heat time/date on SKF 11/1/01	Temperature 11/1/01
Heat time/date off	Temperature

11/1/01 8:30 a.m. added 1 drop of DI water to evaluate if ppt will form. - No ppt, reachin

5.5 Tare the capped receiver portion and upper reservoir section of a 1-L filtration apparatus.
Capped receiver tare 200.942
Upper reservoir tare 115.194 (with lid)

5.6 Place the filter apparatus in secondary containment. Stabilize the filter apparatus with a ring stand and clamps.

5.7 Ascertain the AZ-102 solution has reached room temperature.
Record the solution temperature NA Solution cooled for >24 hrs.

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Record the hot cell temperature 25 °C

5.8 Transfer the AZ-102 solution into the upper reservoir filter apparatus in nominal 500-mL increments while vacuum is applied.

5.9 When 1-L has been filtered, transfer filtrate to a tared 2-L bottle labeled AZ-102C.[3]
Record 2-L AZ-102C bottle tare 310.7g

5.10 Continue the filtration and transferring until the entire volume has been processed.

5.11 Weigh the upper reservoir filter chamber while wet. Record the mass. 118.814g lower res: 202.9g
Calculate the net residual sample mass in the filter chamber 3.62
Record observations.
mass of beaker + wet solids = 952.3g (13:00 11/5/01); (950.7g 15:50 11/6/01) ①
filtrate is clear, ppt had 2 components: floating layer and mostly settled solids.

NOTE: If there are significant solids, they will need to be scraped from the filter paper and collected (wet) into an LSC vial for later analysis. See Cognizant Scientist to make this call.

5.12 Weigh the bottle containing AZ-102C. 2340.7 g
Calculate the net mass of AZ-102C 2030. g (note. not including 10 mL taken in duplicate for density determination)

5.13 Determine the AZ-102C density in duplicate:

a) Tare a 10-mL vol. Flask 17.7443 g
Add AZ-102C from the beaker into the vol flask labeled AZ-102C-A
Measure the gross flask mass 30.4881
Calculate the net mass 12.7438
Determine the solution density 1.2744 g/mL
Hot cell temperature 25°C

b) Tare a 10-mL vol. Flask 17.8084 g
Add AZ-102C from the beaker into the vol flask labeled AZ-102C-B
Measure the gross flask mass 30.4811
Calculate the net mass 12.6727
Determine the solution density 1.2673
Hot cell temperature 25°C

$\bar{x}$ = 1.2709 g/mL

5.14 Pour the 10-mL density check solutions into glass LSC vials labeled AZ-102C-A and AZ-102C-B and submit for analysis according to Tables 3 and 4 using an ASR.

5.15 Assign the composited, concentrated AZ-102C sample the RPL number on the ASR indicated in 5.14.
Identify the RPL number here 02-00751 ASR = 6280

Final volume AZ102C: $$\frac{(2030g + 12.7g + 12.7g)}{1.27\ g/mL} = 1618\ mL$$

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[3] The "C" indicates concentrated sample.

①
949.9g 03:37 11/8/01
949.1g 09:13 11/9/01 (still wet)
934.8g 13:45 11/12/01 (looks dry)
935.0g 08:30 11/13/01

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Table 3. Minimum Reportable Quantities for Liquid Samples (supernatant/filtrate)

Analyte	Minimum Reportable Quantity, mg/L	Analysis Method/ Driver
Al	7.50E+01	ICP-AES [1]
Ca	1.50E+02	
Cr	1.50E+01	
K	7.50E+01	
Li	2.3E+00	
Na	7.50E+01	
U	6.00E+02	
U	7.8E+02	Kin. Phosphorescence
TOC	1.50E+03	Silver catalyze persulfate and furnace oxidation method
TIC	1.50E+02	Silver catalyze persulfate and furnace oxidation method
Cl	3.00E+02	IC Anions [1]
F	1.50E+02	
NO_2	3.00E+03	
NO_3	3.00E+03	
PO_4	--[1]	
SO_4	--[1]	
total and free OH	1.70E+01	Titration
Density	0.9 to 1.7 g/mL	Gravimetry
Total Cs[2]	1.5E+00	ICP-MS
^{137}Cs	5.00E-02	GEA [1]

[1] Report any additional analytes on an opportunistic basis.

[2] Total Cs is typically reported as a sum of ^{133}Cs, ^{135}Cs and ^{137}Cs.

