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Vitrification and Product Testing of AZ-101 Pretreated High-Level Waste Envelope D Glass

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September 2004

Prepared for Bechtel National Inc.
By Battelle—Pacific Northwest Division
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9/27/04
for W. Tamosaitis

ACCEPTED FOR
PROJECT USE

September 2004

Test Specification: 24590-HLW-TSP-RT-02-009, Rev 0
Test Plan: TP-RPP-WTP-190, Rev 0
R&T Focus Area: Waste Form Qualification
Test Scoping Statement(s): B-26
Test Exceptions: 24590- WTP -TEF-RT-03-002 and 24590-HLW-TEF-RT-03-002

Battelle—Pacific Northwest Division
Richland, Washington 99352

COMPLETENESS OF TESTING

This report describes the results of work and testing specified by Test Specification 24590-HLW-TSP-RT-02-009, Rev 0, Test Exceptions: 24590- WTP -TEF-RT-03-002 and 24590-HLW-TEF-RT-03-002, and Test Plan TP-RPP-WTP-190, Rev 0. 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

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Abbreviations and Acronyms

AEA	alpha energy analysis
ALO	analytical laboratory operations
AMU	atomic mass unit
ARG	analytical reference glass
ASO	Analytical Service Operations
ASR	analytical service request
ASTM	American Society for Testing and Materials
BNI	Bechtel National, Inc.
CCB	continuing calibration blank
CCC	canister centerline cooling
CCV	continuing calibration verification
CFR	Code of Federal Regulations
CMC	chemical management center
CUA	Catholic University of America
CVAA	cold vapor atomic absorption spectroscopy
DIW	deionized water
DOE	U.S. Department of Energy
DOE-EM	U.S. Department of Energy, Office of Environmental Management
DWPF	Defense Waste Processing Facility
EA	environmental assessment
EDS	energy dispersive spectroscopy
EPA	Environmental Protection Agency
EQL	estimated quantitation limit
GEA	gamma energy analysis
HLRF	High-Level Radiochemistry Facility
HLW	high-level waste
ICB	initial calibration blank
ICN	interim change notice
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectroscopy
ICV	initial calibration verification
IDL	instrument detection limit
IHLW	immobilized high-level waste
ILAW	immobilized low-activity waste
LAW	low activity waste

LCS	laboratory control standard
LDR	land disposal restrictions
LEPS	low-energy photon spectrometry
LRM	low-activity test reference material
MDA	minimum detectable activity
MDL	method detection limit
MF	mass fraction
MRQ	minimum reportable quantity
M&TE	measuring and test equipment
NIST	National Institute of Standards and Technology
NUREG	nuclear regulation
ORP	Office of River Protection
PCT	product consistency test
PNNL	Pacific Northwest National Laboratory
PNWD	Battelle—Pacific Northwest Division
ppt(s)	precipitate(s)
QA	quality assurance
QAPjP	quality assurance project plan
QC	quality control
QARD	Quality Assurance Requirements and Description
RCRA	Resource Conservation Recovery Act
RD	relative difference
RPD	relative percent difference
RPG	Radiochemical Processing Group
RPL	Radiochemical Processing Laboratory
RPP-WTP	River Protection Project Waste Treatment Plant
RSD	relative standard deviation
SAL	Shielded Analytical Laboratory
SD	serial dilution
SEM	scanning electron microscopy
TC	total carbon
TCLP	Toxicity Characteristic Leaching Procedure
TIC	total inorganic carbon
TOC	total organic carbon
TRU	transuranic
UHC	underlying hazardous constituents
UTS	universal treatment standards
VSL	Vitreous State Laboratory

WAPS	Waste Acceptance Product Specifications
WASRD	Waste Acceptance System Requirements Document
WTP	Hanford Waste Treatment and Immobilization Plant
WTPSP	Waste Treatment Plant Support Project
XRD	X-ray diffraction

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Testing Summary

The U.S. Department of Energy (DOE) Office of River Protection (ORP) has contracted with Bechtel National Inc. (BNI) to design, construct, and demonstrate the Hanford Waste Treatment and Immobilization Plant (WTP) (DOE-ORP 2000). The WTP will separate the Hanford radioactive tank waste into low-activity waste (LAW) and high-level waste (HLW) and will separately vitrify these wastes into borosilicate glasses. To demonstrate the feasibility of vitrification and the durability of the glass, Battelle—Pacific Northwest Division (PNWD) has been contracted to produce and test a vitrified AZ-101 Envelope D[(a)] HLW sample previously supplied to the WTP project by DOE. This document describes work performed in accordance with the PNWD test plan, TP-RPP-WTP-190 Rev 0 (Smith 2002).

Objectives

The ultimate goal of this task is to help demonstrate the WTP project's ability to satisfy the product requirements concerning chemical composition, radionuclide content, waste loading, identification and quantitation of crystalline and noncrystalline phases, and waste-form leachability. The primary objective is to fabricate a HLW glass sample from a pretreated AZ-101 HLW sludge (Envelope D). Table S.1 summarizes the seven specific objectives stated in the test plan (Smith 2002). These objectives were all met. Table S.1 also provides additional information regarding relevant details as to how the individual objectives were met and the outcome of testing.

Test Exceptions

Three interim change notices (ICNs) were issued: ICN-TP-RPP-WTP-190.1 (1/28/2003), which corrected a typo in the document header, ICN-TP-RPP-WTP-190.2 (2/25/2003), and ICN-TP-RPP-WTP-190.3 (5/27/2004). The latter two ICNs were issued in response to the test exceptions listed in Table S.2. Stated test objectives were not affected by these exceptions.

(a) Envelope D waste is the HLW tank waste slurry.

Table S.1. Summary of Test Objectives and Results

Test Objective	Objective Met	Discussion
Produce an AZ-101 HLW glass sample with a composition matching HLW98-95 and batched with WTP glass forming chemicals.	Y	Enough AZ-101 HLW sludge was available to produce 173 g of glass with a composition close to HLW98-95 and batched with WTP glass forming chemicals. Of this, 163 g was usable; 10 g were lost in processing. Section 5.2
Measure AZ-101 HLW glass chemical composition.	Y	AZ-101 HLW glass composition was obtained with ICP-AES and three sample preparation methods. Results were statistically refined. Section 6.1
Measure AZ-101 HLW glass radiochemical composition.	Y	The content of radionuclides in AZ-101 HLW glass was determined by radiochemistry and ICP-MS. Section 6.2
Determine AZ-101 HLW loading in glass.	Y	The waste loading of 34.84 mass% was determined as an average from mass balances of key waste components. $Fe_2O_3 + Al_2O_3 + ZrO_2$ = 23.97 wt% compared to a minimum loading requirement of 21 wt%. See Section 6.1
Identify/quantify crystalline phases expected in AZ-101 HLW glass canister.	Y	6.8±0.95 mass% of 0.5 to 3-μm crystals of $(Ni,Zn,Fe)(Fe,Mn,Cr)_2O_4$ spinel was detected by quantitative XRD and SEM-EDS with image analysis. Homogenous glass was the only noncrystalline phase identified. Section 6.3
Measure 7-day 90°C PCT normalized releases of B, Li, Na, and Si.	Y	The glass passed with remarkably low normalized releases of B, Li, Na, and Si. (0.26 g/m^2, 0.33 g/m^2, 0.256 g/m^2, and 0.15 g/m^2). Section 6.4
Perform the TCLP.	Y	All analyte concentrations were far below the UTS limits, with Cd the closest at 58% of the UTS limit. Section 6.5

ICP-AES = inductively coupled plasma-atomic emission spectroscopy
ICP-MS = inductively coupled plasma-mass spectrometry
XRD = X-ray diffraction
SEM-EDS = scanning electron microscopy with energy-dispersive spectroscopy
PCT = Product Consistency Test
TCLP = Toxicity Characteristic Leach Procedure
UTS = universal treatment standards

Table S.2. Test Exceptions

Test Exceptions	Description
24590-WTP-TEF-RT-03-002	Issued to revise glass-fabrication target amounts and to direct batching adjustments needed because of limited amounts of some waste components.
24590-HLW-TEF-RT-03-002	1) Reporting of boron shall be included in the analysis of the TCLP extract on an opportunistic basis. 2) Changed method detection limit (MDL) to estimated quantitation limit (EQL) in Paragraph 2 of "Additional quality assurance (QA) Requirements." Changed "Table 8" to "Tables 6 and 7" in the same sentence. 3) Deleted requirement to perform cyanide analysis.

Results and Performance Against Success Criteria

Table S.3 lists the success criteria and reviews how these criteria were met through AZ-101 HLW glass fabrication and testing. All seven success criteria were met.

Table S.3. Summary of Success Criteria for AZ-101 HLW Glass

Success Criterion	How the Criterion Was Met
1) Inorganic components present at concentrations >0.5 mass% are identified and quantified.	Glass composition was statistically evaluated from ICP-AES results. The following components exceeded 0.5 mass% in AZ-101 HLW glass: SiO_2, Na_2O, Fe_2O_3, B_2O_3, Al_2O_3, Li_2O, ZrO_2, ZnO, UO_3, CdO, and NiO. See Section 6.1
2) Waste loading is consistent with the minimum concentration of waste-component limits.	The waste-loading fraction of AZ-101 HLW glass, 34.84 mass%, exceeded the target (31.75 mass%) and the contract limits. $Fe_2O_3 + Al_2O_3 + ZrO_2 = 23.97$ wt% compared to a minimum loading of 21 wt%. See Section 6.1
3) U and Pu isotopes are identified and quantified.	U and Pu isotopes were identified and quantified by radiochemistry and ICP-MS. A WTP canister filled with 1.18 m^3 of AZ-101 HLW glass will contain 16.2 kg of U (137 g of ^{235}U) and 160 g of Pu (149 g of ^{239}Pu) at 136 g of Pu per m^3. Uranium contains 0.0067% ^{234}U, 0.84% ^{235}U, 0.062% ^{236}U, and 99.1% ^{238}U. Plutonium contains 92.7% ^{239}Pu, 7.21% ^{240}Pu, and 0.08% ^{241}Pu. See Section 6.2
4) The radionuclides determined as significant per NUREG/BR-0204 (NRC 1998) and 49 CFR 172.101 Table A.2 in Appendix A are identified and quantified.	Radionuclides were determined (Section 6.3, Test Specification) by radiochemistry and ICP-MS. Radionuclides with $t_{1/2} > 10$ years present in AZ-101 HLW glass are ^{63}Ni, ^{90}Sr, ^{99}Tc, ^{137}Cs, ^{151}Sm, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{242}Pu, ^{241}Am, ^{243}Cm, and ^{244}Cm. The 2004 and 2015 activity is mainly due to $^{90}Sr + {}^{90}Y$ (62%) and $^{137}Cs + {}^{137m}Ba$ (38%); in 3115, the main sources of radioactivity will be ^{241}Am (71.4%), ^{239}Pu (16.4%), ^{99}Tc (7.6%), and ^{240}Pu (4.3%). A complete evaluation of each decay chain was made and ^{231}Pa was the only additional reportable radionuclide. See Section 6.2
5) Crystalline and noncrystalline phases are identified and quantified.	By XRD and SEM-EDS, AZ-101 HLW canister-centerline cooled glass contains 6.81±0.95 mass% of spinel crystals that are 0.5 to 3 μm in size. A trace of spinel was detected in the quenched glass. Homogenous glass was the only noncrystalline phase identified. See Section 6.3
6) PCT releases of Li, Na, and B satisfy WAPS requirements.	The 7-day 90°C PCT normalized releases of B, Li, and Na (0.26 g/m^2, 0.33 g/m^2, and 0.256 g/m^2) from AZ-101 HLW glass are 5 to 11% of the corresponding releases of the environmental assessment (EA) standard reference glass. See Section 6.4
7) Generate data for the evaluation of the glass form against Land Disposal Restrictions of the Washington Dangerous Waste Regulations and RCRA LDR.	AZ-101 HLW glass passed the UTS limits for all listed elements. No measurable concentration was detected for Ag, As, Be, Cr, Cu, Hg, Sb, Se, Tl, and V with detection limits below UTS levels. Concentrations of Ba, Ni, and Zn were <10% of the UTS limit. The Pb concentration was 23% of the UTS limit, and the Cd concentration was 58% of the UTS limit. See Section 6.5

Quality Requirements

Application of RPP-WTP Quality Assurance Requirements

PNWD implements the River Protection Project Waste Treatment Plant (RPP-WTP) quality requirements by performing work in accordance with the PNWD Waste Treatment Plant Support Project quality assurance project plan (QAPjP) approved by the RPP-WTP Quality Assurance (QA) organization. This work was performed to the quality requirements of NQA-1-1989 Part I, Basic and Supplementary Requirements, NQA-2a-1990, Part 2.7 and QARD, Revision 13. These quality requirements are implemented through PNWD's *Waste Treatment Plant Support Project (WTPSP) Quality Assurance Requirements and Description Manual.* The analytical requirements are implemented through WTPSP's Statement of Work (WTPSP-SOW-005) with the Radiochemical Processing Laboratory (RPL) Analytical Service Operations (ASO).

A matrix that cross-references the NQA-1, 2a and QARD requirements with the PNWD's procedures for this work is given in Table 2.1. (Applicable Quality Assurance Procedures) It includes justification for those requirements not implemented.

Conduct of Experimental and Analytical Work

Experiments that were not method-specific were performed in accordance with PNWD's procedures QA-RPP-WTP-1101 "Scientific Investigations" and QA-RPP-WTP-1201 "Calibration Control System," ensuring that sufficient data were taken with properly calibrated measuring and test equipment (M&TE) to obtain quality results.

The work was conducted as specified in Test Specification 24590-LAW-TSP-RT-02-009, Rev 0. BNI's QAPjP, PL-24590-QA00001, Rev 0, is applicable to the TCLP activities since the work might be used in support of environmental/regulatory compliance.

The applicable quality control (QC) parameters for chemical analysis are delineated in Test Plan TP-RPP-WTP-190, Rev 0, Table 3 and 7.

Internal Data Verification and Validation

PNWD addresses internal verification and validation activities by conducting an independent technical review of the final data report in accordance with PNWD's procedure QA-RPP-WTP-604. This review verifies that the reported results are traceable, that inferences and conclusions are soundly based, and that the reported work satisfies the Test Plan objectives. This review procedure is part of PNWD's *WTPSP Quality Assurance Requirements and Description Manual*.

R&T Test Conditions

Table S.4 summarizes the principle test conditions called out by the test plan for this work.

Table S.4. R&T Test Conditions

R&T Test Conditions	Test Conditions Followed? Results
1. Glass Fabrication	Yes. Following the Vitreous State Laboratory (VSL) Batching Recipe, a pretreated AZ-101 tank sludge sample was blended with Cs and Tc ion exchange eluates from AZ-101 and AP-101 low activity waste supernatant pretreatment and mixed with the following mineral additives: borax, calcium carbonate, chromium oxide, potassium carbonate, lithium carbonate, sodium carbonate, silica, zinc oxide, and uranium oxide (Table S.5). The resulting AZ-101 melter feed was dried, calcined, and melted at 1150°C for 2.5 hours.
2. Glass Centerline Cooling	Yes. A 20.01-g AZ-101 HLW glass sample was heat-treated in a 25×25×25-mm Pt10%Rh box according to the canister centerline cooling (CCC) curve approximated by a series of linear time-temperature segments (See Table 5.12.)
3. Glass Chemical Composition • Concentration ≥ 0.5 wt% • RCRA metals • Corrosive Elements	Yes. The glass was prepared for analysis with Na_2O_2-NaOH fusion in a Zr crucible, KOH-KNO_3 fusion in a Ni crucible, and acid digestion. Cation analysis was performed with ICP-AES. A portion of the Na_2O_2-NaOH fusion samples was used for radiochemical analysis and ICP-MS analysis.
4. Glass Radiochemical Composition	Yes. Activities and concentrations of specified (Section 6.3, Test Specification) radionuclides were measured by specific radiochemical methods and by ICP-MS. Activities of radionuclides with the half-life ($t_{1/2}$) > 10 years are summarized in Table S.6. Table S.7 shows the total masses and concentrations of U and Pu and their isotopes in a WTP canister.

Table S.4 (contd)

R&T Test Conditions	Test Conditions Followed? Results
5. Crystalline and Non-Crystalline Phase Determination	Yes. Crystalline phases were identified with XRD, SEM, and image analysis on a CCC heat-treated sample of AZ-101 HLW glass. Quantitative XRD analysis showed that the glass contained 7.1 mass% of spinel. The spinel content was also evaluated with an image analyzer from SEM micrographs, obtaining 3.55±0.50 vol%, a fraction equivalent to 6.81±0.95 mass%. Spinel crystals were 0.5 to 3 μm in size and contained Fe, Ni, Cr, Mn, and Zn. Homogenous glass was the only noncrystalline phase identified.
6. A 7-day Product Consistency Test (PCT) at 90°C as defined in C1285-97 (ASTM 1997).	Yes. Average normalized releases from AZ-101 HLW glass subjected to the 7-day 90°C PCT are listed in Table S.8. These values are very low, only 5 to 11% of the corresponding releases of the EA standard reference glass.
7. The TCLP procedure for hazardous inorganics was performed on glass samples	Yes. TCLP results are summarized in Table S.9. The AZ-101 HLW glass passed the UTS limits for all listed elements. Out of the UTS-listed elements (plus Cu), no measurable concentration was detected for Ag, As, Be, Cr, Cu, Hg, Sb, Se, Tl, and V. Concentrations of Ba, Ni, and Zn were <10% of the UTS limit. The Pb concentration was 23% of the UTS limit, and the Cd concentration was 58% of the UTS limit.
8. Total Cyanide	No. This activity was deleted per Test Exception (24590-HLW-TEF-RT-03-002).
9. Reporting	Yes. Reporting per the Test Plan (TP-RPP-WTP-190, Rev. 0) as amended by the Test Exceptions (24590-HLW-TEF-RT-03-002 and 24590-WTP-TEF-RT-03-002)

Table S.5 summarizes the targeted composition and the final estimate of AZ-101 HLW glass composition for all components with ≥ 0.5 mass% in glass. Figure S.1 illustrates that reasonable agreement exists between the actual and targeted composition.

Table S.5. AZ-101 HLW Glass Composition in Mass%

	Measured	Target
	(mass%)	
SiO_2	44.30	44.69
Na_2O	10.58	11.87
Fe_2O_3	12.00	11.16
B_2O_3	10.08	10.63
Al_2O_3	8.23	7.33
Li_2O	3.73	3.76
ZrO_2	3.74	3.38
ZnO	1.99	2.01
UO_3	0.90	0.92
CdO	0.68	0.64
NiO	0.54	0.49

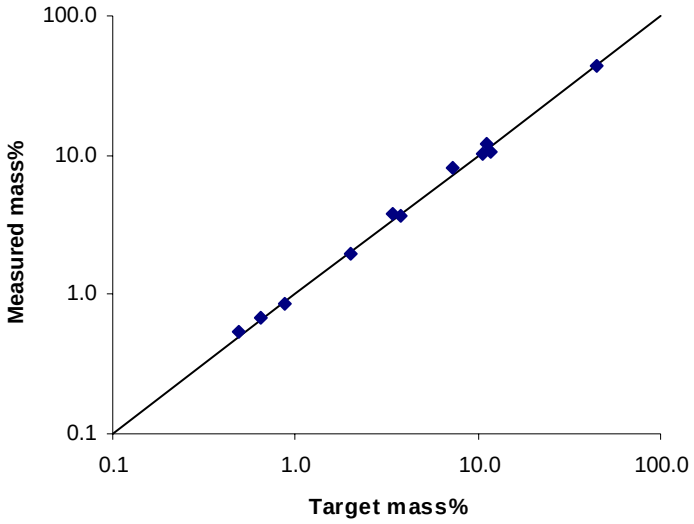

Figure S.1. Analyzed Versus Target AZ-101 HLW Glass Composition (for components with >0.5 mass%)

The waste-loading fraction in the glass was obtained as a weighted average calculated from mass balances for Fe_2O_3, Al_2O_3, ZrO_2, CdO, and CaO. The weighted average was 34.69 mass%, a value higher than the targeted 31.75 mass%.

Table S.6. Activities of Radionuclides Found in AZ-101 HLW Glass (See Section 6.2 for further details)

	$t_{1/2}$, years	A, mCi/kg-glass		$t_{1/2}$, years	A, mCi/kg-glass
^{60}Co	5.27E+00	2.86E+00	$^{238}U^{(a)}$	4.46E+09	1.67E-03
^{63}Ni	1.00E+02	2.46E+00	$^{237}Np^{(a)}$	2.14E+06	4.07E-02
^{79}Se	<6.5E+04	<5.61E-04	^{238}Pu	8.47E+01	4.39E-01
^{90}Sr	2.91E+01	2.49E+04	$^{239+240}Pu$	na	3.55E+00
$^{99}Tc^{(a)}$	2.13E+05	1.28E+00	$^{239}Pu^{(a)}$	2.41E+04	2.84E+00
^{129}I	1.57E+07	<1.75E-03	^{240}Pu	6.54E+03	8.11E-01
^{137}Cs	3.02E+01	1.53E+04	^{241}Pu	1.44E+01	Not measured
^{151}Sm	9.00E+01	4.12E+02	$^{242}Pu^{(a)}$	3.76E+05	1.63E-04
^{154}Eu	8.81E+00	3.34E+01	^{241}Am	4.32E+02	7.14E+01
^{155}Eu	4.96E+00	2.99E+01	$^{241}Am^{(a)}$	4.32E+02	6.94E+01
$^{234}U^{(a)}$	2.45E+05	2.09E-03	$^{243+244}Cm$	na	2.81E-01
$^{235}U^{(a)}$	7.04E+08	9.10E-05	^{243}Cm	2.85E+01	Determined as $^{243+244}Cm$
$^{236}U^{(a)}$	2.34E+07	2.00E-04	^{244}Cm	1.81E+01	Determined as $^{243+244}Cm$
			-	-	-

(a) Based on ICP-MS data

Table S.7. Mass and Concentration of U and Pu per WTP Canister Assuming 1.18 m^3 per Canister

	Mass per Canister, kg	Concentration, kg/m^3		Mass per Canister, g	Concentration, g/m^3
^{234}U	0.0011	0.0009	^{238}Pu	0.082	0.0695
^{235}U	0.137	0.116	^{239}Pu	149	126
^{236}U	0.0100	0.0085	^{240}Pu	11.6	9.8
^{238}U	16.05	13.6	^{242}Pu	0.13	0.11
Total U	16.20	13.7	Total Pu	160.4	136

Table S.8. 7-day 90°C PCT Normalized Releases from AZ-101 HLW Glass

	Normalized Release, g/m^2
B	0.260
Li	0.333
Na	0.256
Si	0.154

Table S.9. TCLP Solution Concentrations and UTS limits

Element		UTS[a] (mg/L-TCLP)	Delisting values[c] (mg/L-TCLP)	Required for LDR	Measured (mg/L-TCLP)
Antimony	Sb	1.15	0.659	yes	0.039 U
Arsenic	As	5.0	3.08	HLVIT	0.052 U
Barium	Ba	21	100	HLVIT	0.19 J
Beryllium	Be	1.22	1.33	yes	0.00021 U
Boron[b]	B	n/a	0.0047	n/a	1.4
Cadmium	Cd	0.11	0.48	HLVIT	0.064 J
Chromium	Cr	0.6	5.0	HLVIT	0.0065 U
Copper	Cu	n/a	5.0	HLVIT	0.025 U
Lead	Pb	0.75	5.0	HLVIT	0.040 U
Mercury	Hg	0.025	0.2	HLVIT	0.000023 U
Nickel	Ni	11	12.1	yes	0.033 J
Selenium	Se	5.7	1.0	HLVIT	0.045 U
Silver	Ag	0.14	3.07	HLVIT	0.0076 U
Thallium	Tl	0.20	0.282	yes	0.000023 J
Vanadium	V	1.6	16.9	n/a	0.0053 U
Zinc	Zn	4.3	225	n/a	0.33 J

(a) UTS = Universal treatment standard, 40 CFR 268.48.
(b) Boron is included for information only and is not a Constituent of Potential Concern.
(c) Kot et al. 2003, 2004.
HLVIT = vitrification has been recognized as the best available technology for immobilizing these elements per 40 CFR 268.40.
n/a = not applicable
LDR = land disposal restrictions
U = Undetected. Analyte was analyzed but not detected (e.g., no measurable instrument response), or response was less than the MDL.
J = Estimated value. Value is below EQL and above MDL.

Simulant Use

It was concluded that the simulated and actual waste glasses appear to have similar durabilities in spite of measurable differences in the level of crystallinity of the CCC heat treated glasses. See Section 6.6.

Discrepancies and Follow-on Tests

None

1.0 Introduction

Radioactive waste currently stored in underground tanks at Hanford will be treated for geologic disposal. The treatment will separate high-level waste (HLW) from low activity waste (LAW) and immobilize these wastes in a glass. Intermediate streams, mainly ion exchange eluates and Sr/transuranic (TRU) precipitate products generated during the separation process will be added to the HLW before vitrification. The HLW product must satisfy a number of performance requirements to be acceptable for disposal.

The U.S. Department of Energy (DOE) Office of River Protection (ORP) has contracted with Bechtel National Inc. (BNI) to design, construct, and demonstrate the Hanford Waste Treatment and Immobilization Plant (WTP) (DOE-ORP 2000). Battelle—Pacific Northwest Division (PNWD) has been contracted to produce and test a HLW waste glass from AZ-101 Envelope D[(a)] HLW samples previously supplied to the WTP project by DOE.

A sludge sample was taken from the AZ-101 tank (a tank of double-shell construction and 1-million gallon capacity). When received, the sample had been processed through pretreatment chemical washing and leaching processes and converted to HLW glass. To produce melter feed, the pretreated sludge was mixed with the composite Cs ion exchange eluates, Tc ion exchange eluates, and mineral additives. The target glass composition was calculated by the Catholic University of America's (CUA's) Vitreous State Laboratory (VSL) based on the analyzed compositions of the pretreated AZ-101 waste.

The primary objective for vitrifying the AZ-101 pretreated HLW sludge sample was to validate the use of simulants and characterize the glass produced from the crucible melts for waste acceptance (WASRD and WAPS), regulatory, and de-listing purposes. Testing of the waste glasses produced from actual tank waste will also show compliance with the WTP contractual requirements such as reporting the chemical and radionuclide analyses, the waste loading, and the values of the key glass properties. The scope of this work consists of glass fabrication, chemical analysis, radiochemical analysis, crystalline phase determination, product consistency test (PCT), and dangerous waste limitations—toxicity characteristic leaching procedure (TCLP).

(a) Envelope D waste is the solid material comprising HLW feed.

2.0 Quality Assurance Requirements

2.1 Application of RPP-WTP Quality Assurance Requirements

PNWD implements the River Protection Project Waste Treatment Plant (RPP-WTP) quality requirements by performing work in accordance with the PNWD Waste Treatment Plant Support Project quality assurance project plan (QAPjP) approved by the RPP-WTP Quality Assurance (QA) organization. This work was performed to the quality requirements of NQA-1-1989 Part I, Basic and Supplementary Requirements, NQA-2a-1990, Part 2.7 and DOE/RW-0333P, Rev 13, *Quality Assurance Requirements and Descriptions* (QARD). These quality requirements are implemented through PNWD's *Waste Treatment Plant Support Project (WTPSP) Quality Assurance Requirements and Description Manual.* The analytical requirements are implemented through WTPSP's Statement of Work (WTPSP-SOW-005) with the Radiochemical Processing Laboratory (RPL) Analytical Service Operations (ASO).

A matrix that cross-references the NQA-1, 2a and QARD requirements with PNWD's procedures for this work is given in Table 2.1. It includes justification for those requirements not implemented.

Table 2.1. Applicable WTPSP Quality Assurance Procedures

NQA-1[a]	QARD[b]	Yes	No	Implementing Procedure Title	Justification for Exclusion
BR 1	Section 1	X		WTPSP Manual Section 1.1, Organization QA-RPP-WTP-101, Communication and Commitment (Interface) Control	
1S-1		X		WTPSP Manual Section 1.1, Organization QA-RPP-WTP-1501, Nonconforming Items	
2	Section 2	X		WTPSP Manual Section 2.1, Quality Assurance Program QA-RPP-WTP-205, Quality Assurance Plans QA-RPP-WTP-208, Applying QA Controls (Grading)	
2S-1			X	WTPSP Manual Section 2.1, Quality Assurance Program	This work does not require qualified inspection and test PNWD staff.
2S-2			X	WTPSP Manual Section 2.1, Quality Assurance Program	NDE is not performed; therefore, qualified NDE PNWD staff members are not required.
2S-3		X		WTPSP Manual Section 18.1, Audits QA-RPP-WTP-1801, Internal Audits	
2S-4		X		QA-RPP-WTP-201, Indoctrination and Training	
BR 3	Section 3		X	WTPSP Manual Section 3.1 QA-RPP-WTP-301, Hand Calculations QA-RPP-WTP-302, Design Control	Design activities will not be performed; however, hand calculations may be performed as per procedure QA-RPP-WTP-301.

Table 2.1 (contd)

NQA-1[a]	QARD[b]	Yes	No	Implementing Procedure Title	Justification for Exclusion
3S-1			X	QA-RPP-WTP-301, Hand Calculations QA-RPP-WTP-302, Design Control	Design activities will not be performed; however, hand calculations may be performed as per procedure QA-RPP-WTP-301.
BR 4	Section 4	X		WTPSP Manual Section 4.1 QA-RPP-WTP-401, Purchase Requisitions QA-RPP-WTP-404, Procurement of Internal Quality Affecting Services	
4S-1		X		QA-RPP-WTP-401, Purchase Requisitions QA-RPP-WTP-404, Procurement of Internal Quality Affecting Services	
BR 5	Section 5	X		WTPSP Manual Section 5.1 QA-RPP-WTP-501, Preparation, Review and Approval of QA Implementing Procedures	
BR 6	Section 6	X		WTPSP Manual Section 6.1 QA-RPP-WTP-601, Document Control QA-RPP-WTP-602, Document Change Control	
6S-1		X		QA-RPP-WTP-601, Document Control QA-RPP-WTP-602, Document Change Control	
BR 7	Section 7	X		WTPSP Manual Section 7.1 QA-RPP-WTP-401, Purchase Requisitions QA-RPP-WTP-404, Procurement of Internal Quality Affecting Services	Purchase specifications will be determined in conjunction with the R&T contact.
7S-1		X		QA-RPP-WTP-401, Purchase Requisitions	
BR 8	Section 8, Supple-ment II	X		WTPSP Manual Section 8.1 QA-RPP-WTP-801, Sample Control	
8S-1		X		QA-RPP-WTP-801, Sample Control	
BR 9	Section 9		X	WTPSP Manual Section 9.1 QA-RPP-WTP-902, Control of Special Processes	Work will be controlled in accordance with BR 5 and BR 11.
9S-1			X	QA-RPP-WTP-902, Control of Special Processes	Work will be controlled in accordance with BR 5 and BR 11.

Table 2.1 (contd)

NQA-1[(a)]	QARD[(b)]	Yes	No	Implementing Procedure Title	Justification for Exclusion
BR 10	Section 10		X	N/A	Design inspection will not be performed; however, reports from the testing will be reviewed in accordance with procedure QA-RPP-WTP-604; independent technical review and testing activities will be performed in accordance with procedure QA-RPP-WTP-1101, Scientific Investigation.
10S-1			X	N/A	Design inspection will not be performed; however, reports from the testing will be reviewed in accordance with procedure QA-RPP-WTP-604; independent technical review and testing activities will be performed in accordance with procedure QA-RPP-WTP-1101, Scientific Investigation.
BR 11	Section 11, Supple-ment III	X		WTPSP Manual Section 11.1 QA-RPP-WTP-1101, Scientific Investigation QA-RPP-WTP-604, Independent Technical Review	
11S-1		X		QA-RPP-WTP-1101, Scientific Investigation QA-RPP-WTP-1102, Generating, Reviewing, Approving, and Issuing Test Plans QA-RPP-WTP-1103, Generating, Reviewing, Approving, and Issuing Test Procedures and Instructions QA-RPP-WTP-1104, Report Generation, Review, Approval, and Publication	
11S-2		X		QA-RPP-WTP-1101, Scientific Investigation QA-RPP-WTP-301, Hand Calculations QA-RPP-WTP-SCP, Software Control	
BR 12	Section 12	X		WTPSP Manual Section 12.1 QA-RPP-WTP-1201, Calibration Control System	
12S-1		X		QA-RPP-WTP-1201, Calibration Control System QA-RPP-WTP-1101, Scientific Investigation	
BR 13	Section 13, Supple-ment II	X		WTPSP Manual Section 13.1 QA-RPP-WTP-1301, Handling, Storage, and Shipping	
13S-1		X		QA-RPP-WTP-1301, Handling, Storage, and Shipping	

Table 2.1 (contd)

NQA-1[(a)]	QARD[(b)]	Yes	No	Implementing Procedure Title	Justification for Exclusion
BR 14	Section 14	X		WTPSP Manual Section 14.1 QA-RPP-WTP-1401, Inspection and Test Status and Tagging	
BR 15	Section 15	X		WTPSP Manual Section 15.1 QA-RPP-WTP-1501, Nonconforming Items	
15S-1		X		QA-RPP-WTP-1501, Nonconforming Items	
BR 16	Section 16	X		WTPSP Manual Section 16.1 QA-RPP-WTP-1601, Trend Analysis QA-RPP-WTP-1602, Corrective Action	
BR 17	Section 17, Supple-ment III	X		WTPSP Manual Section 17.1 QA-RPP-WTP-1701, Records System QA-RPP-WTP-1705, Data Entries for Project Records	
17S-1		X		QA-RPP-WTP-1701, Records System QA-RPP-WTP-1705, Data Entries for Project Records	
BR 18	Section 18	X		WTPSP Manual Section 18.1 QA-RPP-WTP-1801, Internal Audits	
18S-1		X		QA-RPP-WTP-1801, Internal Audits	
N/A	Supple-ment IV		X	Not Applicable	Not applicable; WTPSP does not perform field-survey activities.
N/A	Supple-ment V	X		QA-RPP-WTP-SV, Control of the Electronic Management of Information	

NQA-2a, Part 2.7[(c)]	QARD[2]	Yes	No	Implementing Procedure Title	Justification for Exclusion
1.0	Supple-ment I		X	Not Applicable	See Section 4.0, below
2.0			X	Not Applicable	See Section 4.0, below
3.0			X	Not Applicable	See Section 4.0, below
4.0		X		QA-RPP-WTP-SCP, Software Control, Section 6.0, "Computational Computer Programs" QA-RPP-WTP-604, Independent Technical Review	Commercially available software, such as Word, Excel, and SigmaPlot, will be used for data analysis. Unique computer codes will not be generated as part of these testing activities.
5.0			X	Not Applicable	See Section 4.0, above
6.0			X	Not Applicable	See Section 4.0, above
7.0			X	Not Applicable	See Section 4.0, above
8.0			X	Not Applicable	See Section 4.0, above
9.0			X	Not Applicable	See Section 4.0, above
10.0			X	Not Applicable	See Section 4.0, above
11.0			X	Not Applicable	See Section 4.0, above

(a) NQA-1: ASME/NQA-1, 1989, Quality Assurance Program Requirements for Nuclear Facilities, Basic (BR) and Supplement (S) Requirements.
(b) QARD: DOE/RW-0333P, Rev. 13, U.S. Department of Energy-Office of Civilian Radioactive Waste Management (DOE-OCRWM), Quality Assurance Requirements and Description (QARD).
(c) NQA-2a, 1990, Part 2.7, Quality Assurance Requirements of Computer Software for Nuclear Facility Applications.

2.2 Conduct of Experimental and Analytical Work

Experiments that were not method-specific were performed in accordance with PNWD's procedures QA-RPP-WTP-1101 "Scientific Investigations" and QA-RPP-WTP-1201 "Calibration Control System," verifying that sufficient data were taken with properly calibrated measuring and test equipment (M&TE) to obtain quality results.

As specified in Test Specification, 24590-HLW-TSP-RT-02-009, Rev 0, *AZ-101 (Envelope D)HLW Vitrification, Product Testing, and Regulatory Analyses*, BNI's QAPjP, PL-24590-QA00001, Rev 0 is applicable to the TCLP activities since the work might be used in support of environmental/regulatory compliance.

The applicable quality control (QC) parameters for chemical analysis are delineated in Table 3 and 7 in Test Plan TP-RPP-WTP-190, Rev 0, *AZ-101 (Envelope D) HLW Vitrification, Product Testing and Regulatory Analysis.*

The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis of the AZ-101 immobilized high-level waste (IHLW) (glass) was carried out using a KOH, KNO_3-Ni crucible fusion, a Na_2O_2-NaOH-Zr crucible fusion, and acid dissolution. The only QC issue with the analysis using the KOH, KNO_3-Ni crucible fusion was a low recovery for manganese with one of the laboratory control standards. For the Na_2O_2-NaOH-Zr crucible fusion, the only QC issues arose for Ni and P, which consisted of high and low recoveries, respectively, and for Ni, a relative percent difference (RPD) of over 15%. The levels of Mn, Ni, and P oxides in the glass are about 0.04%, 0.04%, and 0.1%, respectively, and well below the 0.5% contract criteria for quantitation. So these results should be considered acceptable.

TCLP Results for AZ-101 Envelope D Glass are completely summarized in Appendix D, and all QC criteria were met.

2.3 Internal Data Verification and Validation

PNWD addresses internal verification and validation activities by conducting an independent technical review of the final data report in accordance with PNWD's procedure QA-RPP-WTP-604. This review verifies that 1) the reported results are traceable, 2) inferences and conclusions are soundly based, and 3) the reported work satisfies the Test Plan objectives. This review procedure is part of PNWD's *WTPSP Quality Assurance Requirements and Description Manual*.

3.0 Objectives

This work addresses RPP-WTP contract requirements to demonstrate the contractor's ability to satisfy the IHLW product requirements (Specification 1 of the RPP-WTP Tank Waste Remediation System Privatization Contract [DOE-ORP 2000]) with samples of HLW. See 24590-HLW-TSP-RT-02-009, Rev. 0, *AZ-101 (Envelope D) HLW Vitrification, Product Testing, and Regulatory Analyses* and TP-RPP-WTP-190, Rev 0, *AZ-101 (Envelope D) HLW Vitrification, Product Testing, and Regulatory Analyses.* All work was performed to the test plan, which was approved by BNI.

The primary objective for vitrifying the AZ-101 (Envelope D) HLW sample (see 24590-HLW-TSP-RT-02-009, Rev. 0, *AZ-101 (Envelope D) HLW Vitrification, Product Testing, and Regulatory Analyses* and TP-RPP-WTP-190, Rev 0, *AZ-101 (Envelope D) HLW Vitrification, Product Testing, and Regulatory Analyses*) was to generate a glass product for subsequent testing to demonstrate the WTP project's ability to satisfy the product requirements concerning:

- chemical and radionuclide reporting
- waste loading
- identification and quantitation of crystalline phases
- waste-form leachability
- land disposal requirements.

4.0 Success Criteria

The primary success criteria are associated with the product requirements as delineated in Specification 1 of the RPP-WTP project contract (U.S. Department of Energy, Office of River Protection , DOE-ORP, 2000). All work was performed to the test plan, which was approved by BNI. (TP-RPP-WTP-190, Rev 0, *AZ-101 (Envelope D) HLW Vitrification, Product Testing, and Regulatory Analyses*).

These success criteria are as follows:

- Identification and quantification of those chemical constituents present at concentrations greater than 0.5 wt%, consistent with the Waste Acceptance Product Specifications for Vitrified High Level Waste Forms (WAPS), DOE/EM-0093, specifications 1.1 and 3.14.
- The radionuclides determined as significant per NUREG/BR-0204 (NRC 1998) and 49 CFR 172.101 Table A.2 in Appendix A are identified and quantified.
- Product loading shall be consistent with the requirements delineated in the RPP-WTP contract, specification 1.2.2.1.6 concerning minimum concentration of certain waste components and meeting leaching limits.
- Identification and quantification of crystalline and non-crystalline phases shall be consistent with WAPS specification 1.1.1.
- The normalized release rates of lithium, sodium, and boron shall satisfy the requirements delineated in WAPS specification 1.3.1.
- Generate evaluation of the glass form against requirements for Land Disposal under the Washington Dangerous Waste Regulations, WAC 173-303, and RCRA LDR in 40CFR268 (TCLP for hazardous inorganics) and underlying hazardous constituents (UHCs).

5.0 Experimental Method

A pretreated AZ-101 HLW sludge sample was prepared as melter feed to match the target AZ-101 HLW glass composition formulated by VSL (Kot and Pegg. 2003). Section (5.1) describes how the glass was formulated based on the VSL target composition and then made from the AZ-101 sludge sample, Cs and Tc eluates, and mineral additives. It also briefly describes compositional and radiochemical analyses of the glass sample, its phase composition (crystalline and amorphous phases present in a slowly cooled glass), and its leaching characteristics measured with the PCT and TCLP techniques. Note that Appendix A provides the details of the calculation of the glass batch formulation which because of circumstances (actual available secondary wastes were less than those originally anticipated) were more complicated than would be expected.

5.1 Glass Formulation

This subsection provides compositions of the HLW sludge sample, the Cs and Tc eluates, and minerals and the proportions in which these materials were blended to produce a melter-feed sample. According to the VSL formulation, the AZ-101 HLW sludge was to be mixed with the eluates in the proportions corresponding to the tank inventories at which the blend is expected to be vitrified in the WTP. Because insufficient amounts of some the eluates were available to achieve the planned blending ratios, the samples were adjusted, and chemicals were added to make the glass as close in composition as possible to that formulated by the VSL.

5.1.1 Blended AZ-101 HLW

In the WTP, the HLW pretreated sludge, ion exchange column eluates, and Sr/TRU ppts from the pretreatment of LAW were blended and then mixed with glass-forming and modifying additives to form a melter feed that was vitrified. The HLW glass batch was formulated to match the desired processing behavior in the melter, to obtain the glass properties required for the repository, and to achieve the highest waste loading compatible with the glass-property constraints and waste-processing uncertainties. Corrective chemical additions were made to adjust to the VSL recipe when less-than-expected secondary wastes were found to be available (see Table 5.1 and Table 5.2).

The available mass of the AZ-101 dry sludge was 66.5 g. The volumes of eluates needed for this amount of HLW are 475 mL of AP-101 Cs eluate, 269 mL of AZ-101 Cs eluate, 290 mL of AP-101 Tc eluate, and 193 mL of AZ-101 Tc eluate. Since these required amounts were not available, the values of the blended volumes were readjusted.

Table 5.3 and Table 5.4 show the chemical and radiochemical compositions of the dry pretreated (i.e., washed, leached, and rinsed) AZ-101 HLW sludge and the eluates. The chemical composition is given in element (dried sludge) and ion concentrations.

The AZ-101 HLW sludge density was 1.08 g/mL, and the content of solids in the sludge was 11.4 mass% (10.0 mass% glass components, i.e., oxides and halogens, and 10.8 mass% undissolved solids). The densities and mass% of solids in the eluates are given in Table 5.5.

Table 5.1. Blending Mass Fractions for the Cs and Tc Eluates

	Tank	AP-101	AZ-101	AP-101	AZ-101
	Eluate	Cs	Cs	Tc	Tc
Total concentration of glass components	g/L	1.980	1.464	1.035	0.745
Required blending mass fraction	g/g(blend)	0.0172	0.0072	0.0055	0.0026
Actual blending mass fraction	g/g(blend)	0.0063	0.0064	0.0014	0.0018

Table 5.2. Composition of (Actual) Blended HLW, Additives, Corrective Chemicals, and AZ-101 HLW Glass (in mass fraction)

Glass Component	Actual Blended AZ-101 HLW	Mineral Additives	Corrective Chemicals	HLW Glass
	Mass Fraction			
Loading Fraction	**W_B = 0.3122**	**W_{gf} = 0.6825**	**W_C = 0.0053**	**W_B+ W_{gf}+ W_C=1**
Ag_2O	0.0012	---	---	0.0004
Al_2O_3	0.2330	---	0.0132	0.0728
B_2O_3	0.0021	0.1538	0.1341	0.1064
BaO	0.0021	---	0.0002	0.0007
BeO	0.0001	---	---	0.0000
Bi_2O_3	0.0002	---	---	0.0001
Br	0.0001	---	0.0031	0.0000
CaO	0.0133	---	0.0161	0.0042
CdO	0.0205	---	0.0008	0.0064
Ce_2O_3	0.0076	---	---	0.0024
Cl	0.0009	---	0.0006	0.0003
CoO	0.0002	---	---	0.0001
Cr_2O_3	0.0044	---	0.0086	0.0014
CuO	0.0009	---	0.0014	0.0003
F	0.0005	---	0.0008	0.0002
Fe_2O_3	0.3571	---	0.0031	0.1115
K_2O	0.0035	---	0.0473	0.0013
La_2O_3	0.0084	---	---	0.0026
Li_2O	0.0003	0.0549	---	0.0376
MgO	0.0032	---	---	0.0010
MnO_2	0.0105	---	---	0.0033
MoO_3	0.0001	---	---	0.0000
Na_2O	0.1003	0.1245	0.5241	0.1191
Nd_2O_3	0.0062	---	---	0.0019
NiO	0.0157	---	0.0011	0.0049
P_2O_5	0.0127	---	0.0001	0.0040
PbO	0.0023	---	0.0022	0.0007
PdO	0.0033	---	---	0.0010
Rh_2O_3	0.0008	---	---	0.0002
Ru_2O_3	0.0024	---	0.0000	0.0008

Table 5.2 (contd)

Glass Component	Actual Blended AZ-101 HLW	Mineral Additives	Corrective Chemicals	HLW Glass I
	Mass Fraction			
Loading Fraction	**W_B = 0.3122**	**W_{gf} = 0.6825**	**W_C = 0.0053**	**$W_B + W_{gf} + W_C = 1$**
SO_3	0.0036	---	0.0110	0.0012
SiO_2	0.0357	0.6374	0.1575	0.4470
SnO	0.0056	---	---	0.0018
SrO	0.0050	---	---	0.0016
TiO_2	0.0004	---	---	0.0001
UO_2	0.0266	---	0.0747	0.0087
Y_2O_3	0.0006	---	---	0.0002
ZnO	0.0004	0.0293	---	0.0201
ZrO_2	0.1084	---	---	0.0338
Sum	1.0000	1.0000	1.0000	1.0000

Table 5.3. Compositions of Pretreated Tank AZ-101 HLW Sample and the Cs and Tc Eluates in Terms of Element Concentrations

Analyte	AZ-101 Envelope D (µg/g dry waste)	AP-101 Cs Eluate (µg/mL)	AZ-101 Cs Eluate (µg/mL)	AP-101 Tc Eluate (µg/mL)	AZ-101 Tc Eluate (µg/mL)
Ag	902	<0.63	<2.6	<0.64	<0.50
Al	99872.5	12	<6.2	13	<1.20
As	---	---	<26	---	<5.0
B	91	49	9.4	79.8	92.7
Ba	1510	0.32	2.5	<0.25	<0.20
Be	26	<0.25	<1	<0.25	<0.20
Bi	150	<2.5	<10	<2.5	<2.0
Ca	7505	32	27	<6.4	<5.0
Cd	14500	1.8	2	<0.38	<0.30
Ce	5240	<5.1	<21	<5.1	<4.0
Co	127.5	<1.3	<5.2	<1.3	<1.0
Cr	2284.5	14.1	33	<0.51	0.51
Cu	583.5	2.8	<2.6	1	<0.50
Dy	---	---	<5.2	---	<1.0
Eu	---	---	<10	---	<2.0
Fe	202384	5.9	6.8	<0.64	<0.50
K	2000	110	<210	<51	43
La	5807.5	<1.3	<5.2	<1.3	<1.0
Li	115	<0.76	<3.1	<0.76	<0.60
Mg	1540	<2.5	<10	<2.5	<2.0
Mn	5364	<1.3	<5.2	<1.3	<1.0
Mo	66.5	<1.3	<5.2	<1.3	<1.0

Table 5.3 (contd)

Analyte	AZ-101 Envelope D (µg/g dry waste)	AP-101 Cs Eluate (µg/mL)	AZ-101 Cs Eluate (µg/mL)	AP-101 Tc Eluate (µg/mL)	AZ-101 Tc Eluate (µg/mL)
Na	54545	844	803	282	219
Nd	4290	<2.5	<10	<2.5	<2.0
Ni	9992	1.9	<3.1	1.1	<0.60
P	4505	<2.5	<10	<2.5	<2.0
Pb	1727.5	6.1	<10	<2.5	<2.0
Se	---	---	<26	---	<5.0
Si	13055	100	<52	169	19
Sn	3600	<38	<150	<38	<10.0
Sr	3411.5	<0.38	<1.6	<0.38	<0.30
Te	---	---	<150	---	<10.0
Th	---	---	<100	---	<20.0
Ti	177.5	<0.63	<2.6	<0.64	<0.50
Tl	---	---	<52	---	<10.0
U	18500	200	<210	<51	<40.0
V	---	---	<5.2	---	<1.0
W	---	---	<52	---	<10.0
Y	385	<1.3	<5.2	<1.3	<1.0
Zn	277.5	<1.3	<10	<1.3	<1.0
Zr	65050	<1.3	<5.2	<1.3	<1.0
F^-	390	<63	<13	2.7	2
Cl^-	703	<63	180	2.2	0.57
Br^-	<170	<63	<130	<0.7	44.3
NO_2^-	7268	<125	<26	31	0.34
NO_3^-	2178	29250	31,000	102	42.6
PO_4^{2-}	<340	<125	<26	<1.4	1.4
SO_4^{2-}	2410	<125	300	5.1	12.7
$C_2O_4^-$	518	<125	170	<1.4	0.89

Table 5.4. Radiochemical Composition of AZ-101 HLW (in µCi/g dry solids) and AP-101 and AZ-101 ^{137}Cs and ^{99}Tc Eluates (in µCi/mL)

Isotope	AZ-101 Pretreated HLW	AP-101 Cs Eluate	AP-101 Tc Eluate	AZ-101 Cs Eluate
	µCi/g dry solids	µCi/mL		
^{54}Mn	na	<0.02	na	na
^{60}Co	8.43	$<5\times10^{-3}$	$<3\times10^{-5}$	<0.07
^{63}Ni	na	8.88×10^{-4}	$<3\times10^{-5}$	na
^{79}Se	na	3.52×10^{-6}	$<3.58\times10^{-7}$	$<2.2\times10^{-4}$
^{90}Sr	6.1×10^{4}	0.0295	$<1.26\times10^{-4}$	3.3
^{95}Nb	<0.3	<0.02	na	<0.2
^{99}Tc[(a)]	2.53	na	0.416	na

Table 5.4 (contd)

Isotope	AZ-101 Pretreated HLW	AP-101 Cs Eluate	AP-101 Tc Eluate	AZ-101 Cs Eluate
^{106}Ru	<3.0	<0.7	$<3\times10^{-3}$	<9
^{113}Sn	<0.7	<0.2	$<3\times10^{-4}$	<3
^{134}Cs	<0.3	0.156	$<3\times10^{-4}$	4.39
^{137}Cs	641	765	$<2\times10^{-4}$	1.30×10^{4}
^{125}Sb	38.6	<0.4	$<7\times10^{-4}$	<6
$^{126}Sn^{(b)}$	<0.6	0.269	4.15×10^{-3}	<3
$^{126}Sn^{(a)}$	0.21	na	na	na
$^{129}I^{(a)}$	<0.0668	na	na	na
^{144}Ce	<5.0	<0.6	$<2\times10^{-3}$	<8
^{151}Sm	900	2.24×10^{-4}	2.38×10^{-5}	na
^{152}Eu	1.58	<0.01	$<2\times10^{-4}$	<0.3
^{154}Eu	101.2	<0.03	$<7\times10^{-5}$	<0.2
^{155}Eu	119.5	<0.3	$<9\times10^{-4}$	<4
^{232}Th	<1.0	<0.2	$<4\times10^{-4}$	<3
$^{241}Am^{(b)}$	197.5	3.05×10^{-5}	7.22×10^{-7}	2.30×10^{-4}
$^{241}Am^{(c)}$	165	na	na	na
^{242}Cm	0.298	$<2\times10^{-7}$	$<4\times10^{-8}$	$<3\times10^{-6}$
$^{243}Cm+^{244}Cm$	0.298	7.3×10^{-6}	$<4\times10^{-8}$	2.00×10^{-5}
$U^{(d)}$	1.21×10^{4}	206	6.79×10^{-3}	160
$^{233}U^{(a)}$	0.47	na	na	na
^{236}Pu	<0.2	$<2\times10^{-7}$	$<4\times10^{-8}$	$<9\times10^{-6}$
^{238}Pu	1.1	6.07×10^{-5}	$<6\times10^{-8}$	8.30×10^{-4}
$^{239}Pu+^{240}Pu$	9.58	4.68×10^{-4}	1.62×10^{-7}	7.90×10^{-3}
$^{239}Pu^{(a)}$	129	na	na	na
$^{240}Pu^{(a)}$	9.87	na	na	na
^{241}Pu	47.1	3.1×10^{-3}	$<1\times10^{-5}$	na
$^{242}Pu^{(a)}$	0.112	na	na	na
$^{237}Np^{(a)}$	192	na	na	na
Gross β	na	na	na	1.40×10^{4}
Gross α	187.5	9.13×10^{-4}	$<2\times10^{-6}$	7.20×10^{-3}
Sum of α	176	5.61×10^{-4}	8.84×10^{-7}	9.00×10^{-3}

(a) ICP-MS value in µCi/g
(b) GEA value
(c) AEA value
(d) ICP-MS value in µg/mL
na = not available

Table 5.5. Density (in g/mL) and Solid Content (in mass%) in AZ-101 and AP-101 Eluates

	units	AP-101 Cs	AP-101 Tc	AZ-101 Tc	AZ-101 Cs
Density	g/mL	1.017 (±0.005)	0.996 (±0.005)	0.998	1.012
Solid content	mass%	0.34 (±0.02)	0.06 (±0.02)	0.1[(a)]	0.48 (±0.05)
Glass components	mass%	0.4 (±0.2)	0.3 (±0.2)		0.19 (±0.07)
(a) Estimated value.					

5.1.2 HLW Glass Composition

To make glass, the HLW blend (Table 5.1 and Table 5.6) is mixed with glass-forming and modifying additives as summarized in Table 5.2.

Table 5.6. Compositions of Pretreated Tank AZ-101 HLW Sample, the Cs and Tc Eluates, and the Actual Blended HLW[(a)]

	AZ-101 Envelope D (g/kg)[(b)]	AP-101 Cs Eluate (g/ kg)	AZ-101 Cs Eluate (g/ kg)	AP-101 Tc Eluate (g/ kg)	AZ-101 Tc Eluate (g/ kg)	Blended AZ-101 (g/ kg)
Component mass fraction	0.9841	0.0063	0.0064	0.0014	0.0018	1.0000
Eluate volume (L/ kg)[(c)]	---	3.182	4.372	1.353	2.416	---
Ag_2O	1.21	---	---	---	---	1.20
Al_2O_3	236.61	11.45	---	23.74	---	232.96
B_2O_3	0.37	79.68	20.68	248.30	400.47	2.06
BaO	2.11	0.18	1.91	---	---	2.09
BeO	0.09	---	---	---	---	0.09
Bi_2O_3	0.21	---	---	---	---	0.21
Br	---	---	---	---	59.43	0.10
CaO	13.17	22.61	25.81	---	---	13.26
CdO	20.77	1.04	1.56	---	---	20.45
Ce_2O_3	7.70	---	---	---	---	7.57
Cl	0.88	---	---	2.13	0.76	0.87
CoO	0.20	---	---	---	---	0.20
Cr_2O_3	4.19	10.41	32.96	---	1.00	4.40
CuO	0.92	1.77	---	1.21	---	0.91
F	0.49	---	---	2.61	2.68	0.49
Fe_2O_3	362.77	4.26	6.64	---	---	357.08
K_2O	3.02	66.92	---	---	69.49	3.52
La_2O_3	8.54	---	---	---	---	8.40
Li_2O	0.31	---	---	---	--	0.31
MgO	3.20	---	---	---	---	3.15
MnO_2	10.64	---	---	---	---	10.47
MoO_3	0.10	---	---	---	---	0.10
Na_2O	92.19	574.55	739.60	367.30	396.04	100.29

Table 5.6 (contd)

	AZ-101 Envelope D (g/kg)	AP-101 Cs Eluate (g/kg)	AZ-101 Cs Eluate (g/kg)	AP-101 Tc Eluate (g/kg)	AZ-101 Tc Eluate (g/kg)	Blended AZ-101 (g/kg)
Nd_2O_3	6.27	---	---	---	---	6.17
NiO	15.95	1.22	---	1.35	---	15.70
P_2O_5	12.94	---	---	---	1.40	12.74
PbO	2.33	3.32	---	---	---	2.32
PdO	3.32	---	---	---	---	3.26
Rh_2O_3	0.79	---	---	---	---	0.78
Ru_2O_3	2.48	---	---	---	---	2.44
SO_3	2.52	---	170.84	4.11	14.20	3.60
SiO_2	35.01	108.01	---	349.26	54.52	35.73
SnO_2	5.73	---	---	---	---	5.64
SrO	5.06	---	---	---	---	4.98
TiO_2	0.37	---	---	---	---	0.37
UO_2	26.31	114.58	---	---	---	26.62
Y_2O_3	0.61	---	---	---	---	0.60
ZnO	0.43	---	---	---	---	0.43
ZrO_2	110.17	---	---	---	---	108.42

(a) The VSL spreadsheet reported oxides of Mn, Sn, Ru, and U as MnO_2, SnO, Ru_2O_3, and UO_2. This convention is followed in this table. The final content of Mn, Sn, Ru, and U is represented in terms of MnO, SnO_2, RuO_2, and UO_3.

(b) (g/kg)—grams of oxide per kilogram of oxide

(c) (L/kg)—liters of eluate per kg of waste oxides

The mass of glass to be made from 66.5 g AZ-101 dry sludge, which is 79.76 wt% oxides and contains 98.41 wt% of the oxides in the blended waste, is 173 grams. This is calculated as follows: $66.5/(0.3122 \times 0.9841) = 173$, where 0.3122 is the weight fraction of waste oxides from the blended waste from Table 5.2, and 0.9841 is the mass fraction of waste oxides from the waste sludge in the blended waste.

5.1.3 HLW Feed Composition

To make glass, glass-forming and modifying additives and corrective chemicals were mixed together. Table 5.7 lists batch chemicals that were used for 173 g glass. The following minor components were deleted for the corrective chemicals listed in Table 5.2: BaO, Br, CdO, Cl, CuO, F, Fe_2O_3, NiO, P_2O_5, PbO, and SO_3. Although Al_2O_3 was not deleted from the list of additives, it is not included in Table 5.7 because, as Table 5.8 shows, there is more Al_2O_3 in the silica sand as an impurity than the amount of Al_2O_3 from missing eluates. The values listed in Table 5.8 are based on chemical analyses for the material providing the glass-forming and modifying components ($Na_2B_4O_7 \cdot 10H_2O$, Li_2CO_3, Na_2CO_3, SiO_2, and ZnO). For other additions ($CaCO_3$, Cr_2O_3, K_2CO_3, and U_3O_8), the data are based on stoichiometry and corrected for manufacturer-certified composition and measured humidity.

Table 5.7. Chemical Additives for 173 g Glass

Chemical	Mass, g
$Na_2B_4O_7 \cdot 10H_2O$	48.4598
$CaCO_3$	0.0126
Cr_2O_3	0.0063
K_2CO_2	0.0596
Li_2CO_3	16.0759
Na_2CO_3	11.9073
SiO_2	75.1787
U_3O_8	0.0671
ZnO	3.4432
Total	155.2107

Table 5.8. Mass Fractions of Glass Component Oxides in the Batch Chemicals Listed in Table 5.9. Note that species such as water or carbonate are not included because they do not contribute to the final glass composition.

	Borax	Calcium Carbonate	Chromium Oxide	Potassium Carbonate	Lithium Carbonate	Sodium Carbonate	Silica	Uranium Oxide	Zinc Oxide
	Mass fraction of the listed oxides in each batch chemical								
Al_2O_3	---	---	---	---	---	---	0.0014	---	---
B_2O_3	0.3750	---	---	---	---	---	---	---	---
CaO	---	0.5582	---	---	---	---	0.0001	---	---
CdO	---	---	---	---	---	---	---	---	0.0001
Cl	---	---	---	---	0.0001	0.0002	---	---	---
Cr_2O_3	---	---	1.0000	---	---	---	---	---	---
Fe_2O_3	---	---	---	---	0.0004	---	0.0002	---	---
K_2O	---	---	---	0.676	---	---	---	---	---
Li_2O	---	---	---	---	0.4012	---	---	---	---
MgO	---	---	---	---	0.0010	---	0.0001	---	---
Na_2O	0.1670	---	---	---	---	0.5839	---	---	---
NiO	---	---	---	---	---	---	---	---	---
PbO	---	---	---	---	---	---	---	---	---
SiO_2	---	---	---	---	---	---	0.9970	---	---
TiO_2	---	---	---	---	---	---	0.0001	---	---
U_3O_8	---	---	---	---	---	---	---	1.0000	---
ZnO	---	---	---	---	---	---	---	---	0.9990

5.2 Glass Fabrication

The pretreated high-level waste sludge was processed and vitrified in the RPL in the High Level Radioactive Facility (HLRF) (see Figure 5.1 and Figure 5.2). The pretreated high-level waste sludge and secondary wastes described in the previous sections were mixed with glass-forming chemicals, which are listed in Table 5.7. Table 5.8 gives the oxide content of each of these chemicals, which is needed to properly calculate the amount of each chemical added to the glass batch to give the target glass

composition. The WTP will use commercially available chemicals. Table 5.9 lists such chemicals that were used in producing waste glass evaluated in this report. See Appendix A for the calculations using the data in Table 5.8 to determine the amounts of batch chemicals given in Table 5.7.

Table 5.9. AZ-101 Mineral and Chemical Glass-Former Additives

Mineral	Grade	Company	Telephone No.
10-M Borax	Technical	U.S. Borax Valencia, CA 91355-1847	805-287-5400 www.borax.com
Calcium carbonate[(a)]	Reagent	Fisher 99.1% pure Lot# 005661	na
Chromium oxide[(a)]	Reagent	Fisher Lot# 007112	na
Potassium carbonate[(a)]	Reagent	Fisher Lot# 851377	na
Sodium carbonate	Dense Soda Ash Anhydrous	Solvay Minerals Houston, TX	713-525-6800 FAX: 713-525-7805 www.solvayminerals.com
Lithium carbonate	Technical	Chemettal-Foote Kings Mt, NC	704-734-2501, 704-734-2670 www.chemetal lithium.com
Silica	SIL-CO-SIL-75	U.S. Silica, Mill Creek OK 74856-0036	800-243-7500, 304-258-2500 FAX: 304-258-8295 www.u-s-silica.com
Uranium oxide[(b)]	~50 mesh\99% pure	Cerac Milwaukee, WI 53201	414-289-9800 FAX: 414-289-9805
ZnO	Kadox 920	Zinc Corp Amer. Monaca, PA	800-962-7500, 724-774-1020 horseheadinc.com

(a) Used as corrective chemicals, see Table 5.2.
(b) U_3O_8 was used as a substitute for Sr/TRU precipitate.

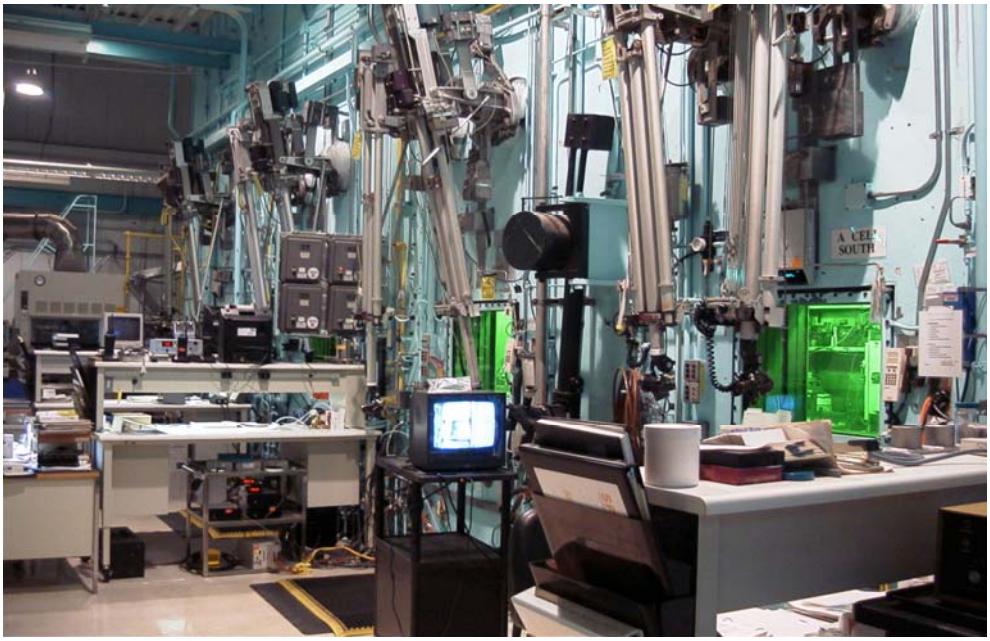

Figure 5.1. View of the HLRF Gallery (the front face of the hot cells)

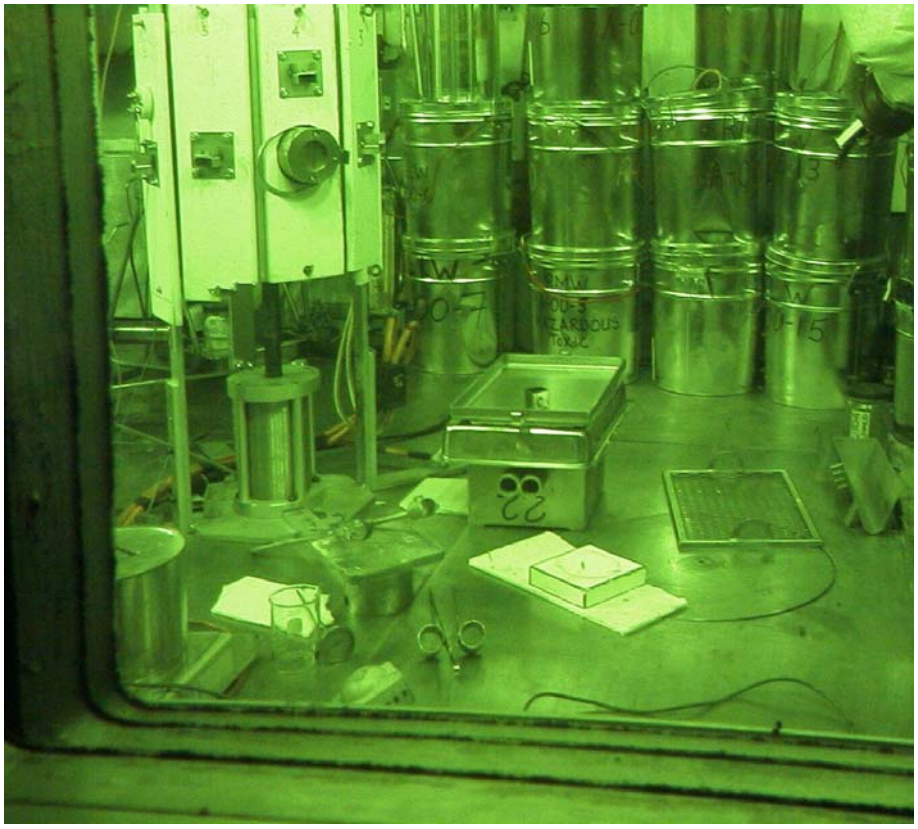

Figure 5.2. View Through "A-South" Hot-Cell Window
(the high-temperature furnace is on the left)

The pretreated sludge was emptied into a 2-L stainless steel vessel, stirred vigorously for 25 minutes with a magnetic stir bar on a stir plate, and heated to reduce its volume. The AP-101 and AZ-101 Cs and Tc eluates were added to the boiling sludge, while heating and stirring continued for 3 hours. The amounts of eluates added are listed in Table 5.1. The blended HLW was stirred and heated for additional 60 minutes. The mineral additives (borax, lithium carbonate, sodium carbonate, silica, and zinc oxide), corrective chemicals (calcium carbonate, chromium oxide, and potassium carbonate), and uranium oxide were premixed in an agate milling chamber for 4 minutes (see Table 5.8 and Table 5.9 for the composition and sources of the minerals and corrective additions). The premixed additives were then added to the blended HLW in the amounts shown in Table 5.7.

The resulting melter feed slurry was heated and stirred for 155 minutes on a hot plate to evaporate water. To prevent segregation, the slurry was vigorously mixed with a magnetic stirrer for 95 minutes and then manually with a stainless steel spatula. The thickened slurry (Figure 5.3) was transferred to a 200-mL Pt10%Rh crucible and placed in an oven preheated at 200°C. Drying continued for 127 minutes while the temperature was gradually increased to 300°C. The crucible was then placed into a furnace at 600ºC and calcined for 1 hour.

The calcined feed was ground in an automated alumina grinder (see Figure 5.4) for 10 minutes and passed through a 40-mesh sieve. Particles that did not pass through the sieve (>425 μm) were ground for 10 minutes and the final residue for 5 minutes until all calcined feed passed through the sieve.

The calcine was added back into the Pt10%Rh crucible and melted in a high-temperature furnace[(a)] at 1150°C for 147 minutes (with a lid after 32 minutes when the gas-evolving reactions were complete); see Figure 5.5. The melt was then poured onto a stainless steel plate (Figure 5.6 and Figure 5.7). All glass was handled in a manner to keep it free of organic contamination and stored in a cleaned stainless steel container. The amount of glass made was 162.95 g. Of this amount, 0.40 g remained attached to crucible walls (Figure 5.8); the rest of the glass (162.55 g) was usable. The 10-g difference between the calculated and actually prepared glass (see Section 5.1.3 and Table 5.7) is due to process losses, e.g., the transfer of dry feed form stainless steel beaker to platinum crucible, feed removal from stirring tools, grinding, and sieving the calcine.

(a) Del Tech high-temperature bottom-loading furnace equipped with a Eurotherm programmer/controller and the temperature monitored with a calibrated Type R thermocouple and an Omega, Model 660 thermocouple readout.