Notes:
11/13/01
Transfer solids (dried) ~~from~~ precipitated from AZ102 evaporation.
Vial tare. 58.6098 g
Gross vial mass 75.4
net vial mass
AZ102C solids

precipitate is white

Additional vial needed for ppt. volume. AZ102C solids B
Vial tare 53.5160
Gross vial mass 69.4
net vial mass

Final beaker mass after bulk solids removed 907.2g S.K. Fiskum

Table 4. QC Parameters for AZ-102 Supernatant/Filtrate

Liquid Fraction	Analytical Technique	QC Acceptance Criteria		
		LCS %Recovery[a]	**Spike %Recovery**[b]	**Duplicate RSD**[c]
all requested analytes except Na	ICP/AES	80 - 120%	75 - 125%	<15%
Na	ICP/AES	80 - 120%	75 - 125%	<3.5%
All requested analytes	ICP/MS	80 - 120%	70 - 130%	<15%
All requested anions	IC	80 - 120%	75 - 125%	<15%
U (total)	Kinetic Phosphorescence	80 - 120%	75 - 125%	<15%
OH^-	Potentiometric titration	80 - 120%	N/A	<15%
TIC/$CO_3^=$	Persulfate and combustion furnace	80 - 120%	75 - 125%	<15%
TOC	Silver catalyzed persulfate and combustion furnace	80 - 120%	75 - 125%	<15%
Density		N/A	N/A	N/A
Radiochemical Analytes/Methods				
^{137}Cs	GEA	NP	N/A[d]	<15%

Acronyms:

GEA	– Gamma Energy Analysis
IC	– Ion Chromatography
ICP/AES	– Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP/MS	– Inductively Coupled Plasma Mass Spectroscopy
LCS	– Laboratory Control Standard
N/A	– Not applicable
NP	– Not performed
RSD	– Relative Standard Deviation

Footnotes:

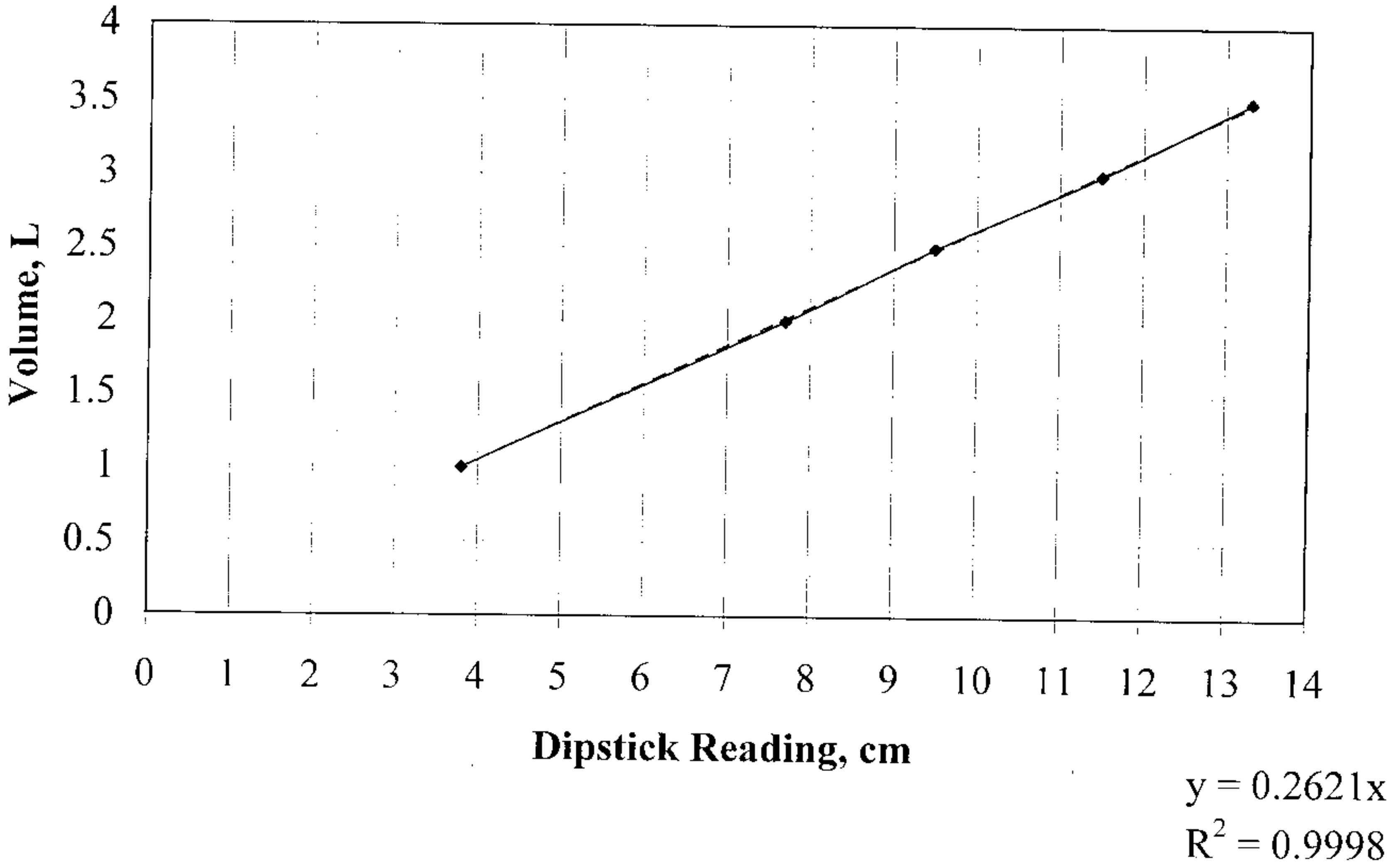
[a] LCS = Laboratory Control Standard. This standard is carried through the entire method. The accuracy of a method is usually expressed as the percent recovery of the LCS. The LCS is a matrix with known concentration of analytes processed with each preparation and analyses batch. It is expressed as percent recovery; i.e., the amount measured, divided by the known concentration, times 100.