Figure 5.3. Dried Melter Feed in Platinum Crucible

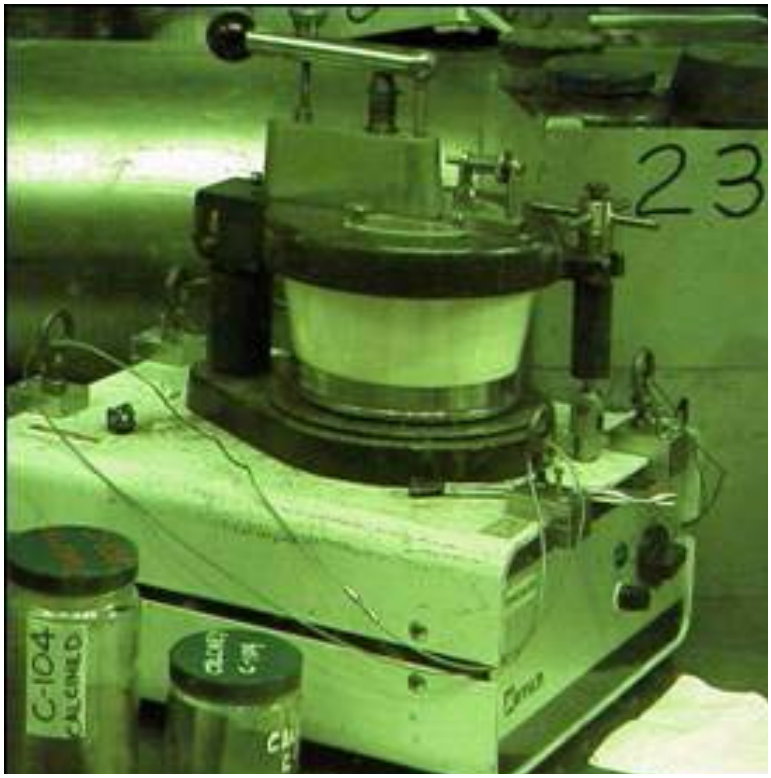

Figure 5.4. The Automated Grinder with a Sintered-Alumina Mortar and Pestle

Figure 5.5. Inspecting Melt after 2 Hours at 1150°C

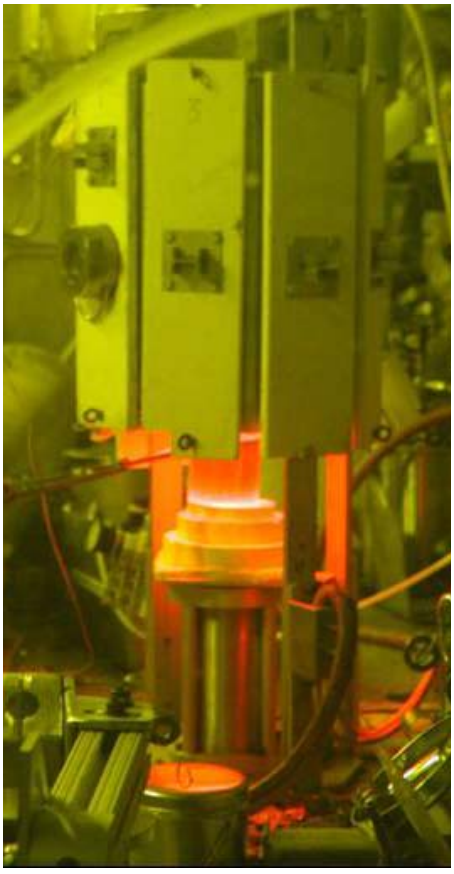

Figure 5.6. Removing Pt Crucible with AZ-101 HLW Glass Melt from the Furnace

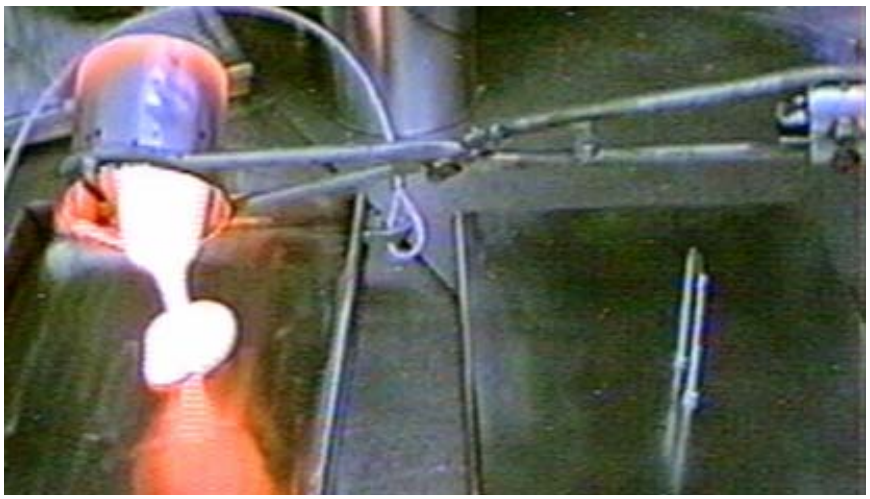

Figure 5.7. Pouring AZ-101 HLW Glass onto Stainless Steel Plate

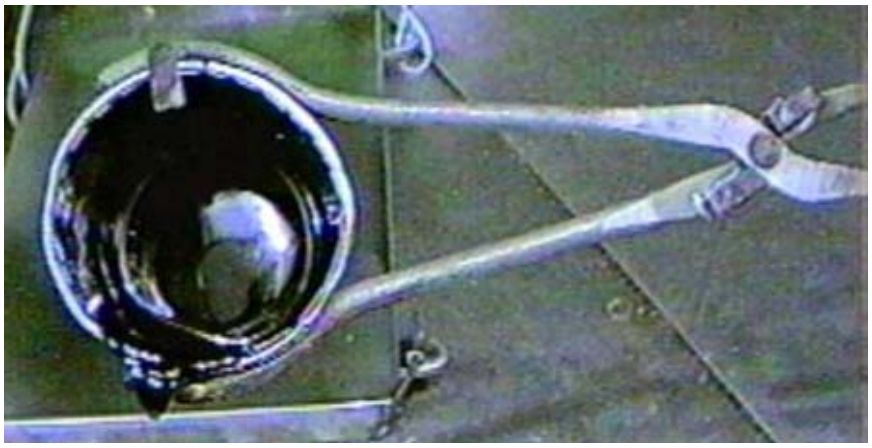

Figure 5.8. Remaining AZ-101 HLW Glass in Platinum Crucible after Pouring. Most of the glass remaining in the crucible (all but 0.4 grams) was removed by causing it to break free by flexing the crucible walls.

5.3 Chemical Analysis

The chemical composition of the AZ-101 HLW glass was measured in duplicate along with an analytical reference glass (ARG-1) reference standard glass (Smith 1993) and low-activity test reference material (LRM) reference standard glass (Ebert and Wolf 1999). Compositions of the standard reference glasses are listed in Table 5.10. The glass was analyzed using a Na_2O_2-NaOH fusion in a Zr crucible according to procedure PNL-ALO-114, a KOH-KNO_3 fusion in a Ni crucible according to procedure PNL-ALO-115, and acid digestion according to PNL-ALO-138. Cation analysis was performed with ICP-AES. A portion of the Na_2O_2-NaOH fusion samples was submitted for radiochemical analysis and inductively coupled plasma-mass spectrometry (ICP-MS) analysis. Corrections to the waste-glass analysis based on standard glass analyses and blanks were performed in six steps as outlined by Weier and Piepel (2002):

1) analyte screening, 2) blank correction, 3) nondetect replacement, 4) relative standard deviation computation, 5) bias correction, and 6) normalization.

The powdered glass sample was prepared for analysis by ICP-AES in the Shielded Analytical Laboratory (SAL). Fusions procedures were done with ~0.10-g sample, and acid digestion was done with a 0.2-g sample. The crucible content was then diluted to a final volume of 100 mL. Prior to analysis by ICP-AES by the ASO, a five-fold serial dilution was conducted on the sample prepared by the fusion processes, and differences in concentration were listed for analytes that had a concentration at or above the estimated quantitation level in the diluted sample. The ICP-AES results were adjusted for all laboratory processing factors and instrument dilutions.

Table 5.10. Compositions (in mg element/g glass) and Standard Deviations of Standard Reference Glasses (Smith 1993; Ebert and Wolf 1999)

	ARG-1		LRM	
	Mean	**Std**	**Mean**	**Std**
	mg element/g glass			
Al	25.03	0.116	50.33	0.630
B	26.93	0.124	24.38	0.453
Ba	0.79	0.009	0.01	0.009
Ca	10.22	0.064	3.86	0.021
Cd	0.00	0.000	1.40	0.026
Cr	0.64	0.007	1.30	0.034
Cu	0.03	0.001	0.00	0.000
Fe	97.92	0.511	9.65	0.294
K	22.50	0.133	12.29	0.066
La	0.00	0.000	0.17	0.004
Li	14.91	0.070	0.51	0.019
Mg	5.19	0.030	0.60	0.024
Mn	14.60	0.076	0.62	0.031
Na	85.31	0.171	148.59	1.847
Ni	8.25	0.047	1.49	0.102
P	0.96	0.048	2.36	0.786
Pb	0.00	0.000	0.93	0.074
Si	223.90	0.734	253.35	3.515
Sr	0.03	0.008	0.00	0.000
Ti	6.89	0.042	0.60	0.024
Zn	0.16	0.129	0.00	0.000
Zr	0.96	0.037	6.88	0.030

QC measurements were required by the controlling QA plan. For fusion processes, two process blanks, two laboratory control samples, and a duplicate were prepared with the samples. For the digestion procedure, a process blank, matrix spike, laboratory-control samples, and duplicate were prepared with the sample. The laboratory-control samples for fusion were prepared using approximately 0.1 g of LRM and ARG-1 reference glasses and for acid digestion with 0.2 g of LRM and ARG-1 reference glasses. Recovery values were listed for all analytes included in the spike that were measured at or above the estimated quantitation level. A matrix spike was prepared using the acid-digestion sample. Duplicate RPDs (relative percent difference) were listed for all analytes that were measured at or above the estimated quantitation level. Analytical spikes were conducted on the sample. Recovery values for analytical and matrix spikes were listed for analytes with measured concentrations above the estimated quantitation level and $\geq$ 25% of that in the sample. Five-fold serial dilution was conducted on the sample for fusion processes, and differences in concentration were listed for analytes that had a concentration at or above the estimated quantitation level in the diluted sample. See Appendix C for more details.

5.4 Radiochemical Composition

The radiochemical composition was obtained with γ energy spectrometry (GEA), α spectrometry, and liquid scintillation counting on a sample of AZ-101 HLW glass solubilized with a NaO_2-NaOH fusion.

For GEA, duplicate samples and blanks were directly aliquoted from the fusion solutions according to procedure RPG-CMC-450. Daily control counts and weekly background checks were measured for each γ detector to ensure the detector performance. The samples were counted for extended counting times, as directed by the analytical service request (ASR), to obtain lower detection limits for isotopes of interest. Detection limits were calculated for all isotopes of interest, i.e., ^{60}Co, ^{95}Nb, ^{113}Sn, ^{125}Sb, ^{126}Sn/Sb, ^{134}Cs, ^{137}Cs, ^{152}Eu, ^{154}Eu, ^{155}Eu, ^{232}Th, and ^{241}Am.

For ^{90}Sr activity, Sr was chemically separated from duplicate samples from the hot cell and a laboratory duplicate according to procedure PNL-ALO-476. The ^{90}Sr activities were measured with an LB4100 gas proportional counter following procedure RPG-CMC-408. A ^{85}Sr tracer was added to each sample to determine the chemical yield by γ counting following procedure RPG-CMC-450.

To obtain ^{63}Ni activity, Ni was chemically separated from the sample according to procedure RPG-CMC-4018, and the ^{63}Ni activity was then measured with liquid scintillation counting on a Packard 2550 following procedure RPG-CMC-474.

Pu and Am/Cm were separated sequentially following procedure PNNL-ALO-417, precipitation plated for counting following procedure PNL-ALO-496, and counted with α spectrometry by procedure RPG-CMC-422. A ^{242}Pu tracer was used to determine the Pu yields. For Am/Cm, an ^{243}Am tracer was used to determine the Am/Cm yields.

The activity of ^{151}Sm was measured in an Am-Cm α-counting mount by liquid scintillation counting by procedure RPG-CMC-474. Because ^{90}Y, the ^{90}Sr daughter, is chemically separated with the Am-Cm fraction, several weeks of decay were required to avoid interference with β counting.

For ICP-MS, AZ-101-HLW glass was prepared with four different preparation methods: PNL-ALO-114 (Na_2O_2-NaOH fusion), PNL-ALO-114 I (iodine option), PNL-ALO-115 (KOH-KNO_3 fusion), and PNL-ALO-138 (acid digestion). The prepared samples and batch QC samples were submitted for analysis by ICP-MS. The final results were corrected for laboratory preparation and for dilutions performed during analyses. Results were reported in terms of concentrations (mg/L) in the samples received and in terms of mass fractions in glass (mg/kg glass). The process blanks and blank spikes were reported only in mg/L. The process blank results were multiplied by the sample dilution factor.

The concentrations of the Pu isotopes were determined with a ^{239}Pu calibration standard. Since minor Pu isotope standards were not available, the QC checks for ^{239}Pu were taken to represent the QC check for the other Pu isotopes. The isotope concentrations of the U isotopes were determined with ^{238}U from a natural U calibration standard. Because minor U isotope standards were not available, the QC checks for ^{238}U were taken to represent the other U isotopes.

The instrument detection limit (IDL) was determined with seven standard blank solutions, which were evaluated at the beginning of the analytical run. The method detection limit (MDL) was determined with three standard blank solutions, which were evaluated throughout the analytical run.

The primary success objectives include reporting 1) the inventory of radionuclides with half-lives >10 years that are or will be present in concentrations >0.05% of the total radioactive inventory for the HLW glass as indexed to the years 2015 and 3115, 2) the total and fissile U and Pu content of a canister,

3) the concentration of Pu for a canister, and 4) the mass fractions of Pu and U isotopes in the total element. The Hanford HLW canisters are 4.5 m high and 0.61 m in diameter and will contain approximately 1.18 m^3 of glass.

The radioactive decay was calculated using the standard decay equation:

$$N = N_0 e^{-\lambda t} \tag{5.1}$$

where N_0 is the number of radioactive atoms at the present time, N is the number of radioactive atoms after a specific elapsed time t, and λ is the decay constant. Since $\lambda = 0.693/t_{1/2}$, where $t_{1/2}$ is the half-life of the radioactive isotope, Equation (5.1) can be written in the form

$$N / N_0 = e^{-0.683 t / t_{1/2}} \tag{5.2}$$

Radioactivity is defined as $A = -dN/dt$. Hence, $A = \lambda N = A_0 \exp(-\lambda t)$, where $A_0 = \lambda N_0$. Table 5.11 lists the $t_{1/2}$ values of the main isotopes and their remaining fractions in years 2015 and 3115.

Table 5.11. Radioisotopes with Half-Lives Longer than 10 Years, the N/N_0 Values at t = 11 (2015) and 1111 (3115) Years, and the Principle Daughter Products

	Half-life (years)	2015[(a)] mCi/kg	3115[(a)] mCi/kg	Significant Daughter Radioisotopes	Half-life (years) Daughters
^{90}Sr	28.5	7.7E-01	2.7E-12	Short lived	na
^{99}Tc	213000	1.0E+00	1.0E+00	na	na
^{137}Cs	30	7.8E-01	1.0E-11	Short lived	na
^{151}Sm	90	9.2E-01	2.2E-04	na	na
^{233}U	159220	1.0E+00	1.0E+00	^{229}Th	7.3 E3
^{234}U	245460	1.0E+00	1.0E+00	^{230}Th	7.7E4
^{235}U	7.037E+08	1.0E+00	1.0E+00	Short lived	na
^{236}U	2.3423E+07	1.0E+00	1.0E+00	^{232}Th	1.4E10
^{238}U	4.4685E+09	1.0E+00	1.0E+00	Short lived	na
^{237}Np	2140000	1.0E+00	1.0E+00	^{233}Pa → ^{233}U	27d, 1.59E5
^{238}Pu	87.7	9.2E-01	1.7E-04	^{234}U	2.45E5
^{239}Pu	24110	1.0E+00	9.7E-01	^{235}U	7.04E8
^{240}Pu	6560	1.0E+00	8.9E-01	^{236}U	2.34E7
^{241}Pu	14.4	5.9E-01	1.3E-23	^{237}U → ^{237}Np	6.75d, 2.14E6
^{242}Pu	376000	1.0E+00	1.0E+00	^{238}U	4.47E9
^{241}Am	432.7	9.8E-01	1.7E-01	^{237}Np	2.14E6
^{242}Am	141	9.5E-01	4.6E-03	^{242}Cm → ^{238}Pu → ^{234}U	163d, 87.7y, 2.45E5
^{243}Cm	28.5	7.7E-01	2.7E-12	^{239}Pu	2.41E4

(a) Based on 2004 values.

In-growth of daughter products will be considered in computing inventory totals in Section 6.2 because, as is indicated in Table 5.11, most of the radioisotopes have daughters that are also radioisotopes and therefore must be considered in any inventory for future years. The specific inventory requirements are as follows: "The Producer shall report the inventory of radionuclides (in Curies) that have half-lives

longer than 10 years and that are, or will be, present in concentrations greater than 0.05 percent of the total radioactive inventory for each waste type, indexed to the years 2015 and 3115." Note that the inventory is in terms of activity (Curies) not mass.

5.5 Crystalline Phases

Crystalline phases were identified and measured with X-ray diffraction (XRD) and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) on a 20.01-g AZ-101 HLW glass sample that had been heat treated in a 25×25×25-mm Pt10%Rh box according to the canister centerline cooling (CCC) curve approximated by a series of linear time-temperature segments (Table 5.12). Figure 5.9 compares the targeted cooling curve with the thermocouple reading.

Using a low-speed diamond wafering saw, a triangular prism was cut from the glass monolith perpendicular to the melt surface, leaving an 18.27-g piece of the CCC-treated glass for the PCT. A thin ~1×3-mm sliver of glass was potted in epoxy and polished from the prism for SEM (VG Elemental Shielded PQ2 with EDS). For XRD (Scintag X-ray diffractometer, Model PAD V, employing Cu K∀ radiation), ~20 mg of the CCC glass was crushed, mixed with 3 mg of powdered corundum as an internal standard, blended in the mortar and pestle, and mixed into a collodion solution. The 2-θ scan ranged from 10° to 70°. The scan proceeded at 0.04° steps with a 5-second dwell for the CCC sample and at 0.02° steps with a 20-second dwell for the quenched sample. The method used follows that described in Elements of X-Ray Diffraction, 2nd edition (Cullity, 1978), using Riqas version 4 software.

Table 5.12. CCC Approximated as a Series of Linear Segments[(a)]

Segment Number	Segment End Time (min)	Segment Start Temperature °C	Cooling Rate (°C/min)
1	45	1050	-1.556
2	107	980	-0.806
3	200	930	-0.591
4	329	875	-0.388
5	527	825	-0.253
6	707	775	-0.278
7	1776	725	-0.304

(a) L. Petkus. "Canister Centerline Cooling Data." letter to C. Musick, CCN 071762, RPP/WTP (2003).

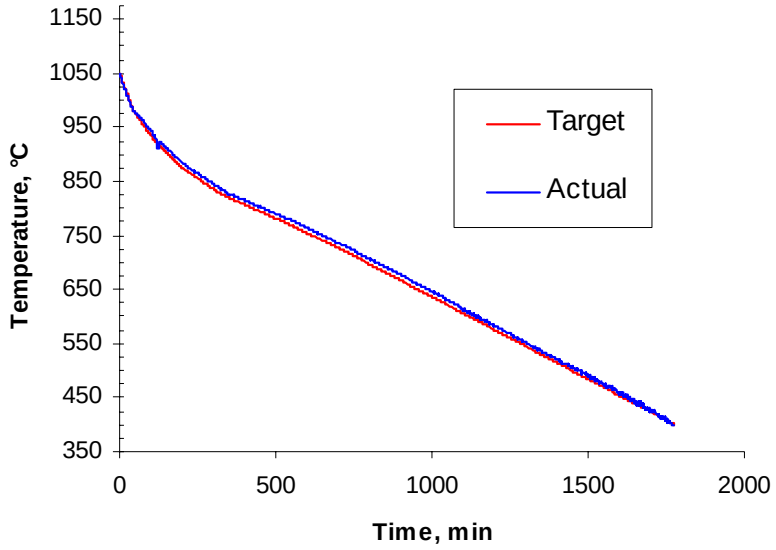

Figure 5.9. CCC Curve. Note that the actual temperature profile almost exactly overlays the target profile.

The main crystalline phase expected in the AZ-101 HLW glass was spinel. Expected spinel components in HLW glass are oxides of Cr, Fe, Mn, Ni, and Zn. Therefore, spinel in HLW glass is a solid solution of a number of simple spinels, such as magnetite, trevorite, nichromite, chromite, franklinite, jakobsite, and zincochromite (see Table 5.13).

5.6 Product Consistency Test

The 18.27-g piece of the CCC glass was used for the 7-day PCT at 90°C following the ASTM procedure C 1285-97. The environmental assessment (EA) standard reference glass (Jantzen et al. 1993) and blanks were tested simultaneously. The glass was ground in an automated alumina grinding chamber and then sieved through -100 to +200 mesh stainless steel sieves to obtain the grain size fraction of 75 μm to 150 μm. The glass particles were cleaned by washing in deionized water (DIW) and ethanol using an ultrasonic cleaner, and dried in an oven at 90°C. Then 1.5 g of the cleaned glass particles was placed into a 22-mL desensitized Type 304L stainless steel container (see Figure 5.10). The initial and final pH values of the solution were taken with an Orion Research Ion Analyzer, Model 720. The pH meters were calibrated with Fisher buffer solutions of pH = 4.00, and 7.00 before use and Oakton buffer solutions 7.00 and 10.00 after use. Aliquots of the solution were filtered through a 0.45-μm filter, acidified with 1 vol% of HNO_3, and submitted for ICP analysis (using a Thermo Jarrell-Ash, Model 61 inductively coupled argon plasma atomic emission spectrometer according to procedure PNL-ALO-211).

Table 5.13. Spinel Minerals

Brunogeierite	$(Ge^{++},Fe^{++})Fe^{+++}{}_2O_4$
Chromite	$Fe^{++}Cr_2O_4$
Cochromite	$(Co,Ni,Fe^{++})(Cr,Al)_2O_4$
Coulsonite	$Fe^{++}V^{+++}{}_2O_4$
Cuprospinel	$(Cu^{++},Mg)Fe^{+++}{}_2O_4$
Franklinite	$(Zn,Mn^{++},Fe^{++})(Fe^{+++},Mn^{+++})_2O_4$
Gahnite	$ZnAl_2O_4$
Galaxite	$(Mn^{++},Fe^{++},Mg)(Al,Fe^{+++})_2O_4$
Hercynite	$Fe^{++}Al_2O_4$
Jacobsite	$(Mn^{++},Fe^{++},Mg)(Fe^{+++},Mn^{+++})_2O_4$
Magnesiochromite	$MgCr_2O_4$
Magnesiocoulsonite	$MgV_2O_{42}O_4$
Magnesioferrite	$MgFe^{+++}{}_2O_4$
Magnetite	$Fe^{++}Fe^{+++}{}_2O_4$
Manganochromite	$(Mn^{++},Fe^{++})(Cr^{+++},V^{+++})_2O_4$
Nichromite	$(Ni,Co,Fe^{++})(Cr^{+++},Fe^{+++},Al)_2O_4$
Qandilite	$(Mg,Fe^{++})_2(Ti,Fe^{+++},Al)O_4$
Ringwoodite	$(Mg,Fe^{++})_2SiO_4$
Spinel	$MgAl_2O_4$
Trevorite	$NiFe^{+++}{}_2O_4$
Ulvospinel	$TiFe^{++}{}_2O_4$
Vuorelainenite	$(Mn^{++},Fe^{++})(V^{+++},Cr^{+++})_2O_4$
Zincochromite	$ZnCr_2O_4$

Figure 5.10. Stainless Steel Container for PCT (vessel, lid, Teflon gasket, nickel-plated brass, nut, and screw)

5.7 Toxicity Characteristic Leaching Procedure

A TCLP test was performed on two AZ-101 HLW glass samples. Extracts were analyzed with ICP(MS for Tl, AES for all other elements of interest) except for Hg that was analyzed with cold vapor atomic absorption spectroscopy (CVAA). The testing was conducted per the Environmental Protection Agency (EPA) SW-846, Method 1311 (EPA 1992) using RPG-CMC-110, Rev 1.

The amount of 33.38 g quenched glass was sieved to pass through a 9.5-mm (USA 3/8 inch Mesh) sieve. Per procedure RPG-CMC-110, a 10-g sample was placed into an extractor vessel with 200 mL of extraction fluid #1. Note that Method 1311 calls for a 100g sample for non-rad materials. The matrix spike aliquots were prepared and then all of the leachate aliquots preserved with concentrated HNO_3. 45-mL aliquots were taken for two acid digestions, one with HNO_3 and HCl, and the other with HNO_3 alone, per procedure RPG-CMC-139. For Hg, approximately 1.5-mL aliquots of the acidified extracts were digested and brought to a digest volume of 25 mL for analysis. For the ICP-AES, ICP/MS and CVAA analytical methods, preparative QC samples included blanks, duplicates, blank spikes, matrix spikes, and laboratory control standards.

The analysis of the extraction solutions and required QC are described in detail in Appendix D.

6.0 Results

6.1 Chemical Composition

Table 6.1 through Table 6.3 list the results of glass-sample analyses. The reported data were used to obtain the final adjusted normalized results for each of the two replicates in each of the three digestions summarized in Table 6.4. Table 6.5 lists the standard deviations (σ_A) for each analysis and each constituent as mass percent. They are multiplied by 10^6 for easier comparison. Table 6.6 summarizes the averages for the two duplicate values for each sample preparation method and the overall average. It also shows, in the last two rows, the sums of squared standard deviations, $\Sigma\sigma_{iA}^2$ for all constituents listed in the target composition and the squared error, $\Sigma(w_{iA} - w_{iT})^2$, where w_A and w_T are the i-the component analyzed and target mass fraction, respectively.

Table 6.1. ICP-AES Data (in mg element/g glass) for AZ-101 HLW Glass Sample Prepared with Na_2O_2-NaOH Fusion in a Zr Crucible[(a)]

	Blank (mg/g)		AZ-101-HLW (mg element/g glass)		ARG-1	LRM
Ag	0.00	0.00	0.18	0.05	0.06	0.00
Al	0.33	0.26	49.50	51.20	25.20	53.80
B	0.00	0.00	33.50	34.60	26.10	25.40
Ba	0.00	0.00	0.65	0.69	0.75	0.01
Bi	0.00	0.00	0.29	0.23	0.22	0.00
Ca	4.30	3.00	7.41	7.30	14.20	7.78
Cd	0.00	0.00	6.28	6.44	0.00	1.46
Ce	0.00	0.00	0.19	0.18	0.00	0.00
Cr	0.07	0.00	0.91	0.92	0.66	1.36
Cu	0.05	0.00	0.34	0.34	0.09	0.00
Fe	2.54	0.59	83.80	86.20	94.50	10.40
K	32.00	20.00	15.00	6.70	44.20	24.00
La	0.00	0.00	2.57	2.70	0.00	0.14
Li	0.13	0.11	17.60	18.30	15.10	0.60
Mg	0.00	0.00	0.90	0.88	5.43	0.74
Mn	0.00	0.00	2.21	2.27	14.40	0.62
Nd	0.00	0.00	1.96	2.06	0.22	0.00
Ni	0.37	0.00	4.18	4.25	8.01	1.53
P	0.54	0.24	3.75	2.61	1.30	2.32
Pb	0.00	0.00	0.77	0.73	0.23	1.10
Rh	0.00	0.00	0.92	0.72	0.00	0.00
Si	1.20	0.00	213.00	219.00	226.00	269.00
Sn	1.50	0.00	2.50	1.90	1.30	1.40
Sr	0.12	0.09	1.68	1.76	0.15	0.14
Ti	0.00	0.00	0.13	0.15	6.24	0.59
U	0.00	0.00	9.70	8.80	0.00	0.00
Y	0.00	0.00	0.17	0.18	0.00	0.00
Zn	0.00	0.00	16.20	16.60	0.23	0.00

(a) Na and Zr fractions are not obtained with this method.

Table 6.2. ICP-AES Data (in mg/g glass) for AZ-101 HLW Glass Sample Prepared with KOH-KNO_3 Fusion in a Ni Crucible[(a)]

	Blank (mg/g)		AZ-101-HLW (mg element/g glass)		ARG	LRM
Ag	0.00	0.07	0.12	0.07	0.05	0.05
Al	1.47	0.67	49.00	48.10	26.50	54.80
B	0.12	0.00	34.30	33.60	27.00	26.20
Ba	0.02	0.04	0.67	0.65	0.76	0.02
Bi	0.25	0.20	0.46	0.33	0.29	0.25
Ca	0.00	0.78	3.80	3.60	10.80	4.20
Cd	0.00	0.00	6.32	6.27	0.00	1.59
Ce	0.00	0.00	0.93	0.64	0.00	0.00
Cr	0.07	0.06	0.91	0.89	0.69	1.42
Cu	0.11	0.13	0.43	0.43	0.21	0.15
Fe	0.90	0.33	88.10	84.50	97.50	10.60
La	0.00	0.00	2.60	2.62	0.00	0.12
Li	0.18	0.36	17.40	16.70	14.50	0.65
Mg	0.35	0.34	0.46	0.93	5.70	1.00
Mn	0.17	0.20	2.50	2.40	15.10	0.79
Na	8.47	13.90	94.60	87.90	90.30	165.00
Nd	0.00	0.00	1.80	2.00	0.19	0.00
P	1.20	0.63	2.50	2.33	1.80	2.99
Pb	0.24	0.30	0.46	0.84	0.38	1.20
Rh	0.00	0.00	1.39	0.30	0.00	0.00
Si	1.80	0.00	212.00	211.00	230.00	272.00
Sn	0.00	0.00	2.32	1.40	1.00	0.94
Sr	0.00	0.00	1.64	1.58	0.04	0.03
Ti	0.00	0.00	0.12	0.15	6.19	0.62
U	0.00	0.00	9.28	7.60	0.00	0.00
Y	0.00	0.00	0.23	0.17	0.00	0.00
Zn	0.00	0.00	15.90	16.00	0.22	0.00
Zr	0.00	0.00	28.20	27.70	0.96	7.04

(a) K and Ni fractions are not obtained with this method.

Table 6.3. ICP-AES Data (in mg/g glass) for AZ-101 HLW Glass Sample Prepared with Acid Digestion[(a)]

	Blank	AZ-101-HLW		ARG	LRM
	(mg/g)	(mg element/g glass)			
Ag	0.00	0.05	0.05	0.01	0.00
Al	0.00	44.80	44.20	25.00	52.70
B	0.00	31.80	29.60	26.40	23.90
Ba	0.00	0.71	0.70	0.81	0.01
Bi	0.00	0.12	0.13	0.11	0.03
Ca	0.00	3.45	3.43	10.60	3.74
Cd	0.00	6.35	6.33	0.00	1.51
Ce	0.00	0.69	0.68	0.00	0.00
Cr	0.00	0.93	0.93	0.67	1.37
Cu	0.00	0.30	0.30	0.04	0.00
Fe	0.02	88.00	87.00	97.50	10.30
K	0.00	0.27	0.25	22.90	12.20
La	0.00	2.70	2.68	0.01	0.09
Li	0.00	17.90	17.70	15.50	0.49
Mg	0.00	0.78	0.79	5.64	0.70
Mn	0.00	2.34	2.32	15.20	0.63
Na	0.10	85.00	84.60	85.60	154.00
Nd	0.00	1.95	1.94	0.00	0.00
Ni	0.00	4.38	4.35	8.43	1.54
P	0.00	2.13	2.13	1.26	2.33
Pb	0.00	0.63	0.61	0.03	0.90
Rh	0.00	0.21	0.22	0.00	0.00
Si[(a)]	---	---	---	---	---
Sn	0.00	0.81	0.86	0.32	0.09
Sr	0.00	1.69	1.68	0.03	0.02
Ti	0.00	0.14	0.14	6.81	0.60
U	0.00	5.43	5.43	0.00	0.00
Y	0.00	0.17	0.17	0.01	0.02
Zn	0.01	15.70	15.60	0.19	0.01
Zr	0.00	29.30	29.20	1.12	7.15
(a) Si fraction is not obtained with this method.					

The mass fraction values from Table 6.6 are graphically displayed in Figure 6.1 and Figure 6.2. Identification and quantitation is required only for the chemical constituents present at concentrations greater than 0.5 mass% (indicated by lines in Figure 6.1). Figure 6.2 compares the analytical values (the best estimates averaged for the two measured duplicate samples) with the target values, showing reasonable agreement for components with mass fractions higher than 0.005 in any Table 6.6 column except SiO_2 that was not included in the plot because of its high mass fraction. Thus Figure 6.2 includes glass components with targeted $g_i \geq 0.005$ (Na_2O, Fe_2O_3, B_2O_3, Al_2O_3, Li_2O, ZrO_2, ZnO, UO_3, and CdO) plus any glass component with a mass fraction ≥ 0.005 as determined by ICP analyses listed in Table 6.6 (NiO, CaO, P_2O_5, MnO, and La_2O_3).

Table 6.4. Best Analytical Estimates for AZ-101 HLW Glass Composition[a] in Mass Fractions

	Na_2O_2-NaOH		$KOH-KNO_3$		Acid Digestion	
	Mass %					
Ag_2O	0.02	0.01	0.01	0	0.01	0.01
Al_2O_3	8.48	8.64	8.3	8.29	7.84	7.83
B_2O_3	10.17	10.19	10.56	10.7	9.64	9.2
BaO	0.08	0.08	0.08	0.08	0.08	0.08
Bi_2O_3	0.03	0.03	0.03	0.01	0.01	0.01
CaO	0.49	0.46	0.48	0.45	0.48	0.48
CdO	0.72	0.74	0.64	0.63	0.67	0.67
Ce_2O_3	0.02	0.02	0.11	0.07	0.08	0.08
Cl[b]	0.03	0.03	0.03	0.03	0.03	0.03
CoO[b]	0.01	0.01	0.01	0.01	0.01	0.01
Cr_2O_3	0.13	0.13	0.12	0.12	0.14	0.14
CuO	0.02	0.02	0.01	0.01	0.03	0.03
F[b]	0.02	0.02	0.02	0.02	0.02	0.02
Fe_2O_3	11.69	11.68	12.26	11.94	12.22	12.21
K_2O[c]	0	0	0.03	0.03	0.03	0.03
La_2O_3	0.37	0.38	0.43	0.44	0.61	0.61
Li_2O	3.72	3.85	3.66	3.53	3.81	3.78
MgO	0.14	0.13	0.02	0.1	0.12	0.13
MnO	0.29	0.29	0.3	0.29	0.3	0.3
Na_2O[c]	10.9	10.79	10.3	10.16	10.52	10.81
Nd_2O_3	0.23	0.24	0.21	0.23	0.23	0.23
NiO[c]	0.54	0.54	0.54	0.54	0.55	0.54
P_2O_5	0.69	0.45	0.33	0.32	0.46	0.47
PbO	0.08	0.08	0.02	0.06	0.07	0.07
PdO[b]	0.1	0.1	0.1	0.1	0.1	0.1
Rh_2O_3	0.11	0.09	0.17	0.04	0.03	0.03
RuO_2[b]	0.04	0.04	0.04	0.04	0.04	0.04
SiO_2[c]	43.46	43.68	43.76	44.65	45.03	45.21
SnO_2	0.2	0.12	0.28	0.18	0.1	0.11
SO_3[b]	0.11	0.11	0.11	0.11	0.11	0.11
SrO	0.19	0.2	0.19	0.19	0.2	0.2
TiO_2	0.02	0.02	0.02	0.03	0.02	0.02
UO_3	1.11	1	1.08	0.91	0.64	0.65
Y_2O_3	0.02	0.02	0.03	0.02	0.02	0.02
ZnO	2.01	2.06	1.98	1.99	1.95	1.94
ZrO_2[c]	3.74	3.74	3.72	3.66	3.8	3.79

(a) Two analyses were performed for each sample preparation method (i.e., Na_2O_2-NaOH, $KOH-KNO_3$, and acid digestion).

(b) Cl, CoO, F, PdO, RuO_2, and SO_3 are unanalyzed and undetected glass components substituted by their assumed target values.

(c) Na and Zr concentrations were not obtained from the analysis using Na_2O_2-NaOH fusion, K and Ni concentrations were not obtained from the analysis using $KOH-KNO_3$ fusion, and Si concentration was not obtained from the analysis using acid digestion; their values were substituted with inverse variance weighted means of the concentrations from the other two methods before the final normalization.

Table 6.5. Values of $10^6\sigma_A$ for Best Analytical Estimates for AZ-101 HLW Glass Composition

	Na_2O_2-NaOH		$KOH-KNO_3$		Acid Digestion	
	$10^6\sigma_A$ based on the data for Table 6.4					
Ag_2O	0.98	0.26	0.63	0.41	0.28	0.28
Al_2O_3	22.66	23.42	22.43	22.01	20.61	20.33
B_2O_3	32.96	33.96	34.03	33.30	30.10	28.40
BaO	0.27	0.28	0.28	0.27	0.18	0.18
Bi_2O_3	0.55	0.44	0.96	0.73	0.23	0.25
CaO	8.11	8.10	1.68	1.64	1.11	1.10
CdO	0.78	0.80	1.54	1.53	1.63	1.62
Ce_2O_3	0.42	0.39	2.00	1.38	1.49	1.46
Cr_2O_3	0.20	0.21	0.22	0.22	0.18	0.18
CuO	0.15	0.15	0.13	0.13	0.08	0.08
Fe_2O_3	34.71	35.64	25.62	24.60	24.73	24.42
K_2O	0.00	0.00	1.79	1.65	1.79	1.65
La_2O_3	1.31	1.38	1.55	1.56	2.19	2.18
Li_2O	8.89	9.25	8.84	8.49	9.01	8.91
MgO	4.07	3.98	2.27	4.30	3.54	3.56
MnO	0.71	0.73	0.91	0.89	0.75	0.74
Na_2O	22.19	22.21	44.42	42.39	34.49	34.08
Nd_2O_3	1.09	1.14	1.00	1.11	1.08	1.08
NiO	0.81	0.82	0.39	0.39	0.76	0.75
P_2O_5	12.77	8.99	9.12	8.58	7.24	7.24
PbO	1.96	1.86	1.26	2.19	1.60	1.56
Rh_2O_3	1.38	1.08	2.09	0.45	0.32	0.32
SiO_2	45.92	46.81	48.79	47.72	28.96	28.83
SnO_2	6.80	5.30	6.09	3.68	2.13	2.26
SrO	0.52	0.54	0.47	0.46	0.49	0.49
TiO_2	0.26	0.30	0.23	0.30	0.27	0.27
UO_3	9.88	8.97	9.46	7.76	5.55	5.55
Y_2O_3	0.28	0.29	0.38	0.28	0.28	0.28
ZnO	2.14	2.19	2.10	2.11	2.07	2.06
ZrO_2	2.54	2.54	5.05	4.96	5.16	5.14

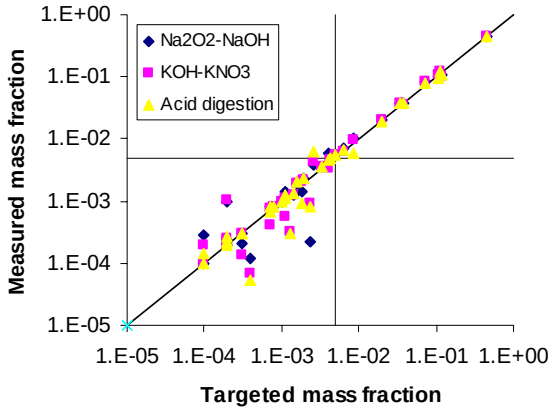

Figure 6.1. Analyzed Versus Target Mass Fractions of AZ-101 HLW Glass Components

Table 6.6. Averaged Best Analytical Estimates for AZ-101 HLW Glass Composition[a] in Mass Fractions Sorted by Target

	Na_2O_2-NaOH	KOH-KNO_3	Acid Digestion	Average	Target
	Mass Fraction				
SiO_2[b]	0.4357	0.4421	0.4512	0.4430	0.4469
Na_2O[b]	0.1084	0.1023	0.1066	0.1058	0.1187
Fe_2O_3	0.1168	0.1210	0.1221	0.1200	0.1116
B_2O_3	0.1018	0.1063	0.0942	0.1008	0.1063
Al_2O_3	0.0856	0.0830	0.0784	0.0823	0.0733
Li_2O	0.0379	0.0360	0.0380	0.0373	0.0376
ZrO_2	0.0374	0.0369	0.0380	0.0374	0.0338
ZnO	0.0204	0.0199	0.0195	0.0199	0.0201
UO_3	0.0105	0.0100	0.0064	0.0090	0.0092
CdO	0.0073	0.0064	0.0067	0.0068	0.0064
NiO[b]	0.0054	0.0054	0.0055	0.0054	0.0049
CaO	0.0048	0.0047	0.0048	0.0047	0.0042
P_2O_5	0.0057	0.0033	0.0047	0.0045	0.0040
MnO	0.0029	0.0029	0.0030	0.0030	0.0027
La_2O_3	0.0038	0.0044	0.0061	0.0047	0.0026
Ce_2O_3	0.0002	0.0009	0.0008	0.0006	0.0024
Nd_2O_3	0.0016	0.0023	0.0011	0.0017	0.0020
SnO_2	0.0024	0.0022	0.0023	0.0023	0.0019
SrO	0.0020	0.0019	0.0020	0.0020	0.0016
Cr_2O_3	0.0013	0.0012	0.0014	0.0013	0.0014
K_2O[b]	0.0000	0.0003	0.0003	0.0002	0.0013
MgO	0.0014	0.0006	0.0013	0.0011	0.0011
SO_3[c]	0.0011	0.0011	0.0011	0.0011	0.0011
PdO[c]	0.0010	0.0010	0.0010	0.0010	0.0010
RuO_2[c]	0.0008	0.0008	0.0008	0.0008	0.0007
BaO	0.0008	0.0004	0.0007	0.0006	0.0007
PbO	0.0004	0.0004	0.0004	0.0004	0.0004
Ag_2O	0.0002	0.0001	0.0001	0.0001	0.0004
Cl[c]	0.0003	0.0003	0.0003	0.0003	0.0003
CuO	0.0002	0.0001	0.0003	0.0002	0.0003
F[c]	0.0002	0.0002	0.0002	0.0002	0.0002
Rh_2O_3	0.0010	0.0011	0.0003	0.0008	0.0002
TiO_2	0.0002	0.0003	0.0002	0.0002	0.0002
Y_2O_3	0.0002	0.0003	0.0002	0.0002	0.0002
Bi_2O_3	0.0003	0.0002	0.0001	0.0002	0.0001
CoO[c]	0.0001	0.0001	0.0001	0.0001	0.0001
$10^2\Sigma\sigma_{iA}{}^2$	0.597	0.697	0.412	0.0140	n/a
$10^2\Sigma(w_{iA}\text{-}w_{iT})^2$	42.57	43.21	44.05	43.27	n/a

(a) Two analyses were performed for each sample preparation method (i.e., Na_2O_2-NaOH, KOH-KNO_3, and acid digestion).

(b) Na and Zr concentrations were not obtained from the analysis using Na_2O_2-NaOH fusion, K and Ni concentrations were not obtained from the analysis using KOH-KNO_3 fusion, and Si concentration was not obtained from the analysis using acid digestion; their values were substituted with inverse variance weighted means of the concentrations from the other two methods before the final normalization.

(c) Cl, CoO, F, PdO, RuO_2, and SO_3 are unanalyzed and undetected glass components substituted by their assumed target values.

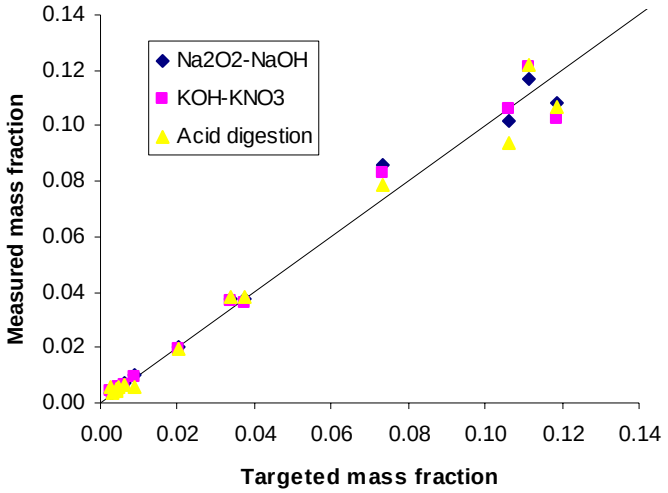

Figure 6.2. Analyzed versus Target Mass Fractions of AZ-101 HLW Glass Components (except SiO_2) with Mass Fractions >0.005

The results of QC measurement can be summarized as follows:

1. Except for Na in the KOH-KNO_3/Ni fusion (Na is known to be present in the KOH-KNO_3/Ni fusion flux), the process blanks concentrations of all components of interest were within the acceptance criteria of the estimated quantitation level or ≤ 5% of the concentration in the sample. In the blanks, the Na ranged from ~10% to ~16% of the level observed in the sample.
2. Laboratory control samples of LRM and ARG-1 reference glasses showed recovery values within the acceptance criteria of 75% to 125% for all elements of interest except for the following minor elements (<0.5 g/L) in samples prepared by acid digestion: Ba and La in the LRM glass and Co in the ARG-1 glass. See Table B.5 in Appendix B.
3. The recovery values for the acid-digestion matrix spiked sample were within the acceptance criterion of 75% to 125% for all components of interest.
4. Except for P in the Na_2O_2-NaOH/Zr fusion, the duplicate RPDs were within the acceptance criteria of ≤ 20% for all components. The RPD for P was ~36%, likely due to a small but variable background level in the fusion flux.
5. The recovery values of spike elements were within the acceptance criterion of 75% to 125% for all components of interest.
6. The fivefold serial dilution differences were within the acceptance criterion of ≤ 10% for all components of interest.
7. Except for B in the interference check standard runs for the acid-digestion sample, all other instrument-related QC tests passed within the appropriate acceptance criteria for all components of interest (B was very slightly above the estimated quantitation level of ~16 µg/mL; this result had no effect on the accuracy of the reported data).

The target waste loading mass fraction in the glass is 0.3122. For oxides that are present only in the blended waste, an estimate of the attained waste loading factor, W_B, can most simply be obtained by

dividing the weight percent of the oxide in the final glass by the weight percent of the oxide measured in the blended waste. If the waste and the glass formers have been weighed out properly and the analytical chemistry is accurate, the waste-loading factor W_B should be close to 0.3122. If an oxide is also present in the glass formers (or in the corrective chemicals also present in this glass batch), then those extra amounts from the other sources must be subtracted out. In terms of an equation, this can be written as follows:

$$W_B = ({}^{g}M_{ox} - {}^{gf}M_{ox} \times W_{gf} - {}^{C}M_{ox} \times W_C)/ {}^{B}M_{ox} \qquad (6.1)$$

where
W_B = waste loading factor
W_{gf} = glass-former loading factor
W_C = corrective chemical loading factor
${}^{g}M_{ox}$ = mass fraction of an oxide in the glass
${}^{gf}M_{ox}$ = mass fraction of an oxide in the glass formers
${}^{C}M_{ox}$ = mass fraction of an oxide in the corrective chemicals
${}^{B}M_{ox}$ = mass fraction of an oxide in the blended waste
$W_B + W_{gf} + W_C = 0.3122 + 0.6825 + 0.0053 = 1.$ (see Table 5.2).

Table 6.7 gives the values of W_B for major oxides found in the waste blend, but not in the glass-former mix. The values expected to be most accurate are those derived from the oxides present in the largest fractions, Fe_2O_3, Al_2O_3, ZrO_2, CdO, and CaO, which give W_B a value of 0.34 to 0.35. More minor component oxides give a much larger spread of values for W_B, ranging from < 0.30 to > 0.50. This indicates that the batching level of the waste blend was higher than planned. One result of higher batching of blended waste is higher loading of the waste glass with Fe_2O_3 , Al_2O_3, and ZrO_2. They sum to 23.97%, 14% higher than the 21% contract limit (see Table 6.8).

Table 6.7. Component Mass Balance-Estimated Waste Loading of AZ-101 HLW Waste Glass

Glass Oxide	${}^{B}M_{ox}$	${}^{gf}M_{ox}$	${}^{g}M_{ox}$	${}^{C}M_{ox}$	W_B
Fe_2O_3	0.3512	0	0.12	0.0031	0.341639
Al_2O_3	0.2293	0	0.0823	0.0132	0.358613
CaO	0.0133	0	0.0047	0.0161	0.346968
ZrO_2	0.1066	0	0.0374	0	0.350844
CdO	0.0202	0	0.0068	0.0008	0.336424
Weighted average waste loading					0.3484

Table 6.8. Table TS-1.1 Minimum Component Limits in High-Level Waste Glass (DOE 2000)

Component	Weight Percent in HLW Glass
Fe_2O_3	12.5
Al_2O_3	11.0
$Na_2O + K_2O$	15.0
ZrO_2	10.0
UO_2	8.0
ThO_2	4.0
CaO	7.0
MgO	5.0
BaO	4.0
CdO	3.0
NiO	3.0
PbO	1.0
TiO_2	1.0
Bi_2O_3	2.0
P_2O_5	3.0
F	1.7
$Al_2O_3 + ZrO_2$	14.0
$Al_2O_3 + ZrO_2 + Fe_2O_3$	21.0
MgO + CaO	8.0
Cr_2O_3	0.5
SO_3	0.5
Ag_2O	0.25
$Rh_2O_3 + Ru_2O_3 + PdO$	0.25
Any single waste oxide (exclusive of Si) not specifically identified in Specification 8, TS-8.1, and -8.4.	0.2
Total of all other waste oxides (exclusive of Si) not specifically identified in this table.	8.0

6.2 Radiochemical Composition

As Table 6.9 shows, quantifiable concentrations were obtained with γ spectrometry for ^{60}Co, ^{137}Cs, ^{154}Eu, ^{155}Eu, and ^{241}Am. No other γ-emitting analytes were found. The principal activity in the samples was from ^{137}Cs. Sample reproducibility was excellent with RPD values below 10%. The two hot-cell process blanks showed miniscule levels of ^{137}Cs, nearly 6 orders of magnitude below the measured sample activities, indicating no contamination of the samples. Minimum reportable quantity (MRQ) values were not provided with the ASR. The AZ-101 HLW glass sample and duplicate analyte concentrations were within 8% RPD.

Table 6.9. Gamma Activity (in mCi/kg) of AZ-101 HLW Glass Radionuclides

Isotope	AZ-101-HLW Glass[(a)]					Process Blank[(a)]			
	Activity	MDA	Activity	MDA	RD	Activity	MDA	Activity	MDA
^{60}Co	2.96±0.33	0.7	2.77±.22	0.4	0.07	n/a	0.005	n/a	0.005
^{95}Nb	n/a	1	n/a	1	n/a	n/a	0.005	n/a	0.005
^{113}Sn	n/a	8	n/a	8	n/a	n/a	0.006	n/a	0.007
^{125}Sb	n/a	0.2	n/a	20	n/a	n/a	0.02	n/a	0.02
^{126}Sn/Sb	n/a	2	n/a	2	n/a	n/a	0.005	n/a	0.005
^{134}Cs	n/a	2	n/a	2	n/a	n/a	0.006	n/a	0.006
^{137}Cs	15300±612	5	15300±612	5	0.00	0.032±0.003	0.006	0.0454±0.004	0.006
^{144}Ce	n/a	30	n/a	30	n/a	n/a	0.03	n/a	0.03
^{152}Eu	n/a	3	n/a	3	n/a	n/a	0.03	n/a	0.03
^{154}Eu	33.0±1.3	3	33.7±1.3	2	0.02	n/a	0.02	n/a	0.02
^{155}Eu	29.7±3.9	20	30.0±3.9	20	0.01	n/a	0.02	n/a	0.02
^{232}Th	n/a	9	n/a	9	n/a	n/a	0.009	n/a	0.010
^{241}Am	70.1±12.6	40	76.0±12.2	40	0.08	n/a	0.02	n/a	0.02

(a) Glass was tested in duplicate; two process blanks were tested.
MDA is minimum detectable activity.
RD is relative difference; RD = |Δ|/(average), where Δ is the difference between duplicate values.
n/a = not applicable because activity below MDA.

For ^{90}Sr, the triplicate results show excellent agreement with an relative standard deviation (RSD) of 1% (Table 6.10). No activity could be seen in either of the hot cell blanks or the lab blank. The reagent spike recovery of 110% was within the blank spike limits of 80 to 110% established by the analytical QA plan. The sample spike recovery could not be determined since the spike activity was too low compared to the sample activity.

The ^{63}Ni activities in the sample, hot-cell prep duplicate, and the laboratory duplicate were in good agreement with an RSD of 12% (Table 6.10). No activity was observed in the hot-cell blanks or the laboratory blank. The reagent and sample spike recoveries of 88% and 89%, respectively, were within the blank spike limits. The process blank had no detectable ^{63}Ni.

Se-79 was analyzed for, but not detected.

The duplicate values of ^{151}Sm were in good agreement with an RPD of 6% (Table 6.10). No ^{151}Sm was detected in the duplicate hot-cell blanks or the lab separation blanks. The reagent spike recovery, 82%, was acceptable. The sample spike recovery, 64%, was low for reasons that are not understood.

Table 6.10. Beta Activity (in mCi/kg) of AZ-101 HLW Glass

	AZ-101-HLW			Blank MDA			Spike fraction	
	Activity[(a)]	MDA	RSD	Hot cell		Lab[(b)]	Reagent	Sample[(c)]
^{79}Se	<0.000561	0.000561	---	---	---	---	---	---
^{90}Sr	24800±500 25200±500 24800±500	100	0.01	0.05	0.05	0.05	1.10	n/a
^{63}Ni	2.46±0.12 2.15±0.11 2.76±0.14	0.20	0.12	0.002	0.002	0.20	0.88	0.89
^{151}Sm	399±40 425±43	1.0	0.06	0.004	0.004	0.004	0.82	0.64

(a) Samples were measured in triplicate.
(b) The ^{90}Sr spike was too weak compared to the sample activity.
(c) The lab blank was calculated using sample dilutions.
MDA is minimum detectable activity.
RSD is relative standard deviation.

As Table 6.11 shows, the duplicate analyses RPD values were within 3% for ^{238}Pu, 11% for ^{241}Am, and within 7% for $^{243+244}$Cm. These values were in agreement within the specified value of 15%. However, the $^{239+240}$Pu RPD values of 24% were higher than the required value of 15%. No apparent reason for this disagreement was recognized. No Pu activities were observed in the hot cell preparation blanks or the laboratory blank. The blank spike and matrix spike recoveries were both 96%. Some ^{242}Pu was seen in the Am/Cm α spectra. However, the presence of Pu in the Am/Cm fraction had no impact on the analysis of ^{241}Am since the ^{238}Pu contribution was negligible. The ^{241}Am activities determined by α spectroscopy are in good agreement with those determined by γ energy analysis. The blank spike recoveries of 94% to 96% were within the acceptance criterion of 80% to 110%. The process blank contained ^{241}Am with activity 6 orders of magnitude lower than the sample.

Table 6.11. Alpha Activity of AZ-101 HLW Glass

Isotope	AZ-101-HLW[(a)]					Blank MDA		Blank MDA
	µCi/g	MDA	µCi/g	MDA	RD	Process[(a)]		Lab
$^{239+240}$Pu[(b)]	3.97 ±0.12	0.02	3.12 ±0.12	0.02	0.24	0.0002	0.0002	0.00004
^{238}Pu	0.446 ±0.033	0.02	0.431 ±0.036	0.02	0.03	0.0002	0.0002	0.00004
^{241}Am[(b)]	65.8 ±7.2	0.06	73.5 ±8.1	0.05	0.11	0.00006	0.0001	0.0001
$^{243/244}$Cm	0.270 ±0.0680	0.06	0.291 ±0.073	0.05	0.07	0.00003	0.00007	0.00005

(a) Glass was tested in duplicate; two process blanks were tested.
Process blank values for ^{241}Am were 0.000114±0.00003 mCi/kg and 0.000137±0.00005 mCi/kg.
(b) Reagent spike values were 0.96 for $^{239/240}$Pu and 0.96 mCi/kg for ^{241}Am.
Sample spike values were 0.96 for $^{239/240}$Pu and 0.94 mCi/kg for ^{241}Am.
MDA is minimum detectable activity.
RD is relative difference; RD = |Δ|/(average), where Δ is the difference between duplicate values.

Table 6.12 lists activity data averaged from Table 6.9 through Table 6.11. Future activities were quantified using the following calculator: WISE Uranium Project (2002). This quantitation was necessary to satisfy the following contract clause: "The Producer shall report the inventory of radionuclides (in Curies) that have half-lives longer than 10 years and that are, or will be, present in concentrations greater than 0.05 percent of the total radioactive inventory for each waste type, indexed to the years 2015 and 3115."

There are about 54 radioisotopes comprising the decay chains of the AZ-101 (D) waste radioisotopes, including the waste isotopes themselves. The detailed results of these calculations are summarized in Appendix B. At 2015, the inventory is dominated by fission products such as ^{90}Sr and its immediate daughter ^{90}Y plus ^{137}Cs and its immediate daughter ^{137m}Ba. Activity at this time is about 63 Ci/kg-glass. At 3115, the fission products have essentially disappeared except for ^{99}Tc. At this time, longer lived TRU radioisotopes dominate, but the total activity is much lower, about 18 mCi/kg-glass. At the longer time, the in-growth of daughter products such as ^{231}Pa is become a reportable part of the radionuclide inventory.

Table 6.13 lists the radiochemical results of the ICP-MS analysis of the AZ-101 HLW glass. The overall average is compared with the ICP-AES data (the averaged best estimates as listed in Table 6.6) and with the target composition. I-129 was analyzed for, but not detected (< 9.91 mg/kg). Note also that ^{241}Pu decays to ^{241}Am and that ICP-MS gave about 20 mg/kg-glass for AMU-241, which is about 70 mCi/kg-glass. Am-241 was measured at about 70 mCi/kg-glass, so very little ^{241}Pu is present Also from Table 6.12, the summarized activity due to ^{99}Tc, uranium, and TRU radioisotopes shows that their fraction of total activity is very small at 2015 (73.2 /62800 = 0.00117) but includes almost all of the activity in 3115 (16.8/18 = 0.933). Details of the analyses are listed in Appendix B, Table B.1 to B.4.

Table 6.12. Averaged Activities in mCi/kg Projected to 2015 and 3115

Radioisotopes in AZ-101 (D) Waste and Significant Daughters	$t_{1/2}$ (years)	2004 mCi/kg	2004[(c)] mCi/kg	2015[(c)] mCi/kg	3115[(c)] mCi/kg
^{63}Ni	1.00E+02	2.46E+00	---	---	---
^{90}Sr	2.91E+01	2.49E+04	2.49E+04	1.93E+04	---
^{90}Y	very short	---	2.49E+04	1.93E+04	---
^{99}Tc[(a)]	2.13E+05	1.28E+00	---	---	1.28
^{137}Cs	3.02E+01	1.53E+04	1.53E+04	1.19E+04	---
^{137m}Ba	very short	---	1.53E+04	1.19E+04	---
^{151}Sm	9.00E+01	4.12E+02	4.12E+02	379	0.59
^{231}Pa	3.28E+04	---	---	---	0.3
^{234}U[(a)]	2.45E+05	2.09E-03	---	---	---
^{235}U[(a)]	7.04E+08	9.10E-05	---	---	---
^{236}U[(a)]	2.34E+07	2.00E-04	---	---	---
^{238}U[(a)]	4.46E+09	1.67E-03	---	---	---
^{237}Np[(a)]	2.14E+06	4.07E-02	---	---	0.3
^{238}Pu	8.47E+01	4.39E-01	---	---	---
^{239}Pu[(a)]	2.41E+04	2.84E+00	---	---	0.72
^{240}Pu[(a)]	6.54E+03	8.11E-01	---	---	2.75
^{242}Pu[(a)]	3.76E+05	1.63E-04	---	---	---
^{241}Am	4.32E+02	7.14E+01	7.14E+01	70	12.02
^{243}Cm[(b)]	2.85E+01	2.81E-01	---	---	---
^{244}Cm[(b)]	1.81E+01	2.81E-01	---	---	---
Total activity	---	---	80900	62800	18

(a) Based on ICP-MS data
(b) Assumes sum of both radioisotopes ^{243}Cm + ^{244}Cm for each.
(c) Reportable as constituting > 0.05% of the total activity present.
--- Implies that a number would be irrelevant, or the value is considered to be negligible

Table 6.13. Uranium and TRU Content of AZ-101 HLW Glass: ICP-MS Data

	PNL-ALO#[(a)]	Sample	Duplicate
		(mg/kg)	
^{234}U	114	0.34±0.11	0.31±0.12
^{234}U	115	0.40±0.06	0.29±0.01
^{234}U	138	0.35±0.05	0.33±0.07
^{235}U	114	41.1±1.30	41.9±0.68
^{235}U	115	40.8±0.43	42.1±1.10
^{235}U	138	45.9±1.20	44.4±0.14
^{236}U	114	3.10±0.10	3.28±0.12
^{236}U	115	2.95±0.14	2.83±0.19
^{236}U	138	3.37±0.28	3.26±0.14
^{238}U	114	4840±38.00	4970±34
^{238}U	115	4770±19.00	4850±20
^{238}U	138	5390±42.00	5270±18
^{237}Np	114	57.6±1.10	57.0±0.62
^{237}Np	115	56.4±0.74	57.1±1.00
^{237}Np	138	61.8±1.40	61.6±1.20
^{239}Pu	114	46.8±0.89	46.0±0.36
^{240}Pu	114	3.61±0.01	3.60±0.05
^{242}Pu	114	0.043±0.003	0.041±0.003
^{241}Am	114	20.0±0.61	19.8±0.39
^{241}Am	115	20.5±0.33	20.2±0.58
^{241}Am	138	21.3±0.40	21.0±0.42

(a) 114—sample prepared with Na_2O_2-NaOH fusion
115—sample prepared with KOH-KNO_3 fusion
138—sample prepared with acid digestion.

The 2004 activities of radionuclides with $t_{1/2} > 10$ years are summarized in Table 6.14. Note excellent agreement between the ^{241}Am activity measured by α spectrometry (71 mCi/kg) and by ICM-MS (69 mCi/kg); also excellent agreement exists between the directly measured $^{239+240}Pu$ activity (3.55 mCi/kg) and that calculated from ICP-MS data (^{239}Pu activity and ^{240}Pu activity sum to 3.65 mCi/kg).

With the glass density of 2.71×10^3 kg/m^3 (see the following section) and 1.18 m^3 of glass per WTP canister, the mass of glass in a canister is 3198 kg. As Table 6.15 shows, the total U in a WTP canister is 16.2 kg (16.1 kg of ^{238}U and 137 g of ^{235}U), and the total Pu is 160 g (149 g of ^{239}Pu). Also listed in Table 6.15 are concentrations of U and Pu and their isotopes. The isotope mass percents of the total U are 0.0067% ^{234}U, 0.84% ^{235}U, 0.062% ^{236}U, and 99.1% ^{238}U. The isotopes mass percents of the total Pu are 92.7% ^{239}Pu, 7.21% ^{240}Pu, and 0.08% ^{241}Pu.

Table 6.14. Activities of Radionuclides in AZ-101 HLW Glass with $t_{1/2}$ > 10 Years (summary table)

	$t_{1/2}$ (years)	A (mCi/kg)
^{63}Ni	1.00E+02	2.46E+00
^{90}Sr	2.91E+01	2.49E+04
^{99}Tc[(a)]	2.13E+05	1.28E+00
^{137}Cs	3.02E+01	1.53E+04
^{151}Sm	9.00E+01	4.12E+02
^{234}U[(a)]	2.45E+05	2.09E-03
^{235}U[(a)]	7.04E+08	9.10E-05
^{236}U[(a)]	2.34E+07	2.00E-04
^{238}U[(a)]	4.46E+09	1.67E-03
^{237}Np[(a)]	2.14E+06	4.07E-02
^{238}Pu	8.47E+01	4.39E-01
$^{239+240}$Pu	n/a	3.55E+00
^{239}Pu[(a)]	2.41E+04	2.84E+00
^{240}Pu[(a)]	6.54E+03	8.11E-01
^{242}Pu[(a)]	3.76E+05	1.63E-04
^{241}Am	4.32E+02	7.14E+01
^{241}Am[(a)]	4.32E+02	6.94E+01
$^{243+244}$Cm	n/a	2.81E-01
^{243}Cm	2.85E+01	n/a
^{244}Cm	1.81E+01	n/a
(a) Based on ICP-MS data.		

Table 6.15. Mass (in g) and Concentration (in kg/m^3) of U and Pu per WTP Canister

	Mass per Canister (g)	Concentration (kg/m^3)
^{234}U	1.09	0.00092
^{235}U	137	0.116
^{236}U	10.0	0.00848
^{238}U	16035	13.6
^{239}Pu	149	0.126
^{240}Pu	11.5	0.00978
^{242}Pu	0.13	0.000114
Total U	16183	13.7
Total Pu	160	0.136

6.3 Crystalline Phases

Crystalline phases in a CCC heat-treated AZ-101 HLW glass sample were identified with XRD and SEM EDS (see Table 5.12 and Figure 5.9 for the CCC heat-treatment schedule). As seen in Figure 6.3 and Figure 6.4, the glass shows a broad amorphous hump with a number of sharp peaks identified in Figure 6.5 as corundum (added as an internal standard) and various spinels. The broad amorphous hump has been subtracted out of the spectrum in Figure 6.5 and Figure 6.6. Two unidentified peaks were reasonably matched with cadmium silicate structure by XRD. However, no evidence of cadmium silicate was found by SEM. According to the quantitative XRD analysis, the AZ-101 HLW glass sample contained 7.1 mass% of spinel, predominantly trevorite. For comparison with spectrum shown in Figure 6.3, see the spectrum for the quenched glass (Figure 6.6). The latter indicates a barely detectable trace of the spinal in the glass.

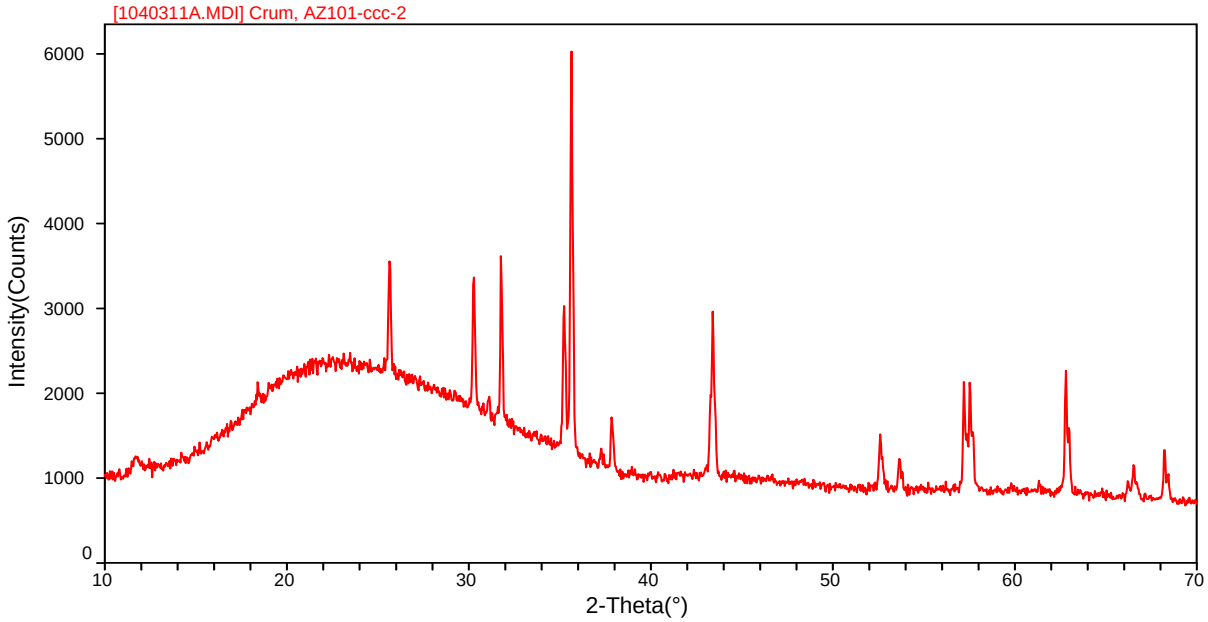

Figure 6.3. AZ-101 HLW CCC Glass XRD Pattern

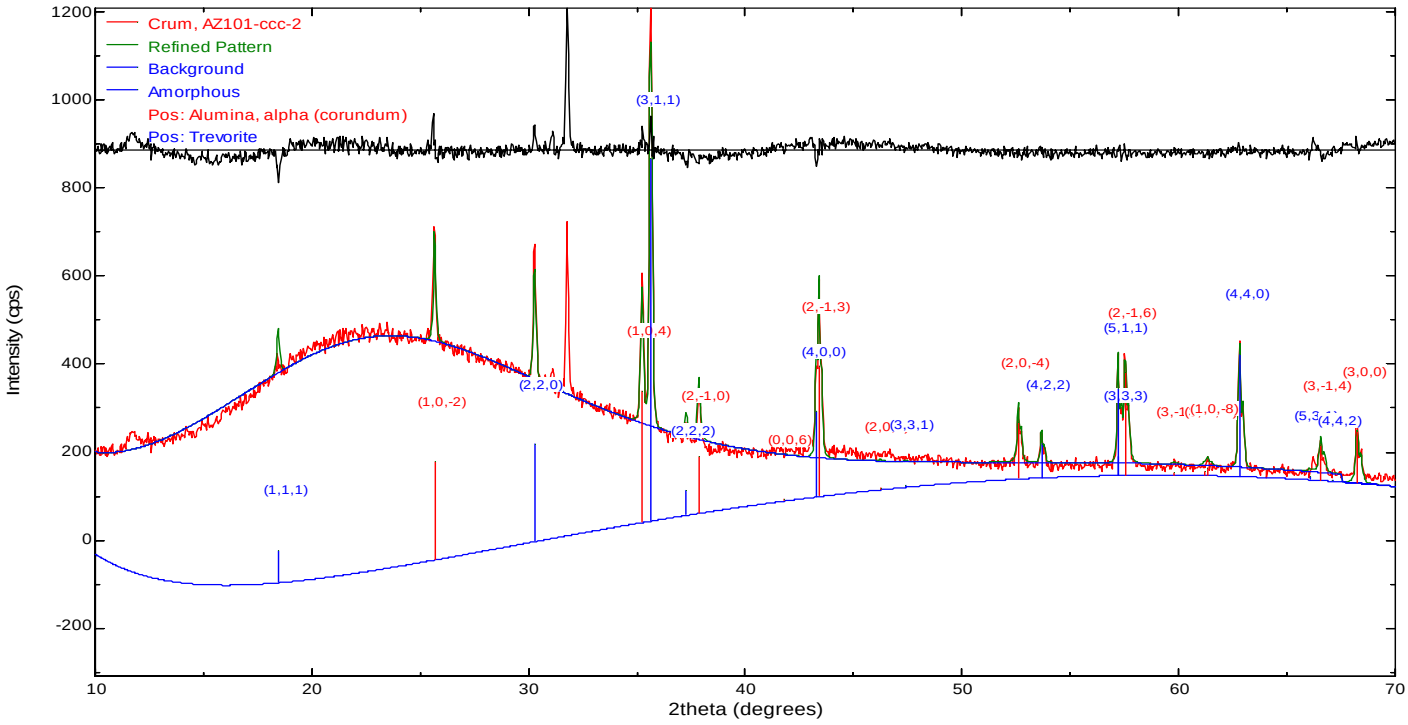

Figure 6.4. Whole Pattern Pitting of AZ-101 HLW CCC Glass XRD Pattern

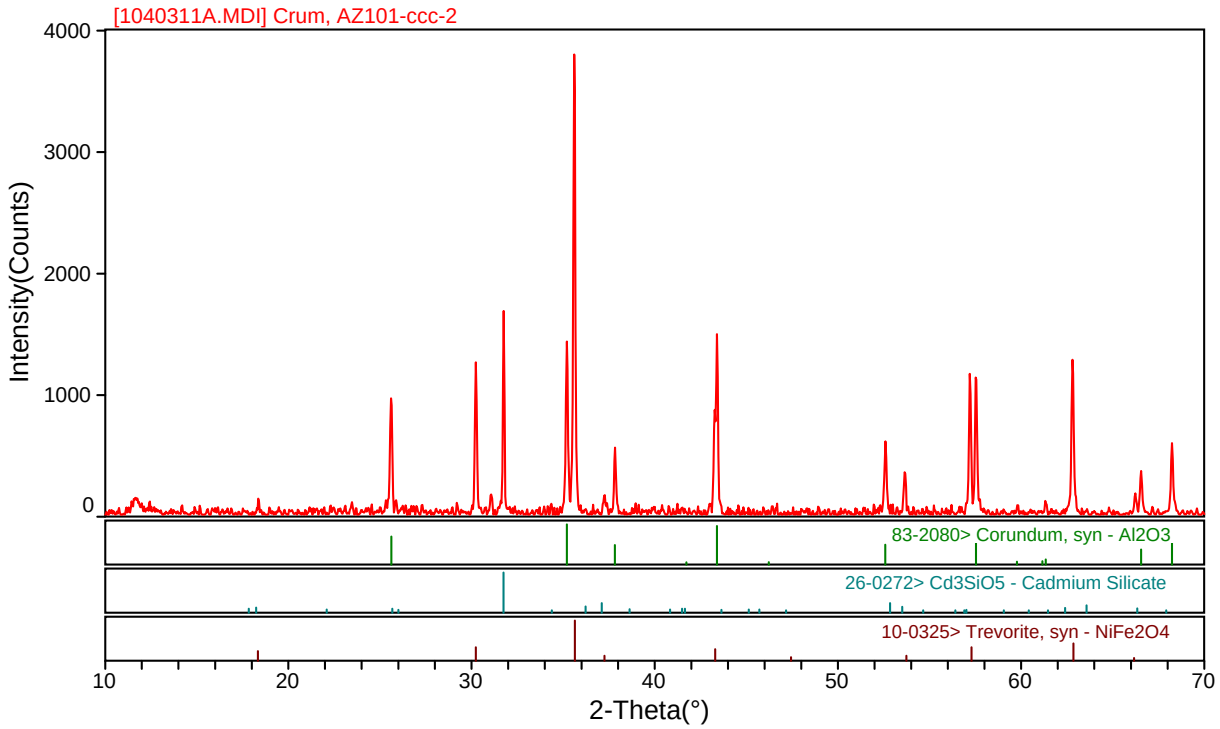

Figure 6.5. AZ-101 HLW CCC Glass XRD Pattern with Crystalline Phases Identified. Note that the broad amorphous peak has been subtracted from the spectrum shown here.