[b] For some methods, the sample accuracy is expressed as the percent recovery of a matrix spike sample. It is expressed as percent recovery; i.e., the amount measured less the amount in the sample, divided by the spike added, times 100. One matrix spike is performed per analytical batch. Samples are batched with similar matrices. For other analytes, the accuracy is determined based on use of serial dilutions.

[c] RSD = Relative Standard Deviation between the samples. Sample precision is estimated by analyzing replicates taken separately through preparation and analysis. Acceptable sample precision is usually <15% RSD if the sample result is at least 10 times the instrument detection limit. %RSD = (standard deviation /mean) x 100

[d] The measurement is a direct reading of the energy and the sample matrix does not affect the analysis; therefore, a matrix spike is not required.

6-L Stainless Steel Beaker for AZ-102 Concentration



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Addendum

Observations During Evaporation, Step 5.4

Date / Time	Temperature °C	Void Space Height, cm	Solution Height, cm	Observations	
p.m. 10/31/01 3:37	43	10			
11/01/01 0630	26.9	~10			
11/01/01 0948	49.5	10.6			
11/01/01 1050	50.1	~10.8			
11/01/01 1140	48.1	11			
11/01/01 1248	49.9	~11.2			~11.75 DEEP
11/01/01 1348	49.1	~11.3			11.5 DEEP
11/01/01 1448	48.6	11.5		clear solution	
11/01/01 1600	49.3	11.75	11.25 DEPTH	doubled Ar flow rate	
11/01/01 1640	48.7	~11.9			
11/02/01 0634	48.6	13	10 DEPTH		
11/02/01 0920	50.1	13.5	9.5 "		
11/02/01 1040	50.2	~13.75	~9.25 "		
11/02/01 15:10	49.4	14	9	thick apparance, ppts formed.	
11/03/01 11:55	50.4	NM	7	Liquid level too low	
11/03/01 12:00	hot plate	turned off		to see in +	
				TC removed, impeller	
				removed, lid installed	
				on pot.	
				S.K Fiskum 11/3/01	

Addendum

After evaporation was complete, analytical results for the as-received material were reported. The AZ-102-AR A and B averaged 2.8 M Na. This feed Na molarity results in nominally a 5.8 M Na product solution. The density was slightly high at 1.271 g/mL.

It is therefore necessary to dilute the feed slightly to produce a final solution density of 1.25 g/mL.

The two density samples AZ-102C-A and AZ-102C-B and the batch contact sample pulled (as delineated in TI-RPP-WTP-132) were combined back into the 2-L feed bottle. Then 200 mL of 0.01M NaOH solution was added to the AZ-102C and the solution mixed. Density samples were re-taken and the batch contact sample was re-taken.

$$\frac{3854\,g}{1.143\,g/mL} * \frac{2.8\,M\,Na}{1618\,mL} = 5.8\,M\ Na$$

The 1618 mL was diluted to 1818 mL to produce a 5.2 M Na solution

AZ102C bottle tare 310.7 g

AZ102C (plus density samples and batch contact samples) 2363.7g

AZ-102C plus 200-mL 0.01M NaOH 2564.1 g

AZ-102C net mass 2253.4 g

Determine the AZ-102C density in duplicate:

a) Tare a 10-mL vol. Flask 17.2013
Add AZ-102C from the bottle into the vol flask labeled AZ-102C-A
Measure the gross flask mass 29.6360
Calculate the net mass 12.4347
Determine the solution density 1.2435
Hot cell temperature 26°C

b) Tare a 10-mL vol. Flask 17.0350
Add AZ-102C from the bottle into the vol flask labeled AZ-102C-B
Measure the gross flask mass 29.5733
Calculate the net mass 12.4883
Determine the solution density 1.2488
Hot cell temperature 26 °C

Pour the AZ-102C-A into a vial with the same label; repeat for AZ-102C-B.

Final volume: $\frac{2253.4\,g}{1.246\,g/mL} = 1{,}808\ mL$ a ~5.2 M Na

Complete 11/05/01
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Appendix D

Target Analyte List, Minimum Reportable Quantities, and QC Acceptance Criteria

Test Specification 24590-PTF-TSP-RT-01-002
Tables A.1, B.2 and D.2

Appendix D: Target Analyte List, Minimum Reportable Quantities, and QC Acceptance Criteria

Test Specification 24590-PTF-TSP-RT-01-002
Tables A.1, B.2 and D.2

Batch Contacts with Cs Ion Exchange Resin

Note: Batch contacts are to be conducted prior to the small-scale column tests with the radioactive sample to verify that SuperLig 644 and SuperLig 639 resin exchange capacities are consistent with previous batches of these resins. Since these tests create wastes from listed wastes (AZ-101 and AZ-102) they in turn will be regulated as listed wastes and require appropriate disposal.

1. Personnel are to record the solution temperature to ±1°C for the batch contact test. Batch contact tests are to be conducted in duplicate.

2. Personnel are to record the production lot number for the resin samples used in the batch contacts. The resin samples used in the batch contacts are to be from the same production lot as the resin used in the column tests.

3. Personnel are to analyze the AZ-101 feed supernate solution to determine the density, and concentrations of Na, K, free hydroxide, nitrate, fluoride, chloride, nitrite, Cs^{137}, pertechnetate, and total Tc^{99}. The minimum reportable quantity (MRQ) for each analyte is provided in Table A.1. SuperLig 644 and 639 resins have exhibited exchange affinity for these analytes.

Table A.1 Analyte Minimum Reportable Quantity

Analyte	**MRQ (μg/mL)**
Na or K	7.5E+01
Cs	1.0 E+01
Al	7.5E+01
Ca	1.5E+02
Free Hydroxide	1.7E+01
Nitrate	3.0E+03
Nitrite	3.0E+03
Chloride	3.0E+02
Fluoride	1.5E+02
Radionuclide	**MRQ (μCi/mL)**
Cs^{137}	1.0E-02
Pertechnetate and Total Tc^{99}	3.0E-03

4. Personnel are to analyze the AZ-102 concentrated supernate solutions to determine the density and concentrations of analytes listed on Table A.1. Radionuclide analysis is for ^{137}Cs. The MRQ for each analyte is provided in Table A.1.

5. Personnel are to contact 0.1±0.01-g of SuperLig 644 resin and 0.1±0.01-g of SuperLig 639 resin with 10±0.1-mL of the solutions listed in Table A.2. Batch contacts are to be conducted for a minimum of 24 hr.

d. Personnel are to collect all AZ-102 cesium eluate, composite the eluate, and analyze the eluate to determine the concentrations of the analytes listed in Table B.2. Analytical requirements for the AZ-102 tests are different than for the AZ-101 tests.