The Rietvold method was used to accommodate whole pattern fitting of the data to arrive at the most accurate concentration of unknown phases in the sample. No additional attempts were made to optimize fitting of structural parameters of the unknown phase in the sample. Only scale and peak profile shape fitting parameters were optimized. The following data are calculated by the Riqas software during whole pattern fitting. The accuracy of these data is not known because differences in the composition of the spinel phase used to fit the pattern. Trevorite was used to fit the pattern however the actual sample is a solid solution of many spinels and thus has minor differences in chemistry.

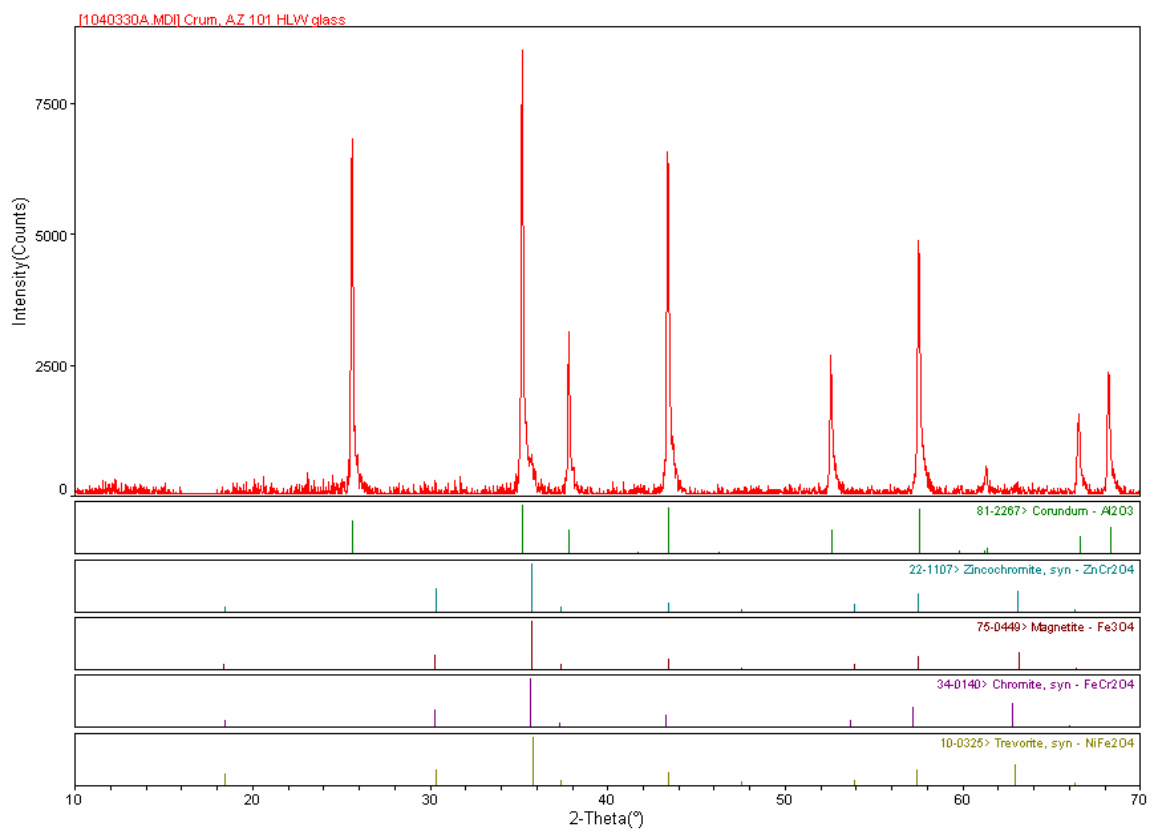

Figure 6.6. AZ-101 HLW Q Glass XRD Pattern with Crystalline Phases Identified. Pattern indicates only a trace of spinel present in the quenched glass. Note that the broad amorphous peak has been subtracted from the spectrum shown here.

The spinel content was evaluated also from SEM micrographs (Figure 6.7). The total of 12 frames was checked to obtain spinel crystal area fraction (Table 6.16). Because spinel crystals are isotropic, the area fraction and volume fraction are identical and equal to 3.55±0.50 vol%. The mass fraction of spinel, c_S, is related to the volume fraction of spinel by the formula

$$c_S = \left[1 + \frac{\rho_M}{\rho_S}\left(\frac{1}{v_S} - 1\right)\right]^{-1} \tag{6.4}$$

where v_S is the spinel volume fraction, and ρ_M and ρ_S are the glass matrix and spinel density, respectively. The trevorite density of 5.165 g/mL was used for spinel density. The glass matrix density can be estimated from composition using the formula

$$\rho_M = \frac{1}{\sum_{i=1}^{n} \frac{v_i m_i}{M_i}} \tag{6.5}$$

where v_i is the i-th glass component partial molar volume (see Table 6.17), m_i is the i-th glass matrix component mass fraction, and M_i is the i-th glass component molecular mass. The composition listed in Table 6.6 is that of the quenched glass without crystals. Equation (6.5) yields for AZ-101 HLW crystal-free glass an estimated density value of $\rho_G = 2.71$ g/mL.

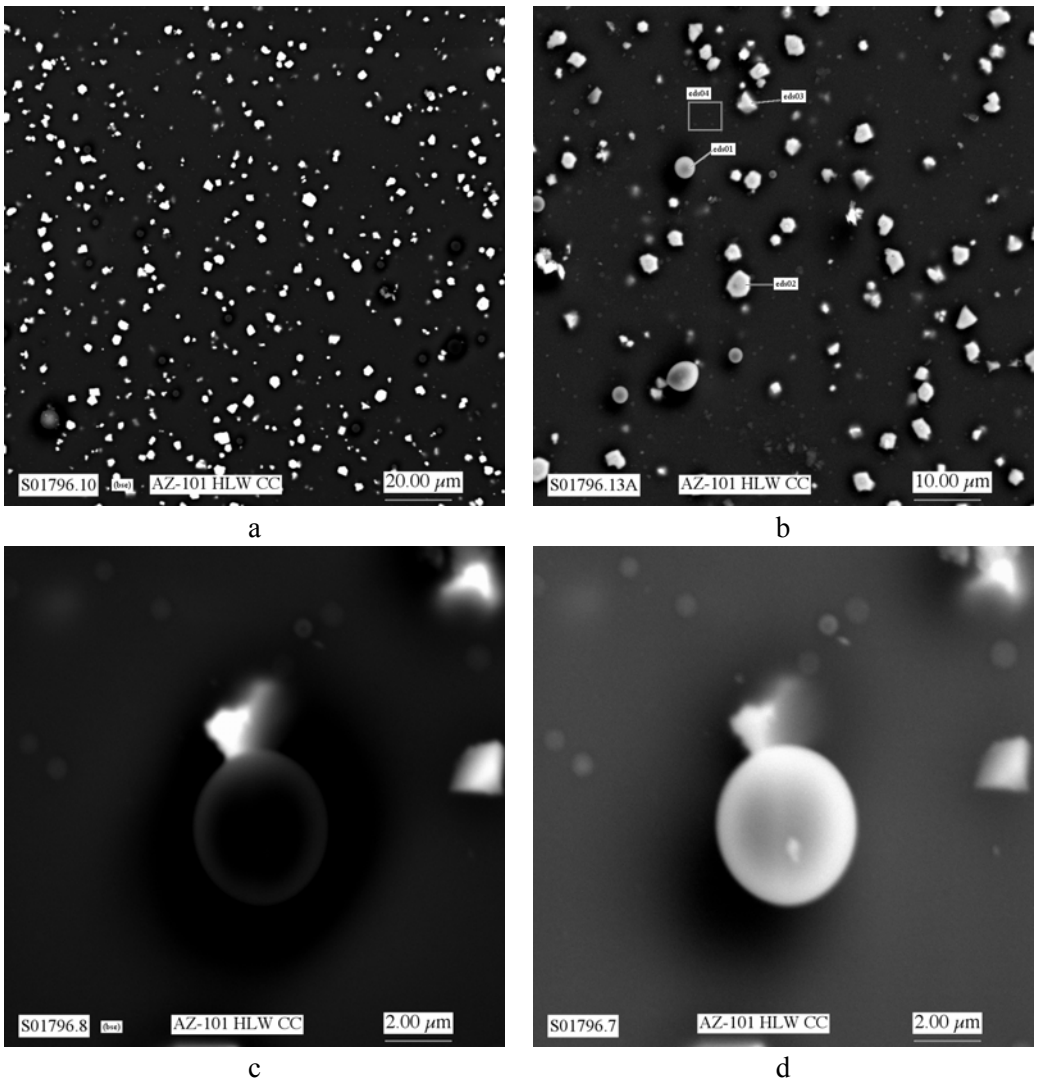

Figure 6.7. AZ-101 HLW Glass SEM Image: (a) and (b) Spinel Crystals and Gas Bubbles; (c) and (d) a Backscattered and a Secondary Electron Image of a Bubble

Table 6.16. Image Analysis of SEM Micrographs for Spinel Fraction in AZ-101 HLW Glass

Spinel area fraction	Average	0.0355
	Minimum	0.0296
	Maximum	0.0470
Standard deviation		0.0050
Relative error		0.14
Number of frames		12
Calculated Quenched glass density, g/mL		2.71
Spinel density, g/mL		5. 165 [(a)]
Spinel mass fraction		0.0663
Standard deviation		0.0093
(a) Density of trevorite (see http://www.webmineral.com/data/Trevorite.shtml)		

Table 6.17. Partial Molar Volumes (in mL/mol) of Glass Components (Vienna et al. 2002)

	mL/mol		mL/mol
Al_2O_3	46.15	MnO_x [(a)]	13.18
B_2O_3	30.05	Na_2O	19.83
BaO	18.87	NiO	12.67
CaO	15.21	SiO_2	25.32
F	7.53	SrO	17.61
Fe_2O_3	39.16	TiO_2	17.96
K_2O	37.74	ZnO	15.07
Li_2O	9.94	ZrO_2	27.08
MgO	13.03	Others [(b)]	42.81

(a) MnO_x = MnO with some $MnO_{1.5}$.
(b) Others are all remaining components.

The CCC glass-matrix composition is different from the quenched (crystal-free) glass and is subjected to the mass-balance equation

$$c_i c_S + m_i(1 - c_S) = g_i \tag{6.6}$$

where g_i is the i-th glass matrix component mass fraction, and c_i is the i-th spinel component mass fraction. Spinel mass fraction in the glass can be obtained from Equations (6.4) to (6.6) provided that the spinel composition is known. As explained below, it was not possible to obtain spinel composition from the EDS analysis. However a semi-quantitative estimate based on the EDS showed that roughly 40% of Fe_2O_3 and 90% of Cr_2O_3, MnO, NiO, and ZnO from glass ended up in spinel; this estimated composition is shown in Table 6.18.

Table 6.18. Estimated Spinel Composition (c_i) in Mass Fractions of Oxides

	Mass Fraction
Cr_2O_3	0.0177
Fe_2O_3	0.6235
MnO	0.0418
NiO	0.0621
ZnO	0.2548

Connecting Equations (6.4) to (6.6) and performing some algebra, the following expression for the spinel mass fraction was obtained:

$$c_S = \frac{v_M}{S + v_C} \tag{6.7}$$

where

$$v_M = \sum_{i=1}^{N} \frac{v_i g_i}{M_i} \tag{6.8}$$

$$v_C = \sum_{i=1}^{N} \frac{v_i c_i}{M_i} \tag{6.9}$$

and

$$S = \frac{1 - v_S}{\rho_S v_S} \tag{6.10}$$

Equations (6.8) to (6.10) define auxiliary variables, of which only v_M, the molar volume of glass with zero spinel content, has a clear physical meaning; v_C can be understood as the partial molar volume of spinel dissolved in glass, and S is the volume of the matrix glass per a mass unit of spinel. Using the above values (ρ_S = 5.163 g/mL, v_S = 0.0355, g_i from Table 6.6, and c_i from Table 6.18), v_M = 0.369 mL/g, v_C = 0.216 mL/g, and S = 5. 260 mL/g were obtained. With these values, by Equation (6.7), the mass fraction of spinel in the AZ-101 HLW glass is 6.73±0.94 mass%. Hence, the c_S value is within the interval of 5.85 and 7.76 mass%; this is in reasonable agreement with 7.1 mass% obtained from quantitative XRD analysis.

Figure 6.7 shows SEM micrographs of the spinel crystals. Most of the crystals are 0.5 to 3 μm in size. The EDS spectrum of a typical crystal, Figure 6.8, indicates that the crystal is spinel containing Fe, Ni, Cr, Mn, and Zn. The sample radiation did not allow quantitative determination of crystal composition. By Table 5.13, the most likely mineral components of spinel in AZ-101 HLW glass are magnetite (Fe_3O_4), trevorite, ($NiFe_2O_4$), nichromite ($NiCr_2O_4$), chromite ($FeCr_2O_4$), franklinite [$Zn(Mn,Fe)_2O_4$], jakobsite [$(Mn,Fe)(Mn,Fe)_2O_4$), and zincochromite ($ZnCr_2O_4$). Provided that the Table 6.18 estimate is realistic, the spinel in AZ-101 HLW glass has a chemical formula:

$$Ni(II)_{0.20}Zn(II)_{0.74}Fe(II)_{0.06}Fe(III)_{1.81}Cr(III)_{0.06}Mn(III)_{0.13}O_4$$

Smooth spherical or elliptical objects can be seen in Figure 6.7a and Figure 6.7b. One of these objects is shown in Figure 6.7c (a backscattered image) and Figure 6.7d (a secondary electron image). The spherical objects were identified as gas bubbles because other possibilities, such as solid spherical particles on the sample surface or liquid-liquid phase separation, were ruled out and because the spherical objects have a composition indistinguishable from the glass matrix (compare the two EDS spectra in Figure 6.9). The cause of a dark halo around the bubble (see Figure 6.7c) is most likely due to localized charging. Bubbles (voids) in sample surfaces can cause localized charging because of difficulties in obtaining a good conductive coating inside of the voids. The contrast was deliberately manipulated in Figure 6.10 to accentuate the halos around crystals and bubbles. While the dark areas around crystals could be interpreted as concentration layers depleted of Fe, Ni, and other spinel-forming components, the larger dark areas around bubbles can hardly be depleted of the same elements. It is, therefore, more likely that the halos are artifacts associated with sample preparation (polishing, coating) resulting in surface charging.

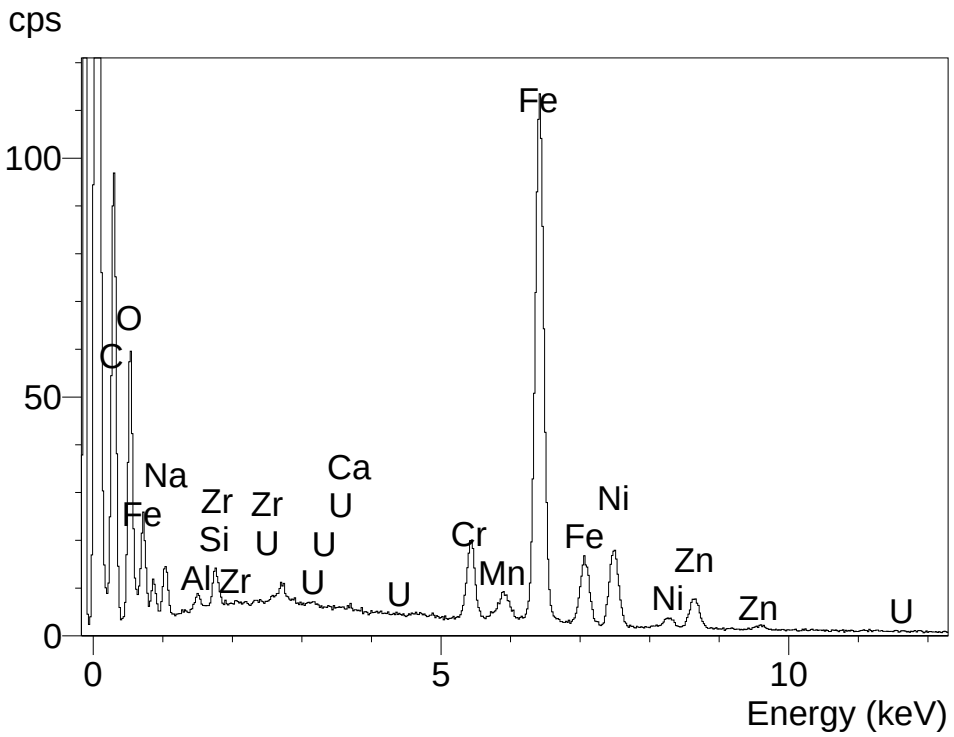

Figure 6.8. EDS Spectrum of Spinel Crystal in AZ-101 HLW Glass

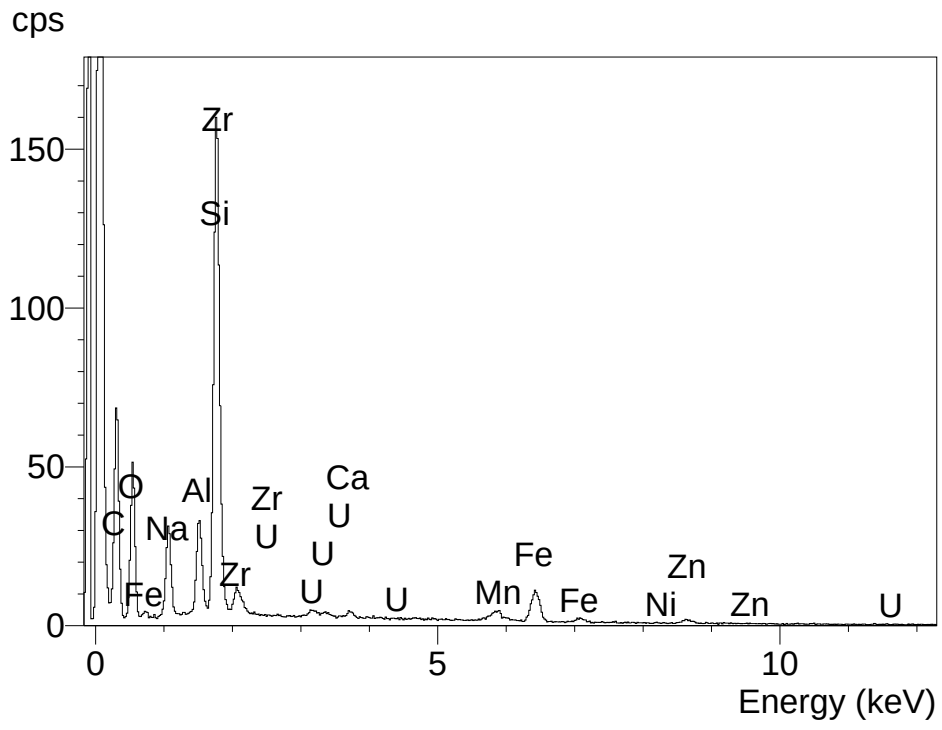

Figure 6.9. EDS Spectra of AZ-101 HLW Glass (top) and Glass Bubble (bottom—next page)

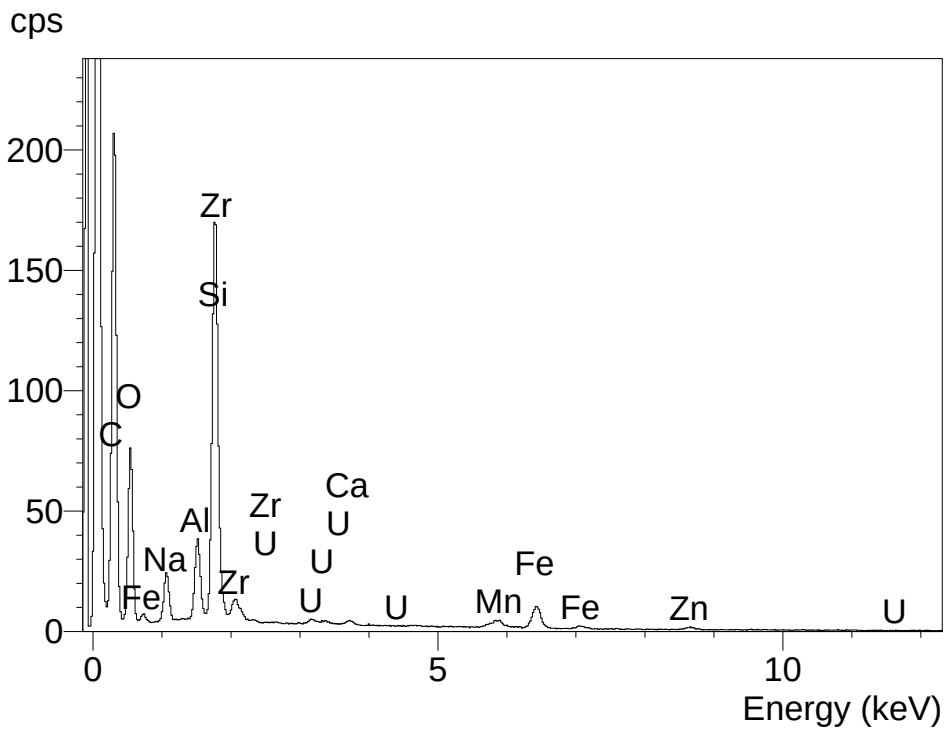

Figure 6.9 (contd)

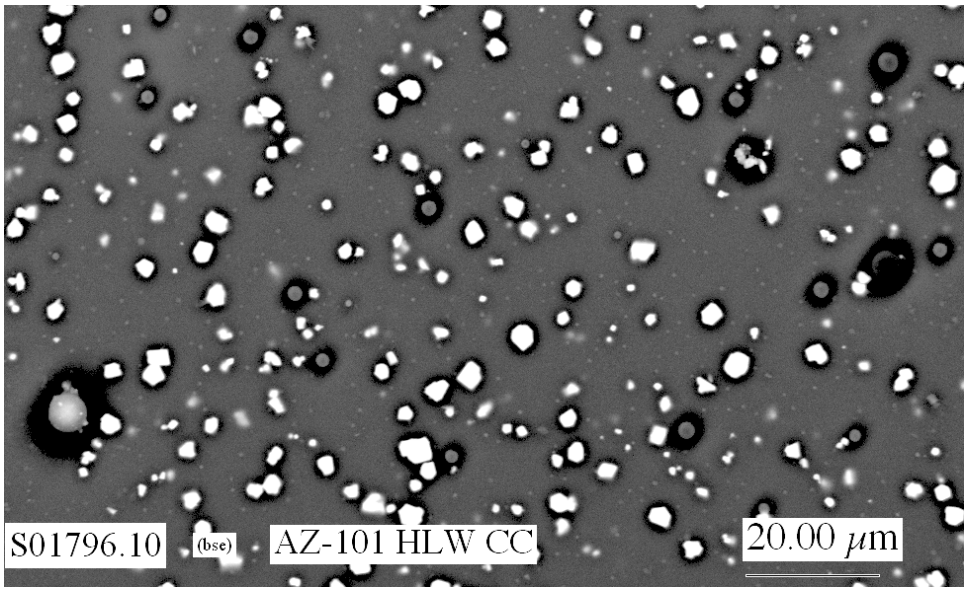

Figure 6.10. AZ-101 HLW Glass SEM Backscattered Image

6.4 Product Consistency Test

Solution concentrations for the 7-day 90°C PCT triplicate measurements are listed in Table 6.19. These triplicate values were averaged and converted to average normalized releases. Table 6.20 summarizes the results for AZ-101 HLW glass and Table 6.21 for EA glass. The normalized releases were calculated using the equation

$$r_i = \frac{c_i - c_{Bi}}{g_i \sigma} \tag{6.11}$$

where r_i is the i-th element normalize release, c_i is the i-the element concentration in PCT solution, c_{Bi} is the i-th element concentration in the blank, g_i is the i-th element mass fraction in glass, and σ is the glass surface-to-solution volume ratio ($\sigma = 2000\ m^{-1}$). The standard deviations in Table 6.20 (AZ-101 HLW) and Table 6.21 (EA) were calculated as SD = SD(c_i)/(2000g_i), where SD(c_i) were obtained from data listed in Table 6.19. Note that the c_i are the g/m^3 values given in Table 6.20.

Table 6.19. PCT Solution Concentrations in g/m^3 and pH Values

	AZ-101 HLW			EA			Blank
	1	2	3	1	2	3	
	(g/m^3)						
B	16.1	17.0	15.8	520	336	338	0.029
Li	11.3	12.2	11.2	144	112	113	0.020
Na	37.4	46.6	37.7	1200	913	913	0.360
Si	65.3	62.4	64.2	827	662	668	0.040
pH	9.33	9.45	9.45	11.67	11.56	11.56	6.61

Table 6.20. PCT Results for AZ-101 HLW Glass

	g_i	c_i	r_i	SD	RSD
	fraction	g/m^3	g/m^2	g/m^2	%
B	0.0313	16.3	0.260	0.010	3.8
Li	0.0173	11.6	0.333	0.016	4.8
Na	0.0785	40.6	0.256	0.033	13.0
Si	0.2070	64.0	0.154	0.004	2.3
pH	n/a	9.41	n/a	n/a	n/a

g_i is the i-th element mass fraction in glass.
c_i is the i-the element concentration in PCT solution.
r_i is the i-th element normalized release.
SD is the standard deviation.
RSD is the relative standard deviation.

Table 6.21. PCT Results for EA Glass

	g_i (fraction)	c_i (g/m^3)	r_i (g/m^2)	SD (g/m^2)	RSD (%)	r_i[(a)] (g/m^2)	SD (g/m^2)
B	0.0351	398	5.67	1.51	26.5	8.36	0.61
Li	0.0198	123	3.11	0.46	14.8	4.80	0.37
Na	0.1246	1009	4.05	0.66	16.4	6.67	0.45
Si	0.2278	719	1.58	0.21	13.0	1.96	0.19
pH	n/a	11.60	n/a	n/a	n/a	11.85	n/a

g_i is the i-th element mass fraction in glass.
c_i is the i-the element concentration in PCT solution.
r_i is the i-th element normalized release.
SD is the standard deviation.
RSD is the relative standard deviation.
(a) Jantzen et al. 1993 data.

As Table 6.20 and Table 6.21 show, normalized releases of B, Li, and Na from AZ-101 HLW glass are 0.26 to 0.33 g/m^2. These very low values are 5 to 11% of the corresponding releases of the EA standard reference glass (3 to 7% of the values reported by Jantzen et al. 1993). Note that hot cell releases from EA glass are somewhat lower (by 20 to 40%) than those measured in a nonradioactive environment by Jantzen et al. (1993). Note that radiolytic effects on the solution in contact with the glass can change the pH of the solution to a more acid condition (Wronkiewicz 1993). This could account for the difference in the EA glass behavior between radioactive and nonradioactive environments.

Measured PCT releases were compared with predictions from a model recently reported by Amidan et al. (2004) and by Piepel and Cooley (2003), according to which

$$r_j = \exp\left(\sum_{i=1}^{N} b_{ij} g_i^N\right) \tag{6.12}$$

where

$$g_i^N = \frac{g_i}{\sum_{i=1}^{N} g_i} \tag{6.13}$$

Here j stands for B, Li, and Na, b_{ij} is the i-th component coefficient for j-th element release, g_i is the i-th component mass fraction in glass, N is the number of components in glass for which the model was fit, and g_i^N is the i-th component normalized mass fraction. The b_{ij} values are listed in Table 6.22.

Table 6.22. PCT Component Coefficients to Obtain r_j ($j \equiv$ B, Li, Na) in g/m^2

	b_{iB}	b_{iLi}	b_{iNa}
	(g/m^2)		
Al_2O_3	-10.19	-7.76	-9.86
B_2O_3	5.58	3.27	2.47
BaO	n/a	16.48	n/a
CaO	-12.40	-17.26	-6.85
Fe_2O_3	-1.90	-4.69	-2.67
K_2O	n/a	120.43	n/a
Li_2O	10.97	11.55	11.71
MgO	n/a	-25.16	n/a
Na_2O	13.00	10.78	16.88
SiO_2	-4.47	-3.06	-4.88
SrO	n/a	-3.40	-11.17
ThO_2	-124.03	n/a	-115.93
TiO_2	n/a	-44.40	n/a
UO_2	n/a	4.12	n/a
ZnO	n/a	-10.46	n/a
ZrO_2	n/a	-7.76	n/a

Calculations were conducted for the target glass, and the averaged analytical composition estimates are listed in Table 6.6. Results of calculation are summarized in Table 6.23 and graphically presented in Figure 6.11. The B release was overpredicted by 65%, the Li release was underpredicted by 14%, and the Na release was overpredicted by 47%. Considering the low release values of AZ-101 HLW glass and the fact that radioactive glasses have lower PCT releases than nonradioactive glasses of the same composition, the model predictions appear satisfactory. Wronkiewicz, 1993 gives a good overview of this kind of behavior.

Table 6.23. Calculated PCT Normalized Releases in g/m^2 from AZ-101 HLW Glass

	Na_2O_2-NaOH	KOH-KNO_3	Acid Digestion	Average	Target
	(g/m^2)				
B	0.451	0.413	0.419	0.428	0.599
Li	0.291	0.284	0.283	0.286	0.445
Na	0.404	0.351	0.377	0.377	0.549

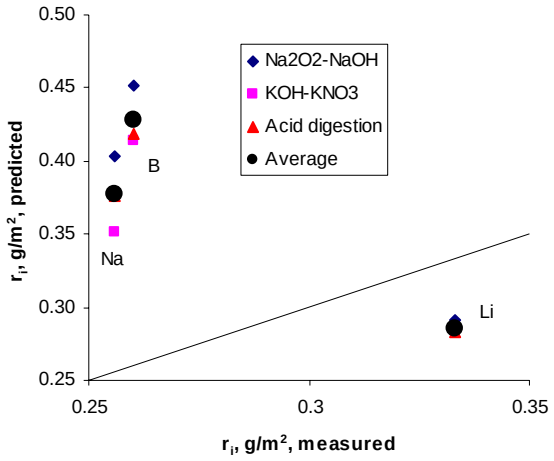

Figure 6.11. Predicted Versus Measured PCT Releases from AZ-101 HLW Glass

It is important to assess the effect of spinel precipitation and the difference between the glass targeted and glass actually made. The CCC-treated AZ-101 HLW glass had 6.81±0.95 mass% of spinel of the estimated composition listed in Table 6.18. Spinel precipitation changes the composition of the amorphous matrix. This impacts the PCT. Because spinel has a high chemical durability, the PCT releases from the glass with spinel are determined by the composition of the remaining amorphous matrix. The matrix composition is given by the formula

$$m_i = \frac{g_i - Cs_i}{1 - C} \tag{6.14}$$

where m_i is the i-th component mass fraction in the amorphous matrix, s_i is the i-th component mass fraction in spinel, and C is the spinel mass fraction in glass. Applying Equation (6.12) and (6.13) to m_i instead of g_i, we obtain after simple rearrangement

$$\ln(r_j) = \frac{\sum_{i=1}^{N} b_{ij} g_i - C\sum_{i-1}^{N} b_{ij} s_i}{\sum_{i=1}^{N} g_i - C\sum_{i-1}^{N} s_i} \tag{6.15}$$

With this equation, the PCT values for the amorphous matrix were calculated as a function of C. The results, based on measured (best average) g_i values listed in Table 6.6, are shown in Figure 6.12. The measured data are also included as data points in Figure 6.12 for $C = 0.071$, a value obtained from XRD analysis.

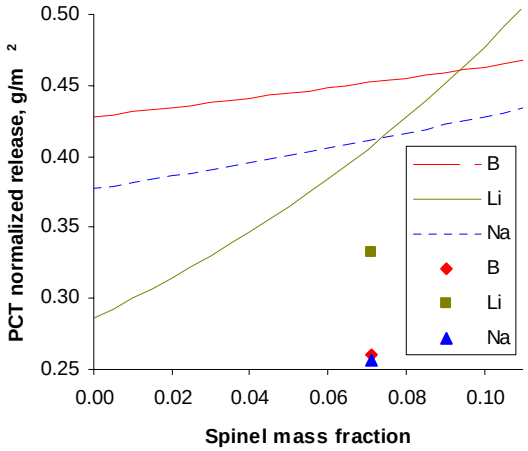

Figure 6.12. Effect of Spinel Mass Fraction on PCT Normalized Releases (lines represent model predictions and data points measured values)

As seen in Table 6.22, the model predicts relatively minor effects of Fe_2O_3 on PCT B and Na releases and a somewhat stronger effect on PCT Li release. A substantial effect is predicted for ZnO on Li release, but negligible effects on B and Na releases. Negligible effects are also predicted for other spinel components (Cr_2O_3, NiO, and MnO). These features are clearly reflected in Figure 6.12, showing that B and Na releases are overpredicted whether the impact of spinel on the amorphous matrix is considered or not. The model provides a slightly more realistic assessment for the Li release. Whereas the spinel-free glass underpredicts the Li release, as shown in Figure 6.11, the Li release from the matrix sharply increases as the spinel fraction increases, resulting in an overpredicted value for $C = 0.071$.

Another important question is "How much were PCT releases affected by the difference between the targeted waste loading (31.75 mass%) and the actual waste loading (34.84 mass%)?" Model calculation shows that the PCT normalized releases are estimated approximately twice as high from the targeted composition as from the actual composition (Table 6.24). Though the models may predict the release values for a particular composition with a relatively low accuracy, the differences between close compositions are usually predicted better. Therefore, the difference in the PCT releases between the glass targeted and the glass made needs to be considered real and calls for explanation, which is given in the following two paragraphs.