Table B.2. Analytical Requirements for AZ-102 Cs Column Effluents and Eluents*

Analyte	**MRQ (µg/mL)**
Al	7.5E+01
Ca	1.5E+02
Cr	1.5E+01
K	7.5E+01
Li	4.0E+00
Na	7.5E+01
U	6.00E+02
TOC	1.5+E03
TIC#	7.5E+01
Cl*	1.0 E+01*
F	1.5E+02
Nitrate	3.0E+03
Nitrite	3.0E+03
Phosphate	3.0E+03
Sulfate	3.0E+03
Total and free OH	1.70E+01
Density	0.9 to 1.7 g/mL
Total Cs	1.5E+00
Radionuclide	**MRQ (µCi/mL)**
Cs^{137}	1.0E-02
Sb-125	----

* Note the MRQ for the Chloride.
# Note: Do not perform the TIC on the AZ-102 eluate.

e. Personnel are to save the cesium eluate solution from both tests for at least 6 months. Personnel are to save the AZ-101 cesium eluate solutions from AZ-101 for combination with HLW sludge for vitrification tests.

9. After eluting and rinsing the lead cesium column, personnel are to regenerate the lead column as follows.

a. Transfer through the lead column 2-total apparatus volumes of 0.25M sodium hydroxide solution at 1 BV/hr.

b. Drain some of the excess liquid from atop the column, leaving approximately 1-BV of sodium hydroxide solution atop the resin bed. Composite and analyze the regeneration solution to determine the concentrations of ^{137}Cs, sodium, and hydroxide in the regeneration solution. Measure the residual concentration of cesium in the columns after elution and regeneration.

c. Personnel are to retain the solution from regeneration of the column.

Table D.2. Quality Control Parameters for Pretreated LAW Analysis

Liquid Fraction	Analytical Technique	QC Acceptance Criteria		
		LCS %Recovery(a)	**Spike %Recovery(b)**	**Duplicate RSD(c)**
Ag, Al, Bi, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Nd, Ni, P, Pb, Pd, Rh, Ru, S, Sr, Si, Ti, U, Zn, Zr	ICP/AES	80 - 120%	75 - 125%	<15%
Na	ICP/AES	80 - 120%	75 - 125%	<3.5%
As, B, Ba, Be, Ce, Co, La, Li, Mo, Pr, Rb, Sb, Se, Ta, Te, Th, Tl, V, W, mass unit 90(d)	ICP/MS	80 - 120%	70 - 130%	<15%
Cl^-, F^-, NO_2^-, NO_3^-, PO_4^{-3}, SO_4^{-2}	IC	80 - 120%	75 - 125%	<15%
CN^-	Distillation Colorimetric	80 - 120%	75 - 125%	<15%
Cs(i), Eu(i)	ICP/MS	N/A	N/A	N/A
Hg	CVAA	80 - 120%	75 - 125%	<15%
NH_3/NH_4^+	ISE, standard additions	80 - 120%	75 - 125%	<15%
OH-	Potentiometric titration	80 - 120%	N/A	<15%
TIC/CO_3^-	Persulfate and combustion furnace	80 - 120%	75 - 125%	<15%
TOC	Silver catalyzed persulfate and combustion furnace	80 - 120%	75 - 125%	<15%
Y	Derived from calculation	N/A	N/A	N/A
^{3}H	Separation/liq. Scintillation	80 - 120%	N/A(e)	<15%
^{14}C	Separation/liq. Scintillation	80 - 120%	75 - 125%	<15%
^{60}Co(f)	GEA	NP	N/A(g)	<15%
^{79}Se	Liq. Scintillation	NP	N/A(e)	<15%
^{90}Sr	Isotopic specific separation/beta count	75 - 125%	N/A(e)	<15%
^{99}Tc	ICP/MS	80 - 120%	70 - 130%	<15%
^{99}Tc (pertechnetate)	Separation/beta count	80 - 120%	70 - 130%	<15%
^{125}Sb	GEA	to be obtained		
^{126}Sn	ICP/MS	80 - 120%	70 - 130%	<15%
^{129}I	ICP/MS or Separation/GEA	NP	N/A(g)	<15%
^{137}Cs	GEA	NP	N/A(g)	<15%
^{152}Eu(f)	GEA	NP	N/A(g)	<15%
^{154}Eu(f)	GEA	NP	N/A(g)	<15%
^{155}Eu(f)	GEA	NP	N/A(g)	<15%
^{231}Pa	ICP/MS	Developed by Laboratory		
^{233}U	ICP/MS	90 - 110%	75 - 125%	<15%
^{234}U	ICP/MS	90 - 110%	75 - 125%	<15%
^{235}U	ICP/MS	90 - 110%	75 - 125%	<15%
^{236}U	ICP/MS	90 - 110%	75 - 125%	<15%
^{238}U	ICP/MS	80 - 120%	70 - 130%	<15%
^{237}Np(e)	ICP/MS	90 - 110%	75 - 125%	<15%
Total Pu	Sum of Isotopes	N/A	N/A	N/A
^{238}Pu, ^{239}Pu, ^{240}Pu(h)	Separation/AEA	NP	N/A(e)	<15%
^{241}Pu/Am, ^{242}Pu	ICP/MS	80 - 120%	70 - 130%	<15%
^{241}Am	Separation/AEA	NP	N/A(e)	<15%
^{242}Cm	Separation/AEA	NP	N/A(e)	<15%
^{243}Am/Cm	ICP/MS	90 - 110%	75 - 125%	<15%
$^{243+244}$Cm	Separation/AEA	NP	N/A(e)	<15%
Total Alpha(h)	Proportional counter	70 - 130%	70 - 130%	<15%
Total Beta	Beta counting	70 - 130%	70 - 130%	<15%
Total Gamma	GEA-Sum of isotopes	N/A	N/A	N/A

Table D.2 (Con't)

Density		N/A	N/A	N/A
Wt% dissolved solids	Gravimetric	80 - 120%	N/A	<21%

Acronyms:

AEA – Alpha Energy Analysis
CVAA – Cold Vapor Atomic Absorption
GEA – Gamma Energy Analysis
IC – Ion Chromatography
ICP/AES – Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP/MS – Inductively Coupled Plasma Mass Spectroscopy
LSC – Laboratory Control Standard
N/A – Not applicable
NP – Not performed
RSD – Relative Standard Deviation
Wt% – Weight percent

Footnotes:

(a) LCS = Laboratory Control Standard. This standard is carried through the entire method. The accuracy of a method is usually expressed as the percent recovery of the LCS. The LCS is a matrix with known concentration of analytes processed with each preparation and analysis batch. It is expressed as percent recovery; i.e., the amount measured, divided by the known concentration, times 100.

(b) For some methods, the sample accuracy is expressed as the percent recovery of a matrix spike sample. It is expressed as percent recovery; i.e., the amount measured less the amount in the sample, divided by the spike added, times 100. One matrix spike is performed per analytical batch. Samples are batched with similar matrices. For other analytes, the accuracy is determined based on use of serial dilutions.

(c) RSD = Relative Standard Deviation between the samples. Sample precision is estimated by analyzing replicates taken separately through preparation and analysis. Acceptable sample precision is usually <15% RSD if the sample result is at least 10 times the instrument detection limit. RSD = (standard deviation of the mean/mean) x 100

(d) ICP-MS mass unit 90 includes ^{90}Sr, ^{90}Y, and ^{93}Zr.

(e) Matrix spike analyses are not required for this method because a tracer is used to correct for analyte loss during sample preparation and analysis. The result generated using the tracer accounts for any inaccuracy of the method on the matrix. The reported results reflect this correction.

(f) An extended counting time in the presence of high ^{137}Cs activity may be required to achieve the minimum reportable quantity for ^{60}Co and ^{152}Eu, ^{154}Eu, ^{155}Eu.

(g) The measurement is a direct reading of the energy and the sample matrix does not affect the analysis; therefore, a matrix spike is not required.

(h) The sum of ^{238}Pu, ^{239}Pu, ^{240}Pu, and ^{241}Am activities will be used as a measurement of alpha-emitting TRU. The selected isotopes account for greater than 95% of the alpha-emitting TRU activity based on previous analysis of Phase I candidate tank waste (Esch 1997a, 1997b, 1997c . Additional isotopes that are defined as alpha-emitting TRU (e.g., ^{237}Np, ^{242}Pu, ^{242}Cm, ^{243}Am, and $^{243+244}$Cm) are not used to calculate total TRU activity because the MDAs for these isotopes are large in comparison with the envelope limits and it is expected that their concentrations are well below the MDA. Note that ^{241}Pu is a beta-emitting TRU whose analysis, along with ^{242}Cm, is required specifically for class C waste determination.