The waste loading may affect the PCT releases in a variety of ways. It is possible to increase the waste loading in glass without changing the glass composition in a significant way by adjusting the composition of the additives. In such a case, the waste loading would have a negligible impact on PCT. Another extreme would be using the same additive mix and blending it with the waste in varied proportions. An example of this, based on the original VSL formulation (Glass I in Table 5.2) is shown in Figure 6.13 in which the model-calculated PCT releases are plotted against the waste loading. The figure shows that the predicted releases of B decrease with increasing waste loading. This is as expected. For example, the PCT normalized release of B from a hypothetical glass made from pure waste would be 0.076 g/m^2, whereas a glass made from the additives without waste would have an order-of-magnitude higher value of 1.27 g/m^2; hence, the PCT Na release would decrease with values between these two extremes.

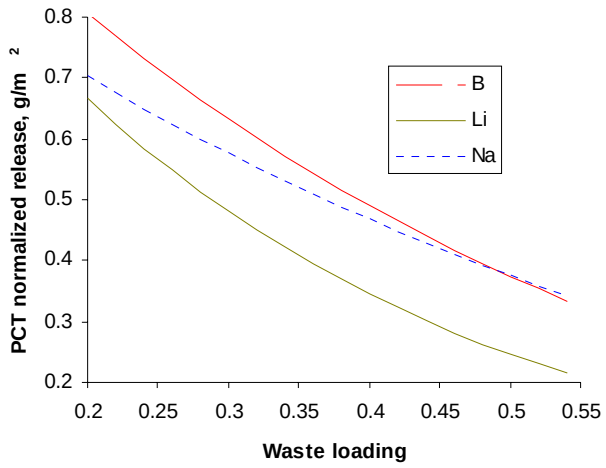

Figure 6.13. Effect of AZ-101 HLW Loading on Glass PCT

Table 6.24. Effect of Waste Loading on PCT Normalized Releases in g/m^2

	Glass I[(a)]			Actual/Target[(b)]		
W	r_B	r_{Li}	r_{Na}	r_B	r_{Li}	r_{Na}
	g/m^2			g/m^2		
0.3347	0.580	0.429	0.537	0.260	0.333	0.256
0.3175	0.605	0.454	0.556	0.599	0.445	0.549

(a) Model calculations for blended HLW mixed with additives as defined in Table 5.2.
(b) Model calculations for actual (averaged) and targeted glass as listed in Table 6.6.

As Figure 6.2 and Table 6.6 show, and as Table 6.7 clearly indicates, the differences between the actual and targeted composition cannot be simply expressed as a result of a difference in waste loading. Table 6.24 reviews model calculations for two waste-loading values and shows that the difference in the waste loading is associated with a relatively mild difference of the PCT outcome in the Glass I example, where the waste and additive compositions were constant, and their ratio was the only variable, compared to the case where a change in waste loading was accompanied by additional changes in glass composition. Focusing on the B normalized release, Table 6.22 shows that Al_2O_3 and Fe_2O_3 decrease B release, whereas B_2O_3 and Na_2O increase it. Table 6.6 shows that the glass made has a higher content of Al_2O_3 and Fe_2O_3 and a lower content of B_2O_3 and Na_2O than the glass targeted. As Table 6.7 indicates, these differences go beyond the mere impact of the waste loading.

6.5 Toxicity Characteristic Leaching Procedure

A summary of the ICP-AES analyses, including QC performance, of the TCLP extracts from HNO_3 and HNO_3 + HCl digestions is given in Appendix D. The TCLP data are summarized in Table 6.25. Concentrations of the universal treatment standards (UTS)-listed elements in the AZ-101 HLW glass are also shown for comparison. The AZ-101 HLW glass passed the UTS limits for all listed elements. Out of the UTS-listed elements (plus Cu), no measurable concentration was detected for Ag, As, Be, Cr, Cu,

Hg, Sb, Se, Tl, and V. Of the remaining UTS-listed elements, concentrations of Ba, Ni, and Zn were below 10% of the UTS limit. The Pb concentration was 23% of the UTS limit, and the Cd concentration was 57.7% of the UTS limit. Note that the project approach is to meet the UTS limit for Sb, Be, Ni, and Tl for LDR variance, where, the requirement is only to document a "...significant reduction in mobility or toxicity." Since, "... significant reduction..." is hard to define. For delisting, the delisting limits must be met.

Apart from the UTS-listed elements and Cu, TCLP solution analysis was performed also for Al, B, Bi, Ca, Ce, Co, Dy, Eu, Fe, K, La, Li, Mg, Mn, Mo, Na, Nd, P, Pd, Rh, Ru, Si, Sn, Sr, Te, Th, Ti, Tl, U, W, Y, and Zr. Of these elements, only Al, B, Ca, Fe, Li, Mg, Mn, Na, Si, and Sr were present in measurable concentrations. A summary of elements with measurable concentrations in the TCLP solution are listed in Table 6.26. Data are sorted by the normalized TCLP concentration, obtained as a ratio of the TCLP solution concentration and the concentration in glass for each element.

Table 6.25. TCLP Results Summary

CAS #	Constituent	Ave. Sample Result (mg/L)[a]	MDL[a] (mg/L)	EQL[b] (mg/L)	Required for LDR	Delisting values (mg/L-TCLP)	UTS Limit (g/m^3)	Fraction of minimum limit (%)
7440-36-0	Antimony	0.039 U	0.039	0.659	yes	0.659	1.15	0.0
7440-38-2	Arsenic	0.052 U	0.052	3.08	HLVIT	3.08	5.000	1.0
7440-39-3	Barium	0.21 J	0.014	100	HLVIT	100	21.000	1.0
7440-41-7	Beryllium	0.00021 U	0.00021	1.22	yes	1.33	1.220	0.0
7440-43-9	Cadmium	0.064 J	0.0047	0.48	n/a	0.48	0.110	58
18540-29-9	Chromium	0.0065 U	0.0065	5.0	HLVIT	0.48	0.600	1.0
7440-50-8	Copper	0.025 U	0.025	29,200	HLVIT	5.0	n/a	n/a
7439-92-1	Lead	0.040 U	0.045	5.0	HLVIT	5.0	0.750	0.9
7439-97-6	Mercury	0.000023 U	0.000023	0.2	HLVIT	0.2	0.025	0.0
7440-02-0	Nickel	0.033 J	0.015	11	yes	12.1	11.00	4.4
7782-49-2	Selenium	0.045 U	0.045	1.0	HLVIT	1.0	5.700	4.0
7440-22-4	Silver	0.0076 U	0.0076	3.07	HLVIT	3.07	0.14	0.01
7440-28-0	Thallium	0.000023 J	0.0000035[c]	0.20	yes	0.282	0.200	0.01
7440-62-2	Vanadium	0.0053 U	0.0053	16.9	n/a	16.9	1.600	0.3
7440-66-6	Zinc	0.33 J	0.11	225	n/a	225	4.300	7.7

U = Undetected. Analyte was analyzed but not detected (e.g., no measurable instrument response) or response was less than the MDL.
J = Estimated value. Value is below EQL and above MDL.
Underlined values are ≥ MDL but have no EQL established for the current method.
(a) MDLs determined per Quality Assurance Plan ASO-QAP-001 Rev. 1 and adjusted by the average sample processing factors.
(b) As no specific estimated quantitation limits (EQL) have been established for TCLP solutions, the EQLs were set equal to the Universal Treatment Standards (UTS) for TCLP analyses or to the quantitation limit specified in the ASR if no UTS value is specified.
(c) The ICP/MS MDL was determined for each analytical run using 3 standard blank solutions which were evaluated throughout the analytical run.

Table 6.26. Concentration Data for Elements Detected in TCLP Solution

	Concentration in kg/m^3		Normalized Concentration - Solution conc/Glass conc[(a)]
	Glass	TCLP Solution	
Pb	1.5	0.178	0.1176
Ba	1.9	0.208	0.1069
Ca	9.1	0.944	0.1037
B	84.8	1.350	0.0159
Sr	4.4	0.047	0.0108
Zn	43.3	0.318	0.0073
Mg	1.8	0.010	0.0056
Li	47.0	0.233	0.0050
Mn	6.2	0.026	0.0042
Cd	16.1	0.065	0.0040
Ni	11.5	0.034	0.0029
Si	561.0	1.109	0.0020
Al	118.0	0.217	0.0018
Fe	227.5	0.342	0.0015
A ratio of the *i*-th component concentration in TCLP solution and and in glass			

The measured TCLP Cd release was compared with a model prediction (see Amidan et al. 2004). The model relating TCLP Cd release concentration (c_{Cd}) to composition was developed by Kot et al. (2003, 2004) in the form

$$c_{Cd} = K g_{CdO}^{b_{CdO}} \tag{6.16}$$

where

$$K = \exp\left(\sum_{i=1}^{N} k_i g_i^N\right) \tag{6.17}$$

Here $b_{CdO} = 0.9085$ is a constant and k_i is the i-th component coefficient; the k_i values are listed in Table 6.27. [Note that k_i's are dimensionless; to be strictly correct, the RHS of Equation (6.17) should have a pre-exponential factor $K_0 = 1$ g/m^3.] This is a preliminary model and is currently being updated.

The results of calculation, based on glass analyses listed in Table 6.6, are summarized in Table 6.28. The delisting limit for c_{Cd} is 0.48 g/m^3. The model predicts 0.16 g/m^3. The measured value was below the estimated quantitation limit of 0.48 g/m^3. Thus, the Cd concentration was overestimated by a factor of 2.5 (based on the average TCLP composition estimate).

Table 6.27. Coefficients Used in Equation (6.17) to Obtain TCLP for c_{Cd} in g/m^3

	$k_i^{(a)}$
Al_2O_3	0.323
B_2O_3	8.675
CdO	21.667
Fe_2O_3	1.014
Li_2O	9.406
MnO	6.447
Na_2O	10.126
SiO_2	-0.942
SrO	6.629
ThO_2	-0.597
UO_2	8.776
ZnO	14.311
ZrO_2	0.681

(a) W. K. Kot et al. 2003. *Regulatory Testing of RPP-WTP HLW Glasses for Compliance with Delisting Requirements*, VSL-03R3780-1, Vitreous State Laboratory, The Catholic University of America, Washington, DC.

Table 6.28. TCLP Solution Concentrations of Cd in g/m^3 Predicted by Applying Formula (6.16) with Coefficients Listed in Table 6.27 to Compositions Listed Table 6.6

Na_2O_2-NaOH	KOH-KNO_3	Acid Digestion	Average
g/m^3			
0.18	0.15	0.14	0.16

The TCLP solution concentration was measured on a quenched glass sample. It is important to assess if spinel crystallization increases or decreases the TCLP release of hazardous elements. For example, the CdO content in glass increases with increasing spinel fraction because CdO is not a component of spinel formed from this melt. In particular, by Equation (6.14), the precipitation of 7.1 mass% spinel increases the CdO content in the amorphous phase from 0.68 mass% (see the average estimate in Table 6.6) to 0.73 mass%. At the same time, the *K* value in Equations (6.16) and (6.17) will decrease because of the decrease in fractions of amorphous phase constituents (ZnO and MnO) that, by Table 6.27, possess high k_i coefficients. Calculation shows that the predicted Cd concentration in TCLP solution decreases from 0.16 g/m^3 to 0.14 g/m^3 as a result of crystallization of 7.1 mass% of spinel. Although the model overpredicts the actual data, the qualitative impact of spinel crystallization (i.e., a decrease rather than increase) is likely to be predicted correctly.

Regarding the effect of waste loading, calculations similar to those performed for PCT were also done for the TCLP. Blending the HLW and additives of compositions listed in Table 5.2 in varied proportions and calculating the Cd concentration in the TCLP solution with the above model show that the Cd release increases as the waste loading increases. The result of the model calculation is displayed in Figure 6.14. In addition, a calculation was performed on the target composition shown in Table 6.6. The model predicts 0.17 g/m^3 of Cd in the TCLP solution. This number may be larger than 0.16 g/m^3 listed in Table 6.28 for the glass actually produced.

Note also that radiolytic effects on the solution in contact with the glass can change the pH of the solution to a more acid condition (Wronkiewicz 1993). This could account for differences in the TCLP results vs model behavior between radioactive and nonradioactive environments.

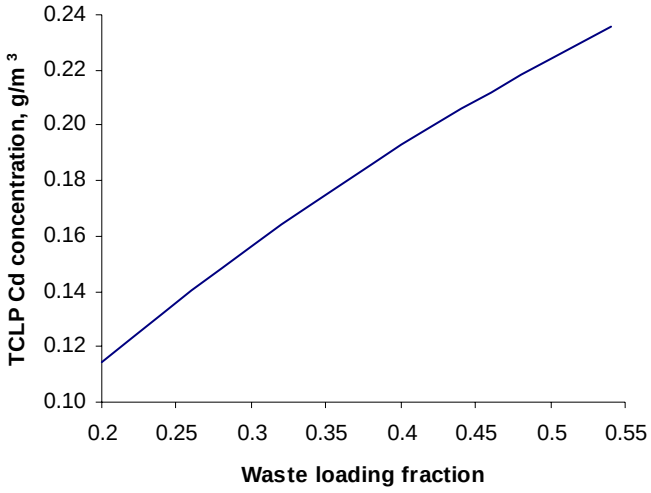

Figure 6.14. Model Predicted Effect of Waste Loading on Cd Concentration in TCLP Solution

6.6 Comparison of the Durability and Crystallinity of Actual and Simulated AZ-101 IHLW

The analyzed composition of the actual AZ-101 IHLW glass and a simulated AZ-101 IHLW version (HLW98-95) produced by VSL (Kot and Pegg 2003) are compared in Table 6.29. In general, they show good agreement in overall composition. Hence, it is believed that they should show comparable chemical durability.

In Table 6.30, the available crystallinity data for the quenched and CCC heat treated simulated and actual waste glasses is presented. Note that the Spinel has about twice the density of the glass (5.21/2.71 = 1.92), so the 1.8 vol% reported by VSL would be equivalent to about 3.5 wt% or the 6.6 wt% reported by PNWD would be about 3.4 vol%.

In Table 6.31, the PCT results for the quenched (Q) and CCC heat treated simulated and actual waste glasses is presented. The release values for both the actual and simulated glasses are comparable and considerably better than those for the EA Glass.

Table 6.29. Averaged Best Analytical Estimates for AZ-101 HLW Glass Composition and VSL Glass HLW98-95

	AZ-101 HLW wt% Glass Average	HLW98-95 (wt %)		AZ-101 HLW wt% Glass Average	HLW98-95 (wt %)
SiO_2	44.30	42.50	SrO	0.20	0.19
Na_2O	10.58	11.82	Cr_2O_3	0.13	0.36
Fe_2O_3	12.00	12.75	K_2O	0.02	0.12
B_2O_3	10.08	10.64	MgO	0.11	0.09
Al_2O_3	8.23	6.43	SO_3	0.11	0.10
Li_2O	3.73	3.76	PdO	0.10	0.07
ZrO_2	3.74	3.91	RuO_2	0.08	0.03
ZnO	1.99	1.91	BaO	0.06	0.10
UO_3	0.90	1.23	PbO	0.04	0.07
CdO	0.68	0.85	Ag_2O	0.01	0.04
NiO	0.54	0.64	Cl	0.03	0.09
CaO	0.47	0.42	CuO	0.02	0.05
P_2O_5	0.45	0.37	F	0.02	-
MnO	0.30	0.47	Rh_2O_3	0.08	0.01
La_2O_3	0.47	0.18	TiO_2	0.02	0.00
Ce_2O_3	0.06	0.29	Y_2O_3	0.02	-
Nd_2O_3	0.17	0.21	Bi_2O_3	0.02	-
SnO_2	0.23				

Table 6.30. Observed Crystallinity of Simulated and Actual Waste Glasses

Property	VSL Simulated HLW Glass		Actual AZ-101 IHLW	
Heat Treatment	CCC	Quenched	CCC	Quenched
Amount of Crystalline Phase	1.8 vol %	None reported[(a)]	3.4 vol%	trace
Crystalline Phase	Spinel		Spinel	Spinel
[(a)] 0.5% spinel after 70 hour soak at 950°C				

Table 6.31. PCT Normalized Release for Actual and Simulated Waste Glasses

		Actual AZ-101 IHLW	VSL Simulated Waste Glass (HLW98-95)
CCC Glass	**Element**	**Normalized Release, g/m^2**	
	B	0.260	0.166
	Li	0.333	0.290
	Na	0.256	0.217
	Si	0.154	0.141
	pH	9.41	11.03
Quenched Glass	B	n/a	0.277
	Li	n/a	0.293
	Na	n/a	0.230
	Si	n/a	0.158
	pH	---	10.34

In Table 6.32, the TCLP results for the simulant and actual glasses are compared. These results are in general agreement except for the cadmium results, which are high for the analysis performed outside PNWD; in general, the results appear to be in agreement for the actual and simulated waste glasses.

Table 6.32. Average TCLP Data for the Glass HLW98-95 and AZ-101 HLW Glass

Element	Symbol	(Glass HLW98-95) Concentration (ppm) of Element in Leachate (VSL Analysis)[a]	AZ-101 HLW Ave. Sample Result (mg/L)	UTS Limit (ppm)	Delisting Limit (ppm)
Antimony	Sb	–	0.039 U	1.15	0.659
Arsenic	As[b]	–	0.052 U	5.00	3.08
Barium	Ba	<0.4	0.21 J	21.00	100.00
Beryllium	Be	–	0.00021 U	–	–
Cadmium	Cd	0.10	0.064 J	0.11	0.48
Chromium	Cr	0.01	0.0065 U	0.60	5.00
Copper	Cu	0.01	0.025 U	NA	29200.00
Lead	Pb	<0.02	0.040 U	0.75	5.00
Mercury	Hg	–	0.000023 U	–	–
Nickel	Ni	0.07	0.033 J	11.00	22.6
Selenium	Se	–	0.045 U	5.70	1.00
Silver	Ag	<0.003	0.0076 U	0.14	3.07
Thallium	Tl	–	0.000023 J	0.20	0.282
Vanadium	V	–	0.0053 U	1.6	16.9
Zinc	Zn	0.39	0.33 J	4.3	225.00

(a) TCLP data collected at VSL do not meet the QAPjP requirements. (Kot et al. 2003)
(b) Not present in glass.
ND - Not detected. NA - Not applicable

In conclusion, the simulated and waste glasses appear to have similar durabilities in spite of noticeable differences in the level of crystallinity of the CCC heat-treated glasses (see Table 6.30).

7.0 Conclusions

A sample of pretreated AZ-101 HLW sludge was mixed with Cs and Tc ion exchange eluates and mineral additives according to the recipe developed by VSL. The resulting melter feed was converted to HLW glass. The glass sample was tested to demonstrate the WTP ability to satisfy the RPP-WTP project contract requirements concerning waste loading, chemical composition, radionuclide content, identification and quantitation of crystalline phases, and waste form leachability by the PCT and TCLP (Smith, 2002). The main results of testing are summarized as follows:

1. The waste loading fraction of AZ-101 HLW glass was 34.84 mass%. This value exceeds the target of 31.75 mass% by 9.73 relative %.

2. Chemical analysis showed that AZ-101 HLW glass composition was close to target. The glass contained, on mass basis, 44.3% SiO_2, 12.0% Fe_2O_3, 10.6% Na_2O, 10.1% B_2O_3, 8.2% Al_2O_3, 3.7% Li_2O, 3.7% ZrO_2, 2.0% ZnO, 0.9% UO_3, and 4.5% of other components. The target composition was 44.7% SiO_2, 11.2% Fe_2O_3, 11.9% Na_2O, 10.6% B_2O_3, 7.3% Al_2O_3, 3.4% ZrO_2, 3.8% Li_2O, 2.0% ZnO, 0.9% UO_3, 4.3% of other components.

3. Radionuclides with $t_{1/2}$ > 10 years currently (in 2004) present in AZ-101 HLW glass are ^{63}Ni, ^{90}Sr, ^{99}Tc, ^{137}Cs, ^{151}Sm, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{237}Np, ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{242}Pu, ^{241}Am, ^{243}Cm, and ^{244}Cm. The 2004 and 2015 activity is mainly due to ^{90}Sr (61%) and ^{137}Cs (38%); in 3115, the main sources of radioactivity will be ^{241}Am (71.4%), ^{239}Pu (16.4%), ^{99}Tc (7.5%), and ^{240}Pu (4.2%). In a WTP canister containing 1.18 m^3 of AZ-101 HLW glass, the total mass of U is 16.2 kg (137 g of ^{235}U) and the total mass of Pu is 160 g (149 g of ^{239}Pu). The concentration of Pu in AZ-101 HLW glass is 136 g/m^3. The isotope mass fractions of the total U are 0.0067% ^{234}U, 0.84% ^{235}U, 0.06% ^{236}U, and 99.1% ^{238}U. The isotope mass fractions of the total Pu are 92.7% ^{239}Pu, 7.21% ^{240}Pu, and 0.08% ^{241}Pu.

4. By quantitative XRD analysis, the AZ-101 HLW CCC glass sample contained 7.1 mass% of spinel, predominantly trevorite. By image analysis applied to SEM micrographs, the volume fraction of crystals was 3.55±0.50 vol%, corresponding to 6.81±0.95 mass%. Most of the crystals were 0.5 μm to 3 μm in size and contained Fe, Ni, Cr, Mn, and Zn.

5. The 7-day 90°C PCT normalized releases of B, Li, and Na from AZ-101 HLW glass were 0.26 g/m^2, 0.33 g/m^2, and 0.256 g/m^2 respectively. These very low values were 5 to 11% of the corresponding releases of the EA standard reference glass.

6. The AZ-101 HLW glass passed the UTS limits for all listed elements. Out of the UTS-listed elements (plus Cu), no measurable concentration was detected for Ag, As, Be, Cr, Cu, Hg, Sb, Se, Tl, and V. Concentrations of Ba, Ni, and Zn were < 10% of the UTS limit. The Pb concentration was 23% of the UTS limit, and the Cd concentration was 58% of the UTS limit.

8.0 Acknowledgements

Several individuals who significantly contributed to this work are not listed as co-authors. However, their important contribution is greatly appreciated. Without making a claim for completeness, their names and contributions are listed as follows:

Michael Krouse helped by producing machined parts.
Dennis F. Smith and Larry D. Lang fabricated key parts for testing.
Michael Tesky modified the test equipment.
Wayne Cosby put the report in its final form.

Appendix A

Glass-Formulation Details

Appendix A: Glass-Formulation Details

This appendix provides compositions of the HLW sludge sample, the Cs and Tc eluates, and minerals and the proportions in which these materials were blended to produce a melter-feed sample. According to the VSL formulation, the AZ-101 HLW sludge was to be mixed with the eluates at the proportions corresponding to the tank inventories at which the blend is expected to be vitrified in the WTP. Since only a limited amount of some of the eluates was available in sufficient quantities, the blending ratios were adjusted, and chemicals were added to make the glass as close as possible to the composition formulated by the VSL.

A.1. Blended AZ-101 HLW

In the WTP, the HLW pretreated sludge, ion exchange column eluates, and Sr/TRU ppts from the pretreatment of LAW will be blended and then mixed with glass-forming and modifying additives to form a melter feed that will be vitrified. The HLW glass batch was formulated to match the desired processing behavior in the melter, to obtain the glass properties required for the repository, and to achieve the highest waste loading compatible with the glass-property constraints and waste-processing uncertainties.

To formulate HLW glass for AZ-101 pretreated sludge blended with ion exchange column eluates, VSL used a double-normalized *i*-th eluate blending ratio defined as

$$\beta_i = b_i \frac{c_{iNa}}{c_{Fe}} \tag{A.1}$$

where c_{Fe} is the Fe mass per unit mass of HLW, c_{iNa} is the Na mass per unit volume of *i*-th eluate, and b_i is the *i*-th eluate blending volume defined as

$$b_i = \frac{V_i}{M} \tag{A.2}$$

where V_i is the *i*-th eluate volume to be mixed with the mass M of dry HLW. Thus, β_i is the mass of Na from the *i*-th eluate per unit mass of Fe in the HLW sludge. Based on this formalism, using the reported waste compositions and expected waste amounts, VSL proposed a formula for the AZ-101 HLW glass batch to be melted by PNWD.

When PNWD put together the actual batching plan for making the AZ-101 HLW glass batch, it was found that the waste components were not available in the ratios assumed by VSL, making it necessary to adjust the glass-batch formulation. Table A.1 presents data from the VSL spreadsheet. The VSL spreadsheet data are expressed in terms of blending volumes of the eluates based on the total radioactivity, R_i, of ^{137}Cs or ^{99}Tc in i-th eluate. Accordingly,

$$b_i = \frac{R_i}{r_i M} \tag{A.3}$$

where r_i is the i-the eluate ^{137}Cs or ^{99}Tc radioactivity density ($r_i = R_i/V_i$). The calculated values of β_i and b_i for each eluate are given in Table A.1. In this table, the eluate concentration is expressed as the ^{137}Cs or ^{99}Tc activity in mCi/L divided by Na concentration in g/L.

Table A.1. Blending Ratios for the Cs and Tc Eluates

		Tank	**AP-101**	**AZ-101**	**AP-101**	**AZ-101**
		Eluate	**^{137}Cs**	**^{137}Cs**	**^{99}Tc**	**^{99}Tc**
Tank inventory ratio (TIR)	$R_i/c_{Fe}M$	mCi/g(Fe in HLW)	27	260	0.00900	0.0533
Eluate activity per sodium (EAS)	$r_i/c_{i\mathrm{Na}}$	mCi/g Na	906	16189	1.48	17
Blend ratio	β_i	g(Na in eluate)/g(Fe in HLW)	0.02980	0.01606	0.00608	0.00314
Na concentration	$c_{i\mathrm{Na}}$	g/L	0.844	0.803	0.282	0.219
Cs/Tc radioactivity density	r_i	mCi/L	765	13000	0.417	3.72
Blending volume	b_i	L(eluate)/kg(dry HLW)	7.146	4.048	4.364	2.897
By Equations (A.1) to (A.3), β_i = TIR/EAS. c_{Fe} = 0.2024 g Fe/g dry HLW b_i values were obtained from Equation (A.2).						

As the last row of Table A.1 shows, according to the anticipated tank inventories, the amounts of eluates to be mixed with AZ-101 slurry containing 100 g dry AZ-101 waste are 715 mL of AP-101 Cs eluate, 405 mL of AZ-101 Cs eluate, 436 mL of AP-101 Tc eluate, and 290 mL of AZ-101 Tc eluate.

The available mass of the AZ-101 dry sludge was M = 66.5 g. The volumes of eluates needed for this amount of HLW are 475 mL of AP-101 Cs eluate, 269 mL of AZ-101 Cs eluate, 290 mL of AP-101 Tc eluate, and 193 mL of AZ-101 Tc eluate. As already indicated, these required amounts were not available. Therefore, the values of the blended volumes were readjusted. Table A.2 shows the available amount (mass and volume) of each eluate. The differences between the required and available volumes and the achievable blending volumes are also listed.

Table A.2. Adjusted Blending Volumes for the Cs and Tc Eluates

		Tank	**AP-101**	**AZ-101**	**AP-101**	**AZ-101**	**Total**
		Eluate	**^{137}Cs**	**^{137}Cs**	**^{99}Tc**	**^{99}Tc**	
Density	ρ_i	kg/L	1.017	1.012	0.996	0.998	---
Available mass	M_i	g	174	238	75	127	---
Available volume	V_i	mL	171	235	75	127	---
Required volumes	V_i	mL	475	269	290	193	---
Adjusted blending volume	b_i	L(eluate)/kg(dry HLW)	2.573	3.537	1.132	1.914	---
Eluate volume deficiency		mL	304	34	215	65	---
Radioactivity required	r_i	mCi	364	3499	0	1	3864
Radioactivity available	r_i	mCi	131	3057	0	0	3189
Radioactivity deficiency		mCi	233	442	0	0	675

The blended HLW composition is calculated from the set of mass-balance equations illustrated by Equation (A.4) for the *j*-th glass component:

$$w_j = Hh_j + \sum_{i=1}^{E} B_i e_{ij} \qquad \text{(A.4)}$$

where

- H is the fraction of glass components (i.e., oxides and halogens that are retained in the glass) in the blended HLW
- B_i is the *i*-th eluate fraction of glass components in the blended HLW
- E is the number of eluates
- h_j is the *j*-th glass component mass fraction in the pretreated HLW
- e_{ij} is the *j*-th glass component mass fraction in the *i*-th eluate
- w_j is the *j*-th glass component of the blended HLW.

Equation (A.4) states that each glass component in the blended waste is the sum of the fractions of that component in each waste stream (HLW and elates) multiplied by the fraction of that waste stream in the blend. This equation is restricted to glass components because these are the only components of interest. A similar equation can also be written for volatile components, such as NO_x, but these components leave the melter into the offgas and are absent in the glass. Some components, such as Cl and Br, may or may not stay in the glass. Because they are present in minute quantities, trace components are treated in subsequent calculations as having little impact on the results.

Compositions of the eluates and HLW sludge are reported in mass fraction concentrations of ions (cations and anions). To use the mass balance as represented by Equation (A.4), the reported components need to be translated into glass components.

First, the term "glass component" needs to be defined. It is assumed that the glass components are in the form of oxides and halides and the halides include F, Cl, and Br, but not I. To simplify calculations, it is customary to represent each oxide by its prevalent valence and treat the halides as elements. Although some components are actually highly volatile (chlorides and bromides), it is assumed that they will be retained in the glass. This may be a realistic assumption considering their minuscule concentrations. The fraction of oxygen in the glass is not accurately represented in the conventional approach to glass composition. An accurate representation of the oxygen fraction is hardly possible considering that the oxidation-reduction state of the glass varies during the vitrification process and depends on the actual feed makeup (such as additions of reducing agents) and melter operation (bubbling). However, selecting the most prevalent oxide forms to represent the glass composition gives a close approximation of the actual oxygen content of the glass. The glass components are also called "non-volatile" components. All waste components except NO_x and CO_x are considered non-volatile, even though, as stated above, some fraction of some components (Cl, Br, SO_x, and Tc) may volatilize during melting.

Second, we need to determine the compositions of HLW and the eluates in terms of the glass components. HLW and eluate component fractions (h_j and e_{ij}) are related to mass fraction concentration of components in the individual streams as follows:

$$h_j = \frac{c_j}{\sum_{j=1}^{G} c_j} \tag{A.5}$$

and

$$e_{ij} = \frac{c_{ij}}{\sum_{j=1}^{G} c_{ij}} \tag{A.6}$$

where c_j is the j-th component mass per unit mass of HLW, c_{ij} is the j-th component mass per unit volume of i-th eluate, and G is the number of components that are retained in HLW glass. Equations (A.5) and (A.6) simply renormalize the reported compositions to obtain mass fractions of nonvolatile components.

Tables A.3 and A.4 show the chemical and radiochemical compositions of the dry pretreated (i.e., washed, leached, rinsed, and dried at 105°C) AZ-101 HLW sludge and the eluates. The chemical composition is given in micrograms of the element per gram for the dried sludge and micrograms of the ion per mL for the eluates.

The AZ-101 HLW sludge density was 1.08 g/mL; the content of solids in the sludge was 11.4 mass % (10.0 mass% glass components, i.e., oxides and halogens, and 10.8 mass% undissolved solids). The densities and fractions of solids in the eluates are in Table A.5.

Table A.6 shows the compositions of the dry AZ-101 HLW and the eluates in terms of glass components. Table A.6 also shows the blended waste composition (w_j) [in mg of glass components per g of the total, i.e., in 1000 multiples of h_j and e_{ij} as defined by Equations (A.5) and (A.6)]. The blended HLW composition (w_j) was calculated using Equation (A.4).

Table A.3. Compositions of Pretreated Tank AZ-101 HLW Sample and the Cs and Tc Eluates in Terms of Element Concentrations

Analyte	AZ-101 Envelope D (µg/g dry waste)	AP-101 Cs Eluate (µg/mL)	AZ-101 Cs Eluate (µg/mL)	AP-101 Tc Eluate (µg/mL)	AZ-101 Tc Eluate (µg/mL)
Ag	902	<0.63	<2.6	<0.64	<0.50
Al	99872.5	12	<6.2	13	<1.20
As	---	---	<26	---	<5.0
B	91	49	9.4	79.8	92.7
Ba	1510	0.32	2.5	<0.25	<0.20
Be	26	<0.25	<1	<0.25	<0.20
Bi	150	<2.5	<10	<2.5	<2.0
Ca	7505	32	27	<6.4	<5.0
Cd	14500	1.8	2	<0.38	<0.30
Ce	5240	<5.1	<21	<5.1	<4.0
Co	127.5	<1.3	<5.2	<1.3	<1.0
Cr	2284.5	14.1	33	<0.51	0.51
Cu	583.5	2.8	<2.6	1	<0.50
Dy	---	---	<5.2	---	<1.0
Eu	---	---	<10	---	<2.0
Fe	202384	5.9	6.8	<0.64	<0.50
K	2000	110	<210	<51	43
La	5807.5	<1.3	<5.2	<1.3	<1.0
Li	115	<0.76	<3.1	<0.76	<0.60
Mg	1540	<2.5	<10	<2.5	<2.0
Mn	5364	<1.3	<5.2	<1.3	<1.0
Mo	66.5	<1.3	<5.2	<1.3	<1.0
Na	54545	844	803	282	219
Nd	4290	<2.5	<10	<2.5	<2.0
Ni	9992	1.9	<3.1	1.1	<0.60
P	4505	<2.5	<10	<2.5	<2.0
Pb	1727.5	6.1	<10	<2.5	<2.0
Pd	2300	<19	<77	<19	<15.0
Rh	512.5	<7.6	<31	<7.6	<6.0
Ru	1600	<28	<110	<28	<22.0
Sb	---	---	<52	---	<10.0
Se	---	---	<26	---	<5.0
Si	13055	100	<52	169	19
Sn	3600	<38	<150	<38	<10.0
Sr	3411.5	<0.38	<1.6	<0.38	<0.30
Te	---	---	<150	---	<10.0
Th	---	---	<100	---	<20.0
Ti	177.5	<0.63	<2.6	<0.64	<0.50
Tl	---	---	<52	---	<10.0
U	18500	200	<210	<51	<40.0

Table A.3 (contd)

Analyte	AZ-101 Envelope D (µg/g dry waste)	AP-101 Cs Eluate (µg/mL)	AZ-101 Cs Eluate (µg/mL)	AP-101 Tc Eluate (µg/mL)	AZ-101 Tc Eluate (µg/mL)
V	---	---	<5.2	---	<1.0
W	---	---	<52	---	<10.0
Y	385	<1.3	<5.2	<1.3	<1.0
Zn	277.5	<1.3	<10	<1.3	<1.0
Zr	65050	<1.3	<5.2	<1.3	<1.0
F^-	390	<63	<13	2.7	2
Cl^-	703	<63	180	2.2	0.57
Br^-	<170	<63	<130	<0.7	44.3
NO_2^-	7268	<125	<26	31	0.34
NO_3^-	2178	29250	31,000	102	42.6
PO_4^{2-}	<340	<125	<26	<1.4	1.4
SO_4^{2-}	2410	<125	300	5.1	12.7
$C_2O_4^-$	518	<125	170	<1.4	0.89

Table A.4. Radiochemical Composition of AZ-101 HLW (in µCi/g dry solids) and AP-101 and AZ-101 ^{137}Cs and ^{99}Tc Eluates (in µCi/mL)

Isotope	AZ-101 Pretreated HLW	AP-101 Cs Eluate	AP-101 Tc Eluate	AZ-101 Cs Eluate
	µCi/g dry solids	µCi/mL		
^{54}Mn	---	<0.02	---	---
^{60}Co	8.43	$<5x10^{-3}$	$<3\times10^{-5}$	<0.07
^{63}Ni	---	8.88×10^{-4}	$<3\times10^{-5}$	---
^{79}Se	---	3.52×10^{-6}	$<3.58\times10^{-7}$	$<2.2\times10^{-4}$
^{90}Sr	6.1×10^{4}	0.0295	$<1.26\times10^{-4}$	3.3
^{95}Nb	<0.3	<0.02	---	<0.2
^{99}Tc[(b)]	2.53	---	0.416	---
^{106}Ru	<3.0	<0.7	$<3\times10^{-3}$	<9
^{113}Sn	<0.7	<0.2	$<3\times10^{-4}$	<3
^{134}Cs	<0.3	0.156	$<3\times10^{-4}$	4.39
^{137}Cs	641	765	$<2\times10^{-4}$	1.30×10^{4}
^{125}Sb	38.6	<0.4	$<7\times10^{-4}$	<6
^{126}Sn[(a)]	<0.6	0.269	4.15×10^{-3}	<3
^{126}Sn[(b)]	0.21	---	---	---
^{129}I[(b)]	<0.0668	---	---	---
^{151}Sm	---	2.24×10^{-4}	2.38×10^{-5}	---
^{152}Eu	1.58	<0.01	$<2\times10^{-4}$	<0.3
^{154}Eu	101.2	<0.03	$<7\times10^{-5}$	<0.2
^{155}Eu	119.5	<0.3	$<9\times10^{-4}$	<4
^{232}Th	<1.0	<0.2	$<4\times10^{-4}$	<3
^{241}Am[(a)]	197.5	3.05×10^{-5}	7.22×10^{-7}	2.30×10^{-4}

Table A.4 (contd)

Isotope	AZ-101 Pretreated HLW	AP-101 Cs Eluate	AP-101 Tc Eluate	AZ-101 Cs Eluate
$^{241}Am^{(c)}$	165	---	---	---
^{242}Cm	0.298	$<2\times10^{-7}$	$<4\times10^{-8}$	$<3\times10^{-6}$
$^{243}Cm+^{244}Cm$	0.298	7.3×10^{-6}	$<4\times10^{-8}$	2.00×10^{-5}
$U^{(d)}$	1.21×10^{4}	206	6.79×10^{-3}	160
$^{233}U^{(b)}$	0.47	---	---	---
^{236}Pu	<0.2	$<2\times10^{-7}$	$<4\times10^{-8}$	$<9\times10^{-6}$
^{238}Pu	1.1	6.07×10^{-5}	$<6\times10^{-8}$	8.30×10^{-4}
$^{238}Pu+^{240}Pu$	9.58	4.68×10^{-4}	1.62×10^{-7}	7.90×10^{-3}
$^{239}Pu^{(b)}$	129	---	---	---
$^{240}Pu^{(b)}$	9.87	---	---	---
^{241}Pu	---	3.1×10^{-3}	$<1\times10^{-5}$	---
$^{242}Pu^{(b)}$	0.112	---	---	---
$^{237}Np^{(b)}$	192	---	---	---
Gross β	---	---	---	1.40×10^{4}
Gross α	187.5	9.13×10^{-4}	$<2\times10^{-6}$	7.20×10^{-3}
Sum of α	176	5.61×10^{-4}	8.84×10^{-7}	9.00×10^{-3}

(a) GEA value
(b) ICP-MS value in μCi/g
(c) AEA value
(d) ICP-MS value in μg/mL
--- = no data.