(i) Total Cs and Eu are sums of all isotopes, therefore spiking and LCS does not apply.

Appendix E

ICP-AES Laboratory Control Sample and Matrix Spike Failures – AZ-102C Solids

Appendix E: ICP-AES Laboratory Control Sample and Matrix Spike Failures – AZ-102C Solids

The Laboratory Control Sample (LCS) processed with the AZ-101C Solids failed to meet the quality control acceptance criterion of 80% to 120% for K, Na, and B. The Matrix Spike failed to meet the QC acceptance criterion of 75% to 125% for K and B, and the Na recovery was not measurable since the sample concentration greatly exceeded the spiking concentration. The reason for each of these failures is described below.

Although the Quality Assurance Plan required re-preparation and re-analysis when the LCS fails, a decision was made not to reanalyze the AZ-102C Solids based on the following.

a) All other QC samples analyzed for K, Na, and B were acceptable.
b) The reasons for the failures could be determined.
c) The failures were not systematic; i.e., the LCS for K, Na, and B did not fail for the AZ-102 as-received analysis or the AZ-102C liquid analysis.
d) The measurement of the AZ-102C solids was performed on an opportunistic basis.
e) The AZ-102 mass balance was reasonably good, based on the AZ-102 as-received, AZ-102C Liquid, and AZ-102C Solids analysis, and the AZ-102C Solids made up only about 1% of the mass.
f) The AZ-102C solids dose levels were significantly high, and additional exposure to staff was not warranted based on data needs.

Potassium Failure Investigation

The LCS and MS were prepared from the same multi-element standard solutions (PBNL-QC-1 and PBNL-QC-2 from Inorganic Ventures, Inc.). The multi-element standard solutions were used over about a 3-month period and were used for the AZ-102 as-received, AZ-102C Liquid, and AZ-102C Solids ICP-AES analyses. The as-received and Liquid analyses were conducted within 1 month of the procurement of the standards, whereas the Solids analysis was conducted about 3 months after procurement. Only the LCS and MS associated with the AZ-102C Solids failed.

Just before preparing the LCS and MS for the AZ-102C Solids analysis, an LCS K failure (~30% recovery) on another batch of samples using the same multi-element solutions prompted an investigation. Based on the investigation, the multi-element standard PBNL-QC-2 was determined to have deteriorated and was removed from service. Unfortunately, this was not in time to restrict its use for the AZ-102C Solids analysis.

During the investigation, the laboratory analyzed the PBNL-QC-2 solution multiple times with an average recovery of about 35% of the certified concentration. The vendor was notified and conducted an independent evaluation of archived material. The vendor measured a K concentration of 1725 μg/mL in the archive, where the certified value was 5000 μg/mL. This evaluation was documented on the vendor's "Inquiry Report Form CL# 4359 (02/04/02)". A copy of this form and the laboratory's results on PBNL-QC-2 after 3 months is included in the ICP-AES system file.

If 1725 µg/mL is used as the basis for the K LCS and MS calculation, the LCS recovers at 100% and the MS at about 70%. However, the 1725 µg/mL is not a certified value and cannot be used for reporting the LCS and MS recoveries.

Sodium and Boron Failure Investigation

The failure of the LCS and MS for Na and B was attributed to blank contamination from processing the AZ-102C Solids in glass using procedure PNL-ALO-129, which requires nitric acid and hydrochloric acid in the digestion process. This procedure typically requires non-glass digestion vessels (e.g., Teflon, polyethylene, etc.) whenever Na, Si, and B (major glass components) are analytes of interest. However, for the AZ-102C Solids acid-digestion, glass-digestion vessels were used for preparing the standards and samples, primarily since the intent of the analysis was to identify the major components of the precipitated solids, and any blank contamination would have a minimal effect.

The Na and B (and Si, which was not identified as an analyte of interest) concentrations in the processing blank were 1.5 to 3.5 times greater than the estimated quantitation limits (EQL). Although the blank contributions were subtracted from the QC samples, the excessively high B and Na LCS recoveries and the B matrix spike recovery were due to variability from single process blank analysis.

Another contributing factor was the result of processing standard solutions containing HF (0.7% added in PBNL QC 2) in glass-digestion vessels. Since the absolute effect of the HF on the glass vessels was likely variable and cannot be quantified, it was not possible to correct the recoveries to account for this effect. Hence the failure was not a systematic problem.

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