Table A.5. Density (in g/mL) and Solid Content (in mass%) in AZ-101 and AP-101 Eluates

	AP-101 Cs	AP-101 Tc	AZ-101 Tc	AZ-101 Cs
Density (g/mL)	1.017 (±0.005)	0.996 (±0.005)	0.998	1.012
	mass%			
Solid content	0.34 (±0.02)	0.06 (±0.02)	0.1[(a)]	0.48 (±0.05)
Glass components	0.4 (±0.2)	0.3 (±0.2)	---	0.19 (±0.07)

(a) Estimated value.

Table A.6. Compositions of Pretreated Tank AZ-101 HLW Sample, the Cs and Tc Eluates, and the Actual Blended HLW in Terms of Mass Fractions of Glass Components[(a)]

	AZ-101 Envelope D $10^3 h_j$ (g/kg)	AP-101 Cs Eluate $10^3 e_{ij}$ (g/kg)	AZ-101 Cs Eluate $10^3 e_{ij}$ (g/kg)	AP-101 Tc Eluate $10^3 e_{ij}$ (g/kg)	AZ-101 Tc Eluate $10^3 e_{ij}$ (g/kg)	Blended AZ-101 $10^3 w_j$ (g/kg)
Ag_2O	1.21	---	---	---	---	1.20
Al_2O_3	236.61	11.45	---	23.74	---	232.96
B_2O_3	0.37	79.68	20.68	248.30	400.47	2.06
BaO	2.11	0.18	1.91	---	---	2.09
BeO	0.09	---	---	---	---	0.09
Bi_2O_3	0.21	---	---	---	---	0.21
Br	---	---	---	---	59.43	0.10
CaO	13.17	22.61	25.81	---	---	13.26
CdO	20.77	1.04	1.56	---	---	20.45
Ce_2O_3	7.70	---	---	---	---	7.57
Cl	0.88	---	---	2.13	0.76	0.87
CoO	0.20	---	---	---	---	0.20
Cr_2O_3	4.19	10.41	32.96	---	1.00	4.40
CuO	0.92	1.77	---	1.21	---	0.91
F	0.49	---	---	2.61	2.68	0.49
Fe_2O_3	362.77	4.26	6.64	---	---	357.08
K_2O	3.02	66.92	---	---	69.49	3.52
La_2O_3	8.54	---	---	---	---	8.40
Li_2O	0.31	---	---	---	---	0.31
MgO	3.20	---	---	---	---	3.15
MnO_2	10.64	---	---	---	---	10.47
MoO_3	0.10	---	---	---	---	0.12
Na_2O	92.19	574.55	739.60	367.30	396.04	100.29
Nd_2O_3	6.27	---	---	---	---	6.17
NiO	15.95	1.22	---	1.35	---	15.70
P_2O_5	12.94	---	---	---	1.40	12.74
PbO	2.33	3.32	---	---	---	2.32
PdO	3.32	---	---	---	---	3.26
Rh_2O_3	0.79	---	---	---	---	0.78
Ru_2O_3	2.48	---	---	---	---	2.44
SO_3	2.52	---	170.84	4.11	14.20	3.60
SiO_2	35.01	108.01	---	349.26	54.52	35.73
SnO_2	5.73	---	---	---	---	5.64
SrO	5.06	---	---	---	---	4.98
TiO_2	0.37	---	---	---	---	0.37
UO_2	26.31	114.58	---	---	---	26.62
Y_2O_3	0.61	---	---	---	---	0.60
ZnO	0.43	---	---	---	---	0.43
ZrO_2	110.17	---	---	---	---	108.42

(a) The VSL spreadsheet reported oxides of Mn, Sn, Ru, and U as MnO_2, SnO, Ru_2O_3, and UO_2. This convention is followed in this table. The final content of Mn, Sn, Ru, and U is represented in terms of MnO, SnO_2, RuO_2, and UO_3.

Finally, the blending ratios can be determined. The B_i values in Equation (A.4) are fractions at which the Cs and Tc eluates are present in the blended HLW. These fractions are defined as the mass of glass components from individual eluates per unit mass of glass components in the blended HLW. Hence, these fractions are independent of the waste loading, which is the fraction of the glass components from the blended HLW in the glass.

The total mass balance is

$$H + \sum_{i=1}^{E} B_i = 1 \tag{A.7}$$

The blending volume, b_i, is the volume of i-th eluate to be mixed with a unit mass of dry HLW. The total concentration of glass components in i-th eluate (in g/L) is $e_i = \sum_{j=1}^{G} c_{ij}$. The total mass of glass components per a unit mass of HLW is $e_{HLW} = \sum_{j=1}^{G} c_j$. Hence, the blending fraction and blending volume are related as

$$B_i = \frac{b_i e_i}{\sum_{j=1}^{G} c_j + \sum_{i=1}^{E} b_i e_i} \tag{A.8}$$

Table A.7 lists the values of the total concentration of glass components (e_i) in the eluates and the blending fractions obtained from Equation (A.8) and the composition data. The value of the total fraction of glass components in the dry AZ-101 (D) pretreated waste is $e_{HLW} = 0.7976$. Both originally required (based on the tank inventory) and availability-based blending fractions are listed. The values of e_{HLW} and e_i for each eluate were obtained starting from the element concentrations listed in Table A.3. The unknown values of concentrations below the ICP detection limits were neglected. The equivalent concentrations of glass components were then calculated. The same glass components were used as those listed in Table A.6. Finally, the concentrations were summed to obtain the totals (Table A.7).

Table A.7. Blending Mass Fractions for the Cs and Tc Eluates

		Tank	**AP-101**	**AZ-101**	**AP-101**	**AZ-101**
		Eluate	**Cs**	**Cs**	**Tc**	**Tc**
Total concentration of glass components	e_i	g/L	1.980	1.464	1.035	0.745
Required blending mass fraction	B_{Ri}	g/g(blend)	0.0172	0.0072	0.0055	0.0026
Actual blending mass fraction	B_{Ai}	g/g(blend)	0.0063	0.0064	0.0014	0.0018

By Equation (A.7), the mass fraction of the dry AZ-101 waste in the blended waste is $H = 0.9841$ when available amounts of eluates are used. Thus, only 1.59 mass% out of the total of glass components is present in the waste blend.

A.1.1 HLW Glass Composition

To make glass, the HLW blend is mixed with glass forming and modifying additives. The mass balance of j-th component is

$$Ww_j + Aa_j = g_j \tag{A.9}$$

where W = waste loading
A = additive fraction in the HLW glass
w_j = j-th component mass fraction in the non-volatile portion of HLW
a_j = j-th component mass fraction in the additive mix
g_j = j-th component mass fraction in the HLW glass.

Equation (A.9) has a similar form as Equation (A.4). It states that each glass component in the product (the HLW glass) is the sum of the fractions of that component in the HLW blend and the mineral mix multiplied by their respective fractions (loadings) in the product. The total mass balance is

$$W + A = 1 \tag{A.10}$$

The waste loading is $W = 0.3175$. This waste loading was determined at the VSL. As mentioned above, it was determined by developing the waste glass that would meet the property constraints and incorporate as much HLW as possible.

The AZ-101 HLW glass composition as previously formulated by VSL is shown in Table A.8 in the "HLW Glass I" column (with minor corrections). To prepare a chemically identical glass with the adjusted HLW, corrective chemical additions were calculated based on the missing amounts of eluates (Table A.2). Because of the impurities in silica sand, the fraction of alumina in the glass is slightly higher as shown in the "HLW Glass II" column (this is discussed below).

Table A.8 shows the fractions of glass-forming and modifying additives copied from the VSL spreadsheet. The corrective additions readjust the feed composition for missing eluates, but were added with the glass-forming chemicals. The loading fraction of corrective chemicals is $S = 0.0053$. Therefore, the fraction of the blended AZ-101 waste is $W - S = 0.3122$. The S value is based on the formula

$$S = W \frac{w_j - d_j}{s_j - d_j} \tag{A.11}$$

where s_j and d_j are j-th component mass fractions in the non-volatile portion of the corrective chemical mix and the actual waste blend, respectively. The value $S = 0.0053$ is obtained for $j \equiv Na_2O$ using the values $w_j = 0.1074$, $d_j = 0.1003$, and $s_j = 0.5241$ (see Table A.8).

Table A.8. Composition of (Actual) Blended HLW, Additives, Corrective Chemicals, and AZ-101 HLW Glass (in mass fractions)[(a)]

Glass Component	Actual Blended AZ-101	Mineral Additives	Corrective Chemicals	HLW Glass I	HLW Glass II
Loading fraction	0.3122	0.6825	0.0053	---	---
	Composition in Mass Fraction of the Oxide				
Ag_2O	0.0012	---	---	0.0004	0.0004
Al_2O_3	0.2330	---	0.0132	0.0728	0.0733
B_2O_3	0.0021	0.1538	0.1341	0.1064	0.1063
BaO	0.0021	---	0.0002	0.0007	0.0007
BeO	0.0001	---	---	0.0000	0.0000
Bi_2O_3	0.0002	---	---	0.0001	0.0001
Br	0.0001	---	0.0031	0.0000	0.0000
CaO	0.0133	---	0.0161	0.0042	0.0042
CdO	0.0205	---	0.0008	0.0064	0.0064
Ce_2O_3	0.0076	---	---	0.0024	0.0024
Cl	0.0009	---	0.0006	0.0003	0.0003
CoO	0.0002	---	---	0.0001	0.0001
Cr_2O_3	0.0044	---	0.0086	0.0014	0.0014
CuO	0.0009	---	0.0014	0.0003	0.0003
F	0.0005	---	0.0008	0.0002	0.0002
Fe_2O_3	0.3571	---	0.0031	0.1115	0.1116
K_2O	0.0035	---	0.0473	0.0013	0.0013
La_2O_3	0.0084	---	---	0.0026	0.0026
Li_2O	0.0003	0.0549	---	0.0376	0.0376
MgO	0.0032	---	---	0.0010	0.0011
MnO_2	0.0105	---	---	0.0033	0.0033
MoO_3	0.0001	---	---	0.0000	0.0000
Na_2O	0.1003	0.1245	0.5241	0.1191	0.1187
Nd_2O_3	0.0062	---	---	0.0019	0.0019
NiO	0.0157	---	0.0011	0.0049	0.0049
P_2O_5	0.0127	---	0.0001	0.0040	0.0040
PbO	0.0023	---	0.0022	0.0007	0.0007
PdO	0.0033	---	---	0.0010	0.0010
Rh_2O_3	0.0008	---	---	0.0002	0.0002
Ru_2O_3	0.0024	---	0.0000	0.0008	0.0008
SO_3	0.0036	---	0.0110	0.0012	0.0011
SiO_2	0.0357	0.6374	0.1575	0.4470	0.4468
SnO	0.0056	---	---	0.0018	0.0018
SrO	0.0050	---	---	0.0016	0.0016
TiO_2	0.0004	---	---	0.0001	0.0002
UO_2	0.0266	---	0.0747	0.0087	0.0087
Y_2O_3	0.0006	---	---	0.0002	0.0002
ZnO	0.0004	0.0293	---	0.0201	0.0201
ZrO_2	0.1084	---	---	0.0338	0.0338
Sum	1.0000	1.0000	1.0000	1.0000	1.0000

(a) The VSL spreadsheet reported oxides of Mn, Sn, Ru, and U as MnO_2, SnO, Ru_2O_3, and UO_2. This convention is followed in this table. The final content of Mn, Sn, Ru, and U is represented in terms of MnO, SnO_2, RuO_2, and UO_3 (see Table 6.4 and Table 6.6).

The mass of glass to be made from 66.5 g AZ-101 dry sludge can now be determined. The fraction of glass components [as defined under Equation (A.4)] in the AZ-101 HLW dry sludge is $e_{HLW} = 0.7976$, and thus 66.5 g will contribute 66.5×0.7976 = 53 g glass components. The glass will contain $W - S = 0.3122$ glass components from the blended waste, which contains $H = 0.9841$ glass components from AZ-101. Hence, the glass has $(W - S)\times H = 0.3122\times 0.9841 = 0.3072$ components from the pretreated AZ-101 dry sludge. Thus, 66.5 g of the pretreated AZ-101 dry sludge will make 53/0.3072 = 173 g glass. This glass is identical in chemistry to the previously approved formulation and, by Table A.2, is 17.5% lower in radioactive component loading.

A1.2 HLW Feed Composition

To make glass, glass-forming and modifying additives and corrective chemicals were mixed together. Table A.9 lists batch chemicals that were used for 173 g glass. The following minor components were deleted for the corrective chemicals listed in Table A.8: BaO, Br, CdO, Cl, CuO, F, Fe_2O_3, NiO, P_2O_5, PbO, and SO_3. Although Al_2O_3 was not deleted from the list of additives, it is not included in Table A.9 because, as Table A.10 shows, there is more Al_2O_3 in the silica sand as an impurity than the amount of Al_2O_3 from missing eluates. As a result, the fraction of Al_2O_3 in the final glass is slightly higher (by 0.05 mass%; see HLW Glass II in Table A.8; see also Table A.11 that lists additional information about the materials). The values listed in Table A.10 are based on chemical analyses for the material providing the glass-forming and modifying components ($Na_2B_4O_7$ $10H_2O$, Li_2CO_3, Na_2CO_3, SiO_2, and ZnO). For other additions ($CaCO_3$, Cr_2O_3, K_2CO_3, and U_3O_8), the data are based on stoichiometry and corrected for manufacturer-certified composition and measured humidity.

Table A.9. Chemical Additives for 173 g Glass

Chemical	Mass, g
$Na_2B_4O_7{\cdot}10H_2O$	48.4598
$CaCO_3$	0.0126
Cr_2O_3	0.0063
K_2CO_2	0.0596
Li_2CO_3	16.0759
Na_2CO_3	11.9073
SiO_2	75.1787
U_3O_8	0.0671
ZnO	3.4432
Total	155.2107

Table A.10. Mass Fractions of Glass Component Oxides in the Batch Chemicals Listed in Table A.11. Note that species such as water or carbonate are not included because they do not contribute to the final glass composition.

	Borax	Calcium Carbonate	Chromium Oxide	Potassium Carbonate	Lithium Carbonate	Sodium Carbonate	Silica	Uranium Oxide	Zinc Oxide
	Mass fraction of the listed oxides in each batch chemical								
Al_2O_3	---	---	---	---	---	---	0.0014	---	---
B_2O_3	0.3750	---	---	---	---	---	---	---	---
CaO	---	0.5582	---	---	---	---	0.0001	---	---
CdO	---	---	---	---	---	---	---	---	0.0001
Cl	---	---	---	---	0.0001	0.0002	---	---	---
Cr_2O_3	---	---	1.0000	---	---	---	---	---	---
Fe_2O_3	---	---	---	---	0.0004	---	0.0002	---	---
K_2O	---	---	---	0.676	---	---	---	---	---
Li_2O	---	---	---	---	0.4012	---	---	---	---
MgO	---	---	---	---	0.0010	---	0.0001	---	---
Na_2O	0.1670	---	---	---	---	0.5839	---	---	---
NiO	---	---	---	---	---	---	---	---	---
PbO	---	---	---	---	---	---	---	---	---
SiO_2	---	---	---	---	---	---	0.9970	---	---
TiO_2	---	---	---	---	---	---	0.0001	---	---
U_3O_8	---	---	---	---	---	---	---	1.0000	---
ZnO	---	---	---	---	---	---	---	---	0.9990

Table A.11. AZ-101 Mineral and Chemical Glass-Former Additives

Mineral	Grade	Company	Telephone No.
10-M Borax	Technical	U.S. Borax Valencia, CA 91355-1847	805-287-5400 www.borax.com
Calcium carbonate[(a)]	Reagent	Fisher 99.1% pure Lot# 005661	---
Chromium oxide[(a)]	Reagent	Fisher Lot# 007112	---
Potassium carbonate[(a)]	Reagent	Fisher Lot# 851377	---
Sodium carbonate	Dense Soda Ash Anhydrous	Solvay Minerals Houston, TX	713-525-6800 FAX713-525-7805 www.solvayminerals.com
Lithium carbonate	Technical	Chemettal-Foote Kings Mt, NC	704-734-2501, 704-734-2670 www.chemetal lithium.com
Silica	SIL-CO-SIL-75	U.S. Silica, Mill Creek OK 74856-0036	800-243-7500, 304-258-2500 FAX 304-258-8295 www.u-s-silica.com
Uranium oxide[(b)]	~50 mesh\99% pure	Cerac Milwaukee, WI 53201	414-289-9800 FAX 414-289-9805
ZnO	Kadox 920	Zinc Corp Amer. Monaca, PA	800-962-7500, 724-774-1020 horseheadinc.com

(a) Used as corrective chemicals, see Table A.8; [(b)]U_3O_8 was used as a substitute for Sr/TRU precipitate.

Appendix B

AZ-101 HLW Glass Chemical Analysis Data

Appendix B: AZ-101 HLW Glass Chemical Analysis Data

Table B.1. Compositions (in mg element/g glass) Standard Reference Glasses (Smith 1993; Ebert and Wolf 1999)

	ARG-1	LRM
	Mean	Mean
	mg element/kg glass	
Al	25030	50330
B	26930	24380
Ba	790	10
Ca	10220	3860
Cd	000	1400
Cr	640	1300
Cu	30	000
Fe	97920	9650
K	22500	12290
La	000	170
Li	14910	510
Mg	5190	600
Mn	14600	620
Na	85310	148590
Ni	8250	1490
P	960	2360
Pb	000	930
Si	223900	253350
Sr	30	000
Ti	6890	600
Zn	160	000
Zr	960	6880

Table B.2. Na_2O_2-NaOH Fusion (PNL-ALO-114)

	Process Blank		AZ-101-HLW		ARG	LRM	IDL	EQL
	mg/kg						g/m^3	
Ag	---	---	[180]	[48]	[59]	---	0.025	0.250
Al	[330]	[260]	49,500	51,200	25,200	53,800	0.060	0.600
B	---	---	33,500	34,600	26,100	25,400	0.050	0.500
Ba	---	---	653	686	748	---	0.010	0.100
Bi	---	---	[290]	[230]	[220]	---	0.100	1.000
Ca	[4,300]	[3,000]	7,410	7,300	14,200	7,780	0.250	2.500
Cd	---	---	6,280	6,440	---	1,460	0.015	0.150
Ce	---	---	---	---	---	---	0.200	2.000
Cr	[69]	---	907	921	656	1,360	0.020	0.200
Cu	[48]	---	[340]	[340]	[85]	---	0.025	0.250
Fe	2,540	585	83,800	86,200	94,500	10,400	0.025	0.250
K	[32,000]	[20,000]	[15,000]	[6,700]	44,200	[24,000]	2.000	20.000
La	---	---	2,570	2,700	---	[140]	0.050	0.500
Li	[130]	[110]	17,600	18,300	15,100	599	0.030	0.300
Mg	---	---	[900]	[880]	5,430	[740]	0.100	1.000
Mn	---	---	2,210	2,270	14,400	[620]	0.050	0.500
Na	---	---	---	---	---	---	0.150	1.500
Nd	---	---	1,960	2,060	[220]	---	0.100	1.000
Ni	[370]	---	4,180	4,250	8,010	1,530	0.030	0.300
P	[540]	[240]	3,750	2,610	[1,300]	2,320	0.100	1.000
Pb	---	---	[770]	[730]	[230]	[1,100]	0.100	1.000
Rh	---	---	[920]	[720]	---	---	0.300	3.000
Si	[1,200]	---	213,000	219,000	226,000	269,000	0.500	5.000
Sn	[1,500]	---	[2,500]	[1,900]	[1,300]	[1,400]	0.500	5.000
Sr	[120]	[88]	1,680	1,760	[150]	[140]	0.015	0.150
Ti	---	---	[130]	[150]	6,240	594	0.025	0.250
U	---	---	[9,700]	[8,800]	---	---	2.000	20.000
Y	---	---	[170]	[180]	---	---	0.050	0.500
Zn	---	---	16,200	16,600	[230]	---	0.050	0.500
Zr	---	---	---	---	---	---	0.050	0.500
M	1881.5		1943.6	1823.2	1988.1	1968.5	---	---

IDL is the instrument detection limit; MDL = IDL*M, where M is the multiplier.
EQL is the estimated quantitation limit.
Bracketed values are within the MDL and the EQL, and have potential uncertainties greater than 15%.
Concentration values < MDL are not listed.

Table B.3. KOH-KNO_3 Fusion (PNL-ALO-115)

	Process Blank		AZ-101-HLW		ARG	LRM	IDL	EQL
	mg/kg						g/m^3	
Ag	---	[65]	[180]	[48]	[59]	---	0.025	0.250
Al	1,470	[670]	49,500	51,200	25,200	53,800	0.060	0.600
B	[120]	---	33,500	34,600	26,100	25,400	0.050	0.500
Ba	[21]	[35]	653	686	748	---	0.010	0.100
Bi	[250]	[200]	[290]	[230]	[220]	---	0.100	1.000
Ca	---	[780]	7,410	7,300	14,200	7,780	0.250	2.500
Cd	---	---	6,280	6,440	---	1,460	0.015	0.150
Ce	---	---	---	---	---	---	0.200	2.000
Cr	[68]	[55]	907	921	656	1,360	0.020	0.200
Cu	[110]	[130]	[340]	[340]	[85]	---	0.025	0.250
Fe	903	[330]	83,800	86,200	94,500	10,400	0.025	0.250
K	---	---	[15,000]	[6,700]	44,200	[24,000]	2.000	20.000
La	---	---	2,570	2,700	---	[140]	0.050	0.500
Li	[180]	[360]	17,600	18,300	15,100	599	0.030	0.300
Mg	[350]	[340]	[900]	[880]	5,430	[740]	0.100	1.000
Mn	[170]	[200]	2,210	2,270	14,400	[620]	0.050	0.500
Na	8,470	13,900	---	---	---	---	0.150	1.500
Nd	---	---	1,960	2,060	[220]	---	0.100	1.000
Ni	---	---	4,180	4,250	8,010	1,530	0.030	0.300
P	[1,200]	[630]	3,750	2,610	[1,300]	2,320	0.100	1.000
Pb	[240]	[300]	[770]	[730]	[230]	[1,100]	0.100	1.000
Rh	---	---	[920]	[720]	---	---	0.300	3.000
Si	[1,800]	---	213,000	219,000	226,000	269,000	0.500	5.000
Sn	---	---	[2,500]	[1,900]	[1,300]	[1,400]	0.500	5.000
Sr	---	---	1,680	1,760	[150]	[140]	0.015	0.150
Ti	---	---	[130]	[150]	6,240	594	0.025	0.250
U	---	---	[9,700]	[8,800]	---	---	2.000	20.000
Y	---	---	[170]	[180]	---	---	0.050	0.500
Zn	---	---	16,200	16,600	[230]	---	0.050	0.500
Zr	---	---	---	---	---	---	0.050	0.500
M	1916.6		1916.6	1823.2	1988.1	1968.5	---	---

IDL is the instrument detection limit; MDL = IDL*M, where M is the multiplier.
EQL is the estimated quantitation limit.
Bracketed values are within the MDL and the EQL and have potential uncertainties greater than 15%.
--- Concentration values < MDL are not listed.

Table B.4. Acid Digestion (PNL-ALO-138)

	Process Blank	AZ-101-HLW		ARG	LRM	IDL	EQL
	mg/kg					g/m^3	
Ag	---	51.1	51.0	[7.6]	---	0.0050	0.069
Al	---	44,800	44,200	25,000	52,700	0.0310	0.446
B	---	31,800	29,600	26,400	23,900	0.0100	0.031
Ba	[1.1]	706	704	811	9.03	0.0011	0.010
Bi	---	[120]	130	[110]	[25]	0.0250	0.250
Ca	---	3,450	3,430	10,600	3,740	0.0450	0.450
Cd	---	6,350	6,330	[2.7]	1,510	0.0038	0.038
Ce	---	693	680	---	---	0.0400	0.400
Cr	---	932	930	667	1,370	0.0060	0.060
Cu	---	295	295	38.5	---	0.0070	0.070
Fe	[15]	88,000	87,000	97,500	10,300	0.0100	0.100
K	---	---	---	22,900	12,200	1.0000	10.000
La	---	2,700	2,680	[11]	87.8	0.0130	0.130
Li	---	17,900	17,700	15,500	488	0.0058	0.058
Mg	---	782	786	5,640	697	0.0250	0.600
Mn	[0.33]	2,340	2,320	15,200	625	0.0006	0.012
Na	[97]	85,000	84,600	85,600	154,000	0.0870	0.870
Nd	---	1,950	1,940	---	---	0.0450	0.250
Ni	---	4,380	4,350	8,430	1,540	0.0130	0.130
P	---	2,130	2,130	1,260	2,330	0.0240	0.236
Pb	---	627	613	[28]	899	0.0230	0.200
Rh	---	214	215	---	---	0.0510	0.300
Si	---	---	---	---	---	0.0300	1.000
Sn	---	[810]	[860]	[320]	[87]	0.1300	2.250
Sr	---	1,690	1,680	30.3	18.4	0.0015	0.010
Ti	---	136	136	6,810	599	0.0025	0.025
U	---	5,430	5,430	---	---	0.5400	4.971
Y	---	172	172	[8.9]	15.7	0.0019	0.020
Zn	[14]	15,700	15,600	192	[9.2]	0.0070	0.050
Zr	---	29,300	29,200	1,120	7,150	0.0043	0.043
M	526.9	549.5	506.1	466.2	478.0	---	---

IDL is the instrument detection limit; MDL = IDL*M, where M is the multiplier.
EQL is the estimated quantitation limit.
Bracketed values are within the MDL and the EQL and have potential uncertainties greater than 15%.
--- Concentration values < MDL are not listed.

Table B.5. Spike Recovery % from LCS for the Three Digestion Techniques Applied to the Reference Glasses

	ARG	LRM	ARG - LCS	LRM - LCS	ARG	LRM	ARG - LCS	LRM - LCS	ARG	LRM	ARG - LCS	LRM - LCS
	µg/g	µg/g	% Rec	% Rec	µg/g	µg/g	% Rec	% Rec	µg/g	µg/g	% Rec	% Rec
Ag	[59]	---	---	---	[54]	[47]	---	---	[7.6]	---	---	---
Al	25200	53800	101	106	26500	54800	102	106	25000	52700	101	105
B	26100	25400	100	104	27000	26200	103	107	26400	23900	101	98
Ba	748	---	96	---	756	[24]	94	---	811	9.03	104	60
Be	---	---	---	---	---	---	---	---	---	---	97	---
Bi	[220]	---	---	---	[290]	[250]	---	---	[110]	[25]	---	---
Ca	14200	7780	95	---	10800	[4200]	106	---	10600	3740	104	97
Cd	---	1460	---	104	---	1590		113	[2.7]	1510	---	108
Ce	---	---	---	---	---	---	---	---	---	---	---	---
Co	---	---	---	---	---	---	---	---	---	---	138	---
Cr	656	1360	80	99	689	1420	86	104	667	1370	92	105
Cu	[85]	---	---	---	[210]	[150]	---	---	38.5	---	120	---
Fe	94500	10400	92	80	97500	10600	97	101	97500	10300	98	107
K	44200	[24,000]	---	---	---	---	---	---	22900	12200	112	100
La	---	[140]	---	---	---	[120]	---	---	[11]	87.8	---	51
Li	15100	599	92	90	14500	649	88	94	15500	488	96	95
Mg	5430	[740]	105	---	5700	[1000]	104	---	5640	697	109	116
Mn	14400	[620]	78	---	15100	[790]	81	---	15200	625	82	101
Na	---	---	---	---	90300	165000	100	106	85600	154000	104	104
Nd	[220]	---	---	---	[190]	---	---	---	---	---	---	---
Ni	8010	1530	92	77	---	---	---	---	8430	1540	102	103
P	[1,300]	2320	---	75	[1800]	2990	---	80	1260	2330	99	99
Pb	[230]	[1,100]	---	---	[380]	[1200]	---	---	[28]	899	---	97
Rh	---	---	---	---	---	---	---	---	---	---	---	---
Si	226000	269000	102	106	230000	272000	104	107	---	---	Si vol.	Si vol.
Sn	[1,300]	[1,400]	---	---	[1000]	[940]	---	---	[320]	[87]	---	---
Sr	[150]	[140]	---	---	[39]	[31]	---	---	30.3	18.4	89	---
Ti	6240	594	88	99	6190	617	87	103	6810	599	96	100
U	---	---	---	---	---	---	---	---	---	---	---	---
V	---	---	---	---	---	---	---	---	---	---	110	---
Y	---	---	---	---	---	---	---	---	[8.9]	15.7	113	---
Zn	[230]	---	---	---	[220]	---	---	---	192	[9.2]	112	---
Zr	---	---	---	---	956	7040	92	102	1120	7150	108	104

Bracketed values are within the MDL and the EQL, and have potential uncertainties greater than 15%.
--- Concentration values < MDL are not listed.

Appendix C

AZ-101 HLW Glass Radiochemical Analysis Data

Appendix C: AZ-101 HLW Glass Radiochemical Analysis Data

Table C.1. ICP-MS Data for ^{99}Tc in AZ-101 HLW Glass

PNL-ALO #	114				
	MF	**SD**	**RPD**	**Rec**	**MDL**
	mg/kg	mg/kg	**%**	**%**	mg/kg
^{99}Tc					
Sample	77.2	0.26	---	---	1.77
Duplicate	76.4	0.51	*1.0*	---	1.66
Process Blank1	---	---	---	---	0.0018
Process Blank2	---	---	---	---	0.0018
LCS/LRM	<1.79	---	---	---	1.79
LCS/ARG-1	<1.81	---	---	---	1.81
Serial Dilution	76.6	0.83	*0.8*	---	8.83
Replicate	75.7	0.4	*1.9*	---	1.77
Post Spike	565	7.5	---	100	1.77

MF is the mass fraction.
SD is the serial dilution, a 5× dilution of the sample solution analyzed if the resulting concentration is above the EQL.
RPD is the relative percent difference.
MDL is the method detection limit.
Rec is the percentage of spike recovery

Table C.2. ICP-MS Data for ^{129}I in AZ-101 HLW Glass

PNL-ALO #	114				
	MF	**SD**	**RPD**	**Rec**	**MDL**
	mg/kg	mg/kg	**%**	**%**	mg/kg
^{129}I					
Sample	<10.7	---	---	---	10.7
Duplicate	<11.4	---	---	---	11.4
Matrix Spike	22.2	2.1	---	103	9.56
Process Blank1	---	---	---	---	0.0117
Process Blank2	---	---	---	---	0.0117
Blank Spike	---	---	---	101	0.0117
Post Spike	83.9	1.7	---	90.0	10.7

MF is the mass fraction
SD is the serial dilution, a 5× dilution of the sample solution analyzed if the resulting concentration is above the EQL
RPD is the relative percent difference
MDL is the method detection limit
Rec is the percentage of spike recovery

Table C.3. ICP-MS Data for U in AZ-101 HLW Glass

PNL-ALO #	114			115			138		
	MF	**SD**	**MDL**	**MF**	**SD**	**MDL**	**MF**	**SD**	**MDL**
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
^{233}U									
Sample	<0.0905	---	0.0905	---	---	---	---	---	---
Duplicate	<0.0849	---	0.0849	---	---	---	---	---	---
Process Blank1	---	---	0.0001	---	---	---	---	---	---
Process Blank2	---	---	0.0001	---	---	---	---	---	---
LCS/LRM	<0.0917	---	0.0917	---	---	---	---	---	---
LCS/ARG-1	<0.0926	---	0.0926	---	---	---	---	---	---
^{234}U									
Sample	0.337	0.110	0.148	0.402	0.064	0.169	0.349	0.046	0.051
Duplicate	0.313	0.120	0.139	0.285	0.012	0.180	0.329	0.066	0.047
Matrix Spike	---	---	---	---	---	---	0.467	0.072	0.049
Process Blank1	---	---	0.00015	---	---	0.00018	---	---	0.00009
Process Blank2	---	---	0.00015	---	---	0.00018	---	---	0.00009
LCS/LRM	<0.150	---	0.150	<0.165	---	0.165	0.0444	---	0.0444
LCS/ARG-1	<0.152	---	0.152	<0.165	---	0.165	0.0433	---	0.0433
Serial Dilution	<0.742	---	0.742	<0.843	---	0.843	0.6	0.14	0.255
Replicate	0.354	0.080	0.148	0.333	0.091	0.169	0.4	0.072	0.051
^{235}U									
Sample	41.1	1.30	0.14	40.80	0.43	0.16	45.9	1.20	0.702
Duplicate	41.9	0.68	0.13	42.10	1.10	0.17	44.4	0.14	0.647
Matrix Spike	---	---	---	---	---	---	66.3	0.23	0.675
Process Blank1	---	---	0.00014	---	---	0.00017	---	---	0.0013
Process Blank2	---	---	0.00014	---	---	0.00017	---	---	---
Blank Spike	---	---	---	---	---	---	---	---	0.0013
LCS/LRM	<0.141	---	0.141	<0.156	---	0.156	0.611	---	0.611
LCS/ARG-1	<0.142	---	0.142	<0.156	---	0.156	0.596	---	0.596
Serial Dilution	41.4	1.30	0.695	39.6	3.30	0.798	45.80	1.30	3.510
Replicate	41.0	0.17	0.139	40.7	0.31	0.160	45.80	0.47	0.702
^{236}U									
Sample	3.10	0.095	0.0703	3.0	0.14	0.123	3.37	0.28	0.0577
Duplicate	3.28	0.120	0.0660	2.83	0.19	0.132	3.26	0.14	0.0531
Matrix Spike	---	---	---	---	---	---	3.71	0.21	0.0554
Process Blank1	---	---	0.00007	---	---	0.00013	---	---	0.0001
Process Blank2	---	---	0.00007	---	---	0.00013	---	---	---
Blank Spike	---	---	---	---	---	---	---	---	0.00011
LCS/LRM	<0.0712	---	0.0712	<0.121	---	0.121	0.0502	---	0.0502
LCS/ARG-1	0.0719	---	0.0719	0.12	---	0.120	0.0489	---	0.0489
Serial Dilution	3.11	0.67	0.3520	2.64	0.700	0.616	3.37	0.57	0.2880
Replicate	3.04	0.19	0.0703	3.01	0.084	0.123	3.26	0.06	0.0577
^{238}U									
Sample	4840	38	1.77	4770	19.0	26.0	5390	42	21.6
Duplicate	4970	34	1.66	4850	20.0	27.8	5270	18	19.9
Matrix Spike	---	---	---	---	---	---	14200	64	20.7
Process Blank1	---	---	0.0018	---	---	0.028	---	---	0.0392
Process Blank2	---	---	0.0018	---	---	0.028	---	---	---
Blank Spike	---	---	---	---	---	---	---	---	0.0392
LCS/LRM	1.80	---	1.80	25.5	---	25.5	18.8	---	18.8
LCS/ARG-1	1.81	---	1.81	25.4	---	25.4	18.3	---	18.3
Serial Dilution	4710	18	8.87	4570	11	130	5400	33	108.0
Replicate	4840	44	1.77	4710	49	26	5370	15	21.6
Post Spike	9680	54	1.77	9180	82	26	10900	120	21.6
MF is the mass fraction. Rec is the percentage of spike recovery.									

Table C.3 (contd)

PNL-ALO #	114		115		138	
	RPD %	Rec %	RPD %	Rec %	RPD %	Rec %
^{233}U						
Sample	---	---	---	---	---	---
Duplicate	---	---	---	---	---	---
^{234}U						
Sample	---	---	---	---	---	---
Duplicate	---	---	---	---	---	---
Matrix Spike	---	---	---	---	---	---
Serial Dilution	---	---	---	---	---	---
Replicate	---	---	---	---	---	---
^{235}U						
Sample	---	---	---	---	---	---
Duplicate	1.9	---	3.10	---	3.400	---
Matrix Spike	---	---	---	---	---	---
Serial Dilution	0.62	---	3.00	---	0.23	---
Replicate	0.24	---	0.14	---	0.23	---
^{236}U						
Sample	---	---	---	---	---	---
Duplicate	5.80	---	3.90	---	3.40	---
Matrix Spike	---	---	---	---	---	---
Serial Dilution	0.34	---	---	---	0.14	---
Replicate	1.80	---	2.0	---	3.20	---
^{238}U						
Sample	---	---	---	---	---	---
Duplicate	2.60	---	1.50	---	2.3	---
Matrix Spike	---	---	---	---	---	107
Blank Spike	---	---	---	---	---	98
Serial Dilution	2.80	---	4.3	---	0.1	---
Replicate	0.10	---	1.3	---	0.5	---
Post Spike	---	100	---	95	---	101

MF is the mass fraction.
Rec is the percentage of spike recovery.

Table C.4. ICP-MS Data for Np, Pu, and AMU in AZ-101 HLW Glass

PNL-ALO #	114			115			138		
	MF	**SD**	**MDL**	**MF**	**SD**	**MDL**	**MF**	**SD**	**MDL**
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
^{237}Np									
Sample	57.6	1.1	0.353	56.4	0.74	0.344	61.8	1.4	1.60
Duplicate	57.0	0.6	0.331	57.1	1.0	0.367	61.6	1.2	1.47
Matrix Spike	---	---	---	---	---	---	65.3	0.5	1.5300
Process Blank1	---	---	0.00036	---	---	0.00037	---	---	0.0029
Process Blank2	---	---	0.00036	---	---	0.00037	---	---	---
Blank Spike	---	---	---	---	---	---	---	---	0.0029
LCS/LRM	0.358	---	0.358	0.336	---	0.336	1.39	---	1.39
LCS/ARG-1	0.361	---	0.361	0.336	---	0.336	1.35	---	1.35
Serial Dilution	55.3	1.60	1.760	52.9	0.3	1.720	63.6	1.2	7.98
Replicate	56.4	0.61	0.353	54.8	1.0	0.344	63.8	1.1	1.6
Post Spike	4870	30	0.353	4580	18	0.344	5550	34	1.6
^{239}Pu									
Sample	46.8	0.89	0.0250	---	---	---	---	---	---
Duplicate	46.0	0.36	0.0234	---	---	---	---	---	---
Process Blank1	---	---	0.000026	---	---	---	---	---	---
Process Blank2	---	---	0.000026	---	---	---	---	---	---
LCS/LRM	0.0253	---	0.0253	---	---	---	---	---	---
LCS/ARG-1	0.0256	---	0.0256	---	---	---	---	---	---
Serial Dilution	46.2	0.79	0.125	---	---	---	---	---	---
Replicate	47.0	0.54	0.025	---	---	---	---	---	---
Post Spike	95.6	0.98	0.025	---	---	---	---	---	---
^{240}Pu									
Sample	3.61	0.0096	0.0010	---	---	---	---	---	---
Duplicate	3.60	0.0540	0.0009	---	---	---	---	---	---
Process Blank1	---	---	0.000001	---	---	---	---	---	---
Process Blank2	---	---	0.000001	---	---	---	---	---	---
LCS/LRM	0.0010	---	0.0010	---	---	---	---	---	---
LCS/ARG-1	0.0016	0.0015	0.0010	---	---	---	---	---	---
Serial Dilution	3.62	0.092	0.0048	---	---	---	---	---	---
Replicate	3.69	0.052	0.0010	---	---	---	---	---	---
^{242}Pu									
Sample	0.0428	0.0029	0.0029	---	---	---	---	---	---
Duplicate	0.0414	0.0030	0.0027	---	---	---	---	---	---
Process Blank1	---	---	0.000003	---	---	---	---	---	---
Process Blank2	---	---	0.000003	---	---	---	---	---	---
LCS/LRM	0.0029	---	0.0029	---	---	---	---	---	---
LCS/ARG-1	0.0029	---	0.0029	---	---	---	---	---	---
Serial Dilution	0.0328	0.0110	0.0143	---	---	---	---	---	---
Replicate	0.0432	0.0033	0.0029	---	---	---	---	---	---
^{241}AMU									
Sample	20.0	0.61	0.0904	20.5	0.33	0.1170	21.3	0.40	0.126
Duplicate	19.8	0.39	0.0848	20.2	0.58	0.1250	21.0	0.42	0.116
Matrix Spike	---	---	---	---	---	---	22.3	0.42	0.121
Process Blank1	---	---	0.00009	---	---	0.00013	---	---	0.00023
Process Blank2	---	---	0.00009	---	---	0.00013	---	---	---
Blank Spike	---	---	---	---	---	---	---	---	0.0002
LCS/LRM	0.0915	---	0.0915	0.114	---	0.114	0.109	---	0.109
LCS/ARG-1	0.0924	---	0.0924	0.114	---	0.114	0.106	---	0.106
Serial Dilution	18.9	0.96	0.4520	18.1	0.69	0.583	22.1	1.10	0.628
Replicate	20.0	0.72	0.0904	20.5	1.0	0.117	22.0	0.80	0.126
Post Spike	503	8.70	0.0904	475	1.5	0.117	572	1.70	0.126
MF is the mass fraction									

Table C.4 (contd)

PNL-ALO #	114		115		138	
	RPD	Rec	RPD	Rec	RPD	Rec
	%	%	%	%	%	%
^{237}Np						
Sample	---	---	---	---	---	---
Duplicate	1.1	---	1.3	---	0.2	---
Matrix Spike	---	---	---	---	---	---
Serial Dilution	4.2	---	6.4	---	2.9	---
Replicate	2.2	---	2.8	---	3.2	---
Post Spike	---	99	---	97	---	100
^{239}Pu						
Sample	---	---	---	---	---	---
Duplicate	1.80	---	---	---	---	---
Serial Dilution	1.30	---	---	---	---	---
Replicate	0.40	---	---	---	---	---
Post Spike	---	103	---	---	---	---
^{240}Pu						
Sample	---	---	---	---	---	---
Duplicate	---	---	---	---	---	---
Serial Dilution	0.20	---	---	---	---	---
Replicate	2.10	---	---	---	---	---
^{242}Pu						
Sample	---	---	---	---	---	---
Duplicate	3.5000	---	---	---	---	---
Serial Dilution	---	---	---	---	---	---
Replicate	0.90	---	---	---	---	---
^{241}AMU						
Sample	---	---	---	---	---	---
Duplicate	0.80	---	1.60	---	1.3000	---
Matrix Spike	---	---	---	---	---	---
Serial Dilution	5.30	---	13.0	---	3.5	---
Replicate	0.10	---	0.1	---	3.2	---
Post Spike	---	99	---	98	---	100
MF is the mass fraction						

Table C5. Calculated Activity of Decay Products per kg in AZ-101 HLW Glass at 2015

		(Parent radionuclide) Fission Products—mCi/kg														
		^{63}Ni	**^{90}Sr**	**^{99}Tc**	**^{137}Cs**	**^{151}Sm**								Sum Activities	% of Total Activity	Activities >0.05% of Total
Daughter Elements	^{63}Ni	2.28	---	---	---	---								2.28	0.003627	---
	^{90}Sr	---	19300	---	---	---								19300	30.7045	30.70450058
	^{90}Y	---	19300	---	---	---								19300	30.7045	30.70450058
	^{99}Tc	---	---	1.28	---	---								1.28	0.002036	---
	^{137}Cs	---	---	---	11900	---								11900	18.93179	18.93179051
	^{137m}Ba	---	---	---	11900	---								11900	18.93179	18.93179051
	^{151}Sm	---	---	---	---	379								379	0.602954	0.602953664
		(Parent radionuclide)Activity of TRU and Uranium and their daughter products—mCi/kg														
		^{244}Cm:	**^{243}Cm:**	**^{241}Am:**	**^{242}Pu:**	**^{240}Pu:**	**^{239}Pu:**	**^{238}Pu:**	**^{238}U:**	**^{237}Np:**	**^{236}U:**	**^{235}U:**	**^{234}U:**			
Daughter elements	^{244}Cm	0.184432	---	---	---	---	---	---	---	---	---	---	---	0.184432	0.000293	---
	^{243}Cm	---	0.215027	---	---	---	---	---	---	---	---	---	---	0.215027	0.000342	---
	^{241}Am	---	---	70.13514	---	---	---	---	---	---	---	---	---	70.13514	0.111578	0.111578461
	^{242}Pu	---	---	---	0.000163	---	---	---	---	---	---	---	---	0.000163	2.59E-07	---
	^{240}Pu	0.000267	---	---	---	0.81	---	---	---	---	---	---	---	0.810267	0.001289	---
	^{239}Pu	---	7.77E-05	---	---	---	2.837838	---	---	---	---	---	---	2.837916	0.004515	---
	^{238}Pu	---	---	---	---	---	---	0.402432	---	---	---	---	---	0.402432	0.00064	---
	^{238}U	---	---	---	2.78E-13	---	---	---	0.040676	---	---	---	---	0.040676	6.47E-05	---
	^{237}Np	---	---	0.000252	---	---	---	---	---	0.00167	---	---	---	0.001922	3.06E-06	---
	^{236}U	4.66E-11	---	---	---	2.64E07	---	---	---	---	0.0002	---	---	0.0002	3.19E-07	---
	^{235}U	---	4.39E-13	---	---	---	3.08E-08	---	---	---	---	0.000091	---	9.1E-05	1.45E-07	---
	^{234m}Pa	---	---	---	2.76E-13	---	---	---	---	0.00167	---	---	---	0.00167	2.66E-06	---
	^{234}Th	---	---	---	2.76E-13	---	---	---	---	0.00167	---	---	---	0.00167	2.66E-06	---
	^{234}U	---	---	---	4.25E-18	---	---	1.31E-05	---	5.15E-08	---	---	0.00209	0.002103	3.35E-06	---
	^{233}Pa	---	---	0.00025	---	---	---	---	0.040676	---	---	---	---	0.040925	6.51E-05	---
	^{233}U	---	---	5.94E-09	---	---	---	---	1.93E-06	---	---	---	---	1.94E-06	3.08E-09	---
	^{232}Th	8.71E-21	---	---	---	7.16E+17	---	---	---	---	1.09E-13	---	---	1.09E-13	1.73E-16	---
	^{231}Pa	---	3.48E-17	---	---	---	3.58E-12	---	---	---	---	2.12E-08	---	2.12E-08	3.37E-11	---
	^{231}Th	---	4.39E-13	---	---	---	3.07E-08	---	---	---	---	0.000091	---	9.1E-05	1.45E-07	---
	^{230}Th:	---	---	---	1.42E-22	---	---	6.58E-10	---	2.53E-12	---	---	2.07E-07	2.08E-07	3.3E-10	---
	^{229}Th	---	---	2.04E-12		---	---	---	9.92E-10	---	---	---	---	9.94E-10	1.58E-12	---

Table C.5 (contd)

(Parent radionuclide) Activity of TRU and Uranium and their daughter products—mCi/kg																
		^{244}Cm:	**^{243}Cm:**	**^{241}Am:**	**^{242}Pu:**	**^{240}Pu:**	**^{239}Pu:**	**^{238}Pu:**	**^{238}U:**	**^{237}Np:**	**^{236}U:**	**^{235}U:**	**^{234}U:**	Sum Activities	% of Total Activity	Activities >0.05% of Total
Daughter Elements	^{228}Ac	2.3E-21	---	---	---	2.34E-17	---	---	---	---	4.84E-14	---	---	4.84E-14	7.7E-17	---
	^{228}Ra	2.3E-21	---	---	---	2.34E-17	---	---	---	---	4.84E-14	---	---	4.84E-14	7.7E-17	---
	^{228}Th	1.11E-21	---	---	---	1.29E-17	---	---	---	---	3.18E-14	---	---	3.18E-14	5.05E-17	---
	^{227}Ac	---	2.88E-18	---	---	---	3.83E-13	---	---	---	---	3.31E-09	---	3.31E-09	5.26E-12	---
	^{227}Th	---	2.77E-18	---	---	---	3.71E-13	---	---	---	---	3.22E-09	---	3.22E-09	5.13E-12	---
	^{226}Ra	---	---	---	3.02E-24	---	---	1.05E-12	---	3.98E-15	---	---	4.92E-10	4.93E-10	7.85E-13	---
	^{225}Ac	---	---	1.99E-12	---	---	---	---	9.75E-10	---	---	---	---	9.77E-10	1.55E-12	---
	^{225}Ra	---	---	2.01E-12	---	---	---	---	9.82E-10	---	---	---	---	9.84E-10	1.57E-12	---
	^{224}Ra	1.1E-21	---	---	---	1.29E-17	---	---	---	---	3.17E-14	---	---	3.17E-14	5.04E-17	---
	^{223}Ra	---	2.72E-18	---	---	---	3.66E-13	---	---	---	---	3.19E-09	---	3.19E-09	5.08E-12	---
	^{222}Rn	---	---	---	3.55E-24	---	---	1.05E-12	---	3.96E-15	---	---	4.91E-10	4.92E-10	7.83E-13	---
	^{221}Fr	---	---	1.99E-12	---	---	---	---	9.75E-10	---	---	---	---	9.77E-10	1.55E-12	---
	^{220}Rn	1.1E-21	---	---	---	1.29E-17	---	---	---	---	3.17E-14	---	---	3.17E-14	5.04E-17	---
	^{219}Rn	---	2.72E-18	---	---	---	3.66E-13	---	---	---	---	3.19E-09	---	3.19E-09	5.08E-12	---
	^{218}Po	---	---	---	3.44E-24	---	---	1.05E-12	---	3.96E-15	---	---	4.91E-10	4.92E-10	7.83E-13	---
	^{217}At	---	---	1.99E-12	---	---	---	---	9.75E-10	---	---	---	---	9.77E-10	1.55E-12	---
	^{216}Po	1.1E-21	---	---	---	1.29E-17	---	---	---	---	3.17E-14	---	---	3.17E-14	5.04E-17	---
	^{215}Po	---	2.72E-18	---	---	---	3.66E-13	---	---	---	---	3.19E-09	---	3.19E-09	5.08E-12	---
	^{214}Bi	---	---	---	1.41E-24	---	---	1.05E-12	---	3.96E-15	---	---	4.91E-10	4.92E-10	7.83E-13	---
	^{214}Pb	---	---	---	4.89E-24	---	---	1.05E-12	---	3.96E-15	---	---	4.91E-10	4.92E-10	7.83E-13	---
	^{214}Po	---	---	---	9.28E-24	---	---	1.05E-12	---	3.96E-15	---	---	4.91E-10	4.92E-10	7.82E-13	---
	^{213}Bi	---	---	1.99E-12	---	---	---	---	9.75E-10	---	---	---	---	9.77E-10	1.55E-12	---
	^{213}Po	---	---	1.94E-12	---	---	---	---	9.54E-10	---	---	---	---	9.56E-10	1.52E-12	---
	^{212}Bi	1.1E-21	---	---	---	1.28E-17	---	---	---	---	3.16E-14	---	---	3.17E-14	5.04E-17	---
	^{212}Po	7.07E-22	---	---	---	8.23E-18	---	---	---	---	2.03E-14	---	---	2.03E-14	3.23E-17	---
	^{212}Pb	1.1E-21	---	---	---	1.28E-17	---	---	---	---	3.16E-14	---	---	3.17E-14	5.04E-17	---
	^{211}Bi	---	2.72E-18	---	---	---	3.66E-13	---	---	---	---	3.19E-09	---	3.19E-09	5.08E-12	---
	^{211}Pb	---	2.72E-18	---	---	---	3.66E-13	---	---	---	---	3.19E-09	---	3.19E-09	5.08E-12	---
	^{210}Bi	---	---	---	7.52E-24	---	---	8.35E-14	---	3.12E-16	---	---	5.12E-11	5.13E-11	8.16E-14	---
	^{210}Po	---	---	---	1.33E-23	---	---	6.94E-14	---	2.58E-16	---	---	4.44E-11	4.45E-11	7.08E-14	---

Table C.5 (contd)

(Parent radionuclide) Activity of TRU and Uranium and their daughter products—mCi/kg																
Daughter Elements		**^{244}Cm:**	**^{243}Cm:**	**^{241}Am:**	**^{242}Pu:**	**^{240}Pu:**	**^{239}Pu:**	**^{238}Pu:**	**^{238}U:**	**^{237}Np:**	**^{236}U:**	**^{235}U:**	**^{234}U:**	Sum Activities	% of Total Activity	Activities >0.05% of Total
	^{210}Pb	---	---	---	1.44E-23	---	---	8.41E-14	9.54E-10	3.14E-16	---	---	5.15E-11	1.01E-09	1.6E-12	---
	^{209}Pb	---	---	1.94E-12	---	---	---	---	---	---	---	---	---	1.94E-12	3.09E-15	---
	^{207}Tl	---	---	---	---	---	3.65E-13	---	---	---	---	3.19E-09	---	3.19E-09	5.07E-12	---
Sum Total														62857.23	100	---

Table C6. Calculated Activity of Decay Products per kg in AZ-101 HLW Glass at 3115

	(Parent radionuclide) fission products—mCi/kg															
Daughter Elements		**^{63}Ni**	**^{90}Sr**	**^{99}Tc**	**^{137}Cs**	**^{151}Sm**								Sum Activities	% of Total Activity	Activities >0.05% of Total
	^{63}Ni	0.00124	---	---	---	---								0.00124	0.007096	---
	^{90}Sr	---	1.18E-07	---	---	---								1.18E-07	6.75E-07	---
	^{90}Y	---	1.18E-07	---	---	---								1.18E-07	6.75E-07	---
	^{99}Tc	---	---	1.28	---	---								1.28	7.325056	7.325056
	^{137}Cs	---	---	---	1.87E-07	---								1.87E-07	1.07E-06	---
	^{137m}Ba	---	---	---	1.87E-07	---								1.87E-07	1.07E-06	---
	^{151}Sm	---	---	---	---	0.59								0.59	3.376393	3.376393
		(Parent radionuclide) Activity of TRU and Uranium and their daughter products—mCi/kg														---
		^{244}Cm:	**^{243}Cm:**	**^{241}Am:**	**^{242}Pu:**	**^{240}Pu:**	**^{239}Pu:**	**^{238}Pu:**	**^{238}U:**	**^{237}Np:**	**^{236}U:**	**^{235}U:**	**^{234}U:**			
Daughter Elements	^{244}Cm:	9.58E-20	---	---	---	---	---	---	---	---	---	---	---	9.58E-20	5.48E-19	---
	^{243}Cm:	---	5.17E-13	---	---	---	---	---	---	---	---	---	---	5.17E-13	2.96E-12	---
	^{241}Am:	---	---	12.01892	---	---	---	---	---	---	---	---	---	12.01892	68.78067	68.78067
	^{242}Pu:	---	---	---	0.000163	---	---	---	---	---	---	---	---	0.000163	0.000931	---
	^{240}Pu:	0.000694	---	---	---	0.720811	---	---	---	---	---	---	---	0.721505	4.128955	4.128955
	^{239}Pu:	---	0.000321	---	---	---	2.748649	---	---	---	---	---	---	2.74897	15.73153	15.73153
	^{238}Pu:	---	---	---	---	---	---	6.78E-05	---	---	---	---	---	6.78E-05	0.000388	---
	^{238}U:	---	---	---	2.81E-11	---	---	---	---	0.00167	---	---	---	0.00167	0.009557	---
	^{237}Np:	---	---	0.011989	---	---	---	---	0.040676	---	---	---	---	0.052665	0.301385	0.301385
	^{236}U:	2.36E-08	---	---	---	2.52E-05	---	---	---	---	0.0002	---	---	0.000225	0.001289	---
	^{235}U:	---	3.44E-10	---	---	---	3.06E-06	---	---	---	---	0.000091	---	9.41E-05	0.000538	---
	^{234m}Pa:	---	---	---	2.81E-11	---	---	---	---	0.00167	---	---	---	0.00167	0.009557	---
	^{234}Th:	---	---	---	2.81E-11	---	---	---	---	0.00167	---	---	---	0.00167	0.009557	---
	^{234}U:	---	---	---	4.41E-14	---	---	0.000157	---	5.24E-06	---	---	2.08E-03	0.002246	0.012852	---
	^{233}Pa:	---	---	0.011989	---	---	---	---	0.040676	---	---	---	---	0.052665	0.301385	0.301385
	^{233}U:	---	---	3.71E-05	---	---	---	---	0.000196	---	---	---	---	0.000233	0.001336	---
	^{232}Th:	6.44E-16	---	---	---	7.03E-13	---	---	---	---	1.1E-11	---	---	1.17E-11	6.68E-11	---
	^{231}Pa:	---	3.88E-12	---	---	---	3.58E-08	---	---	---	---	2.11E-06	---	2.15E-06	1.23E-05	---
	^{231}Th:	---	3.44E-10	---	---	---	3.06E-06	---	---	---	---	0.000091	---	9.41E-05	0.000538	---
	^{230}Th:	---	---	---	1.47E-16	---	---	1.39E-06	---	2.61E-08	---	---	2.08E-05	2.22E-05	0.000127	---

Table C.6 (contd)

	(Parent radionuclide) Activity of TRU and Uranium and their daughter products—mCi/kg															
		^{244}Cm:	**^{243}Cm:**	**^{241}Am:**	**^{242}Pu:**	**^{240}Pu:**	**^{239}Pu:**	**^{238}Pu:**	**^{238}U:**	**^{237}Np:**	**^{236}U:**	**^{235}U:**	**^{234}U:**	Sum Activities	% of Total Activity	Activities >0.05% of Total
Daughter Elements	^{229}Th:	---	---	1.43E-06	---	---	---	---	9.96E-06	---	---	---	---	1.14E-05	6.51E-05	---
	^{228}Ac:	6.35E-16	---	---	---	6.93E-13	---	---	---	---	1.09E-11	---	---	1.16E-11	6.62E-11	---
	^{228}Ra:	6.35E-16	---	---	---	6.93E-13	---	---	---	---	1.09E-11	---	---	1.16E-11	6.62E-11	---
	^{228}Th:	6.31E-16	---	---	---	6.89E-13	---	---	---	---	1.09E-11	---	---	1.15E-11	6.6E-11	---
	^{227}Ac:	---	3.66E-12	---	---	---	3.39E-08	---	---	---	---	2.06E-06	---	2.09E-06	1.2E-05	---
	^{227}Th:	---	3.61E-12	---	---	---	3.34E-08	---	---	---	---	2.03E-06	---	2.06E-06	1.18E-05	---
	^{226}Ra:	---	---	---	1.61E-17	---	---	2.62E-07	---	3.74E-09	---	---	4.29E-06	4.56E-06	2.61E-05	---
	^{225}Ac:	---	---	1.43E-06	---	---	---	---	9.95E-06	---	---	---	---	1.14E-05	6.51E-05	---
	^{225}Ra:	---	---	1.43E-06	---	---	---	---	9.95E-06	---	---	---	---	1.14E-05	6.51E-05	---
	^{224}Ra:	6.31E-16	---	---	---	6.89E-13	---	---	---	---	1.09E-11	---	---	1.15E-11	6.6E-11	---
	^{223}Ra:	---	3.61E-12	---	---	---	3.34E-08	---	---	---	---	2.03E-06	---	2.06E-06	1.18E-05	---
	^{222}Rn:	---	---	---	1.61E-17	---	---	2.62E-07	---	3.74E-09	---	---	4.29E-06	4.56E-06	2.61E-05	---
	^{221}Fr:	---	---	1.43E-06	---	---	---	---	9.95E-06	---	---	---	---	1.14E-05	6.51E-05	---
	^{220}Rn:	6.31E-16	---	---	---	6.89E-13	---	---	---	---	1.09E-11	---	---	1.15E-11	6.6E-11	---
	^{219}Rn:	---	3.61E-12	---	---	---	3.34E-08	---	---	---	---	2.03E-06	---	2.06E-06	1.18E-05	---
	^{218}Po:	---	---	---	1.61E-17	---	---	2.62E-07	---	3.74E-09	---	---	4.29E-06	4.56E-06	2.61E-05	---
	^{217}At:	---	---	1.43E-06	---	---	---	---	9.95E-06	---	---	---	---	1.14E-05	6.51E-05	---
	^{216}Po:	6.31E-16	---	---	---	6.89E-13	---	---	---	---	1.09E-11	---	---	1.15E-11	6.6E-11	---
	^{215}Po:	---	3.61E-12	---	---	---	3.34E-08	---	---	---	---	2.03E-06	---	2.06E-06	1.18E-05	---
	^{214}Bi:	---	---	---	1.61E-17	---	---	2.62E-07	---	3.74E-09	---	---	4.29E-06	4.55E-06	2.61E-05	---
	^{214}Pb:	---	---	---	1.61E-17	---	---	2.62E-07	---	3.74E-09	---	---	4.29E-06	4.55E-06	2.61E-05	---
	^{214}Po:	---	---	---	1.61E-17	---	---	2.62E-07	---	3.74E-09	---	---	4.29E-06	4.55E-06	2.61E-05	---
	^{213}Bi:	---	---	1.43E-06	---	---	---	---	9.95E-06	---	---	---	---	1.14E-05	6.51E-05	---
	^{213}Po:	---	---	1.39E-06	---	---	---	---	9.74E-06	---	---	---	---	1.11E-05	6.37E-05	---
	^{212}Bi:	6.31E-16	---	---	---	6.89E-13	---	---	---	---	1.09E-11	---	---	1.15E-11	6.6E-11	---
	^{212}Po:	4.05E-16	---	---	---	4.42E-13	---	---	---	---	6.95E-12	---	---	7.39E-12	4.23E-11	---
	^{212}Pb:	6.31E-16	---	---	---	6.89E-13	---	---	---	---	1.09E-11	---	---	1.15E-11	6.6E-11	---
	^{211}Bi:	---	3.61E-12	---	---	---	3.34E-08	---	---	---	---	2.03E-06	---	2.06E-06	1.18E-05	---
	^{211}Pb:	---	3.61E-12	---	---	---	3.34E-08	---	---	---	---	2.03E-06	---	2.06E-06	1.18E-05	---
	^{210}Bi:	---	---	---	1.44E-17	---	---	2.46E-07	---	3.44E-09	---	---	4.06E-06	4.31E-06	2.47E-05	---

Table C.6 (contd)

	(Parent radionuclide) Activity of TRU and Uranium and their daughter products—mCi/kg															
Daughter Elements		**^{244}Cm:**	**^{243}Cm:**	**^{241}Am:**	**^{242}Pu:**	**^{240}Pu:**	**^{239}Pu:**	**^{238}Pu:**	**^{238}U:**	**^{237}Np:**	**^{236}U:**	**^{235}U:**	**^{234}U:**	Sum Activities	% of Total Activity	Activities >0.05% of Total
	^{210}Po:	---	---	---	1.44E-17	---	---	2.46E-07	---	3.44E-09	---	---	4.06E-06	4.31E-06	2.47E-05	---
	^{210}Pb:	---	---	---	1.44E-17	---	---	2.46E-07	---	3.44E-09	---	---	4.06E-06	4.31E-06	2.47E-05	---
	^{209}Pb:	---	---	1.39E-06	---	---	---	---	9.74E-06	---	---	---	---	1.11E-05	6.37E-05	---
	^{207}Tl:	---	3.6E-12	---	---	---	3.33E-08	---	---	---	---	2.02E-06	---	2.05E-06	1.18E-05	---
	Sum Total													17.47427	100	---

Appendix D

TCLP QA Report(From RPL)

Appendix D: TCLP QA Report (From RPL)

TCLP Results for AZ-101 Envelope D Glass

Test Plan Number:	TP-RPP-WTP-121 Rev. 0
Preparation Method:	RPG-CMC-110 Rev. 1/RPG-CMC-139 Rev. 0/RPG-CMC-101 Rev.0
Analysis Method:	RPG-CMC-211 Rev. 0 (ICP-AES) RPG-CMC-201 Rev. 0 (Mercury) 329-OP-SC01 Rev. 0 (ICP-MS)
Leach Date:	03/7/2004–03/8/2004
Spreadsheet Author/Date:	M.W. Urie/6-17-04
Spreadsheet Reviewer/Date:	K.N Pool/6-18-04

General

This document provides the information required to satisfy the referenced test plan. Quality control (QC) criteria are defined in the referenced test plan.

Procedure RPG-CMC-110 was used to perform the Toxic Characteristic Leaching Procedure (TCLP) on the AZ-101 high-level waste (HLW) glass sample submitted under Analytical Service Request (ASR) 6834. The TCLP, using TCLP Extraction Fluid #1, was performed in the Radiochemical Processing Laboratory (RPL) Shielded Analytical Laboratory (SAL). The TCLP batch included a sample, duplicate, and a TCLP extraction blank. Following the TCLP extraction processing, a laboratory control sample (LCS) and matrix spikes (MSs) for each glass were prepared from aliquots of the leachates before acidification to a pH of <2 (for laboratory preservation). Once the LCS and MS were prepared, the leachates were acidified, and aliquots were drawn for mercury analysis and for preparation of samples for metal analysis by ICP-AES and ICP-MS.

All TCLP analysis results (Table D.1) are given as mg/L for each detected analyte, and have been adjusted for all laboratory processing factors and instrument dilutions. Process factors were required to adjust for dilution of the TCLP extracts resulting from initial acidification and spike additions, and for dilution resulting from the subsequent sample preparation (i.e., acid digestion). The process factors for each sample were determined from the various process volumes (e.g., TCLP extract, spike solution, final digestate).

A summary of the analysis results for the AZ-101 HLW glass, for all analytes of interest and including QC performance (Table D.2 through D.4), is provided below.

1.0 Sample Analysis Results

Table D.1. TCLP Sample Results

CAS #	Constituent	Sample Result (mg/L)[a]	Duplicate Result (mg/L)[a]	MDL[a] (mg/L)	EQL[b] (mg/L)
Analytes of Interest:					
7440-36-0	Antimony	0.039 U	0.039 U	0.039	0.659
7440-38-2	Arsenic	0.052 U	0.052 U	0.052	3.08
7440-39-3	Barium	0.19 J	0.23 J	0.014	100
7440-41-7	Beryllium	0.00021 U	0.00021 U	0.00021	1.22
7440-43-9	Cadmium	0.065 J	0.062 J	0.0047	0.48
18540-29-9	Chromium	0.0065 U	0.0065 U	0.0065	5.0
7440-50-8	Copper	0.025 U	0.025 U	0.025	29,200
7439-92-1	Lead	0.045 U	0.35 J	0.045	5.0
7439-97-6	Mercury	0.000023 U	0.000023 U	0.000023	0.2
7440-02-0	Nickel	0.029 J	0.036 J	0.015	11
7782-49-2	Selenium	0.045 U	0.045 U	0.045	1.0
7440-22-4	Silver	0.0076 U	0.0076 U	0.0076	3.07
7440-28-0	Thallium	0.000027 J	0.000019 J	0.0000035[c]	0.20
7440-62-2	Vanadium	0.0053 U	0.0053 U	0.0053	16.9
7440-66-6	Zinc	0.35 J	0.30 J	0.11	225
Opportunistic Analytes:					
7429-90-5	Aluminum	0.23	0.22	0.053	N/A
7440-42-8	Boron	1.3	1.5	0.019	0.05
7440-70-2	Calcium	1.5	0.84	0.067	N/A
7723-14-0	Phosphorous	0.047 U	0.047 U	0.047	N/A
7440-09-7	Potassium	1.34 U	1.34 U	1.34	N/A
7440-23-5	Sodium	1500	1600	0.289	N/A

U = Undetected. Analyte was analyzed but not detected (e.g., no measurable instrument response) or response was less than the MDL.

J = Estimated value. Value is below EQL and above MDL.

Underlined values are ≥ MDL but have no EQL established for the current method.

(a) MDLs determined per Quality Assurance Plan ASO-QAP-001 Rev. 1 and adjusted by the average sample processing factors.

(b) As no specific EQLs have been established for TCLP solutions, the estimated quantitation limits (EQL) were set equal to the Universal Treatment Standards (UTS) for TCLP analyses or to the quantitation limit specified in the ASR if no UTS value is specified.

(c) The ICP/MS MDL was determined for each analytical run using 3 standard blank solutions which were evaluated throughout the analytical run.

ICPAES and ICP-MS Analysis

Acid digestion of the TCLP extract solutions was done per procedure RPG-CMC-139 using from 40 to 45 mL of the acidified TCLP extract. Procedure RPG-CMC-139 includes two digestion options, one using nitric and hydrochloric acids and the other using nitric acid alone; samples were prepared using both digestion options. Metals analysis of the acid-digested samples was performed per procedure RPG-CMC-211 (ICPAES) and 329-OP-SC01 (ICP-MS). ICP-AES results for Ag and Sb are from the nitric acid digests; the results for As, Ba, Be, Cd, Cr, Cu, Ni, Pb, Se, V, and Zn are from the combined nitric and hydrochloric acid digests. Results for the opportunistic analytes Al, B, Ca, K, Na, and P for the combined nitric and hydrochloric acid digests are also shown in Tables D.1 and D.2 (process

blank only). No QC data for the opportunistic analytes are given. ICP-MS analysis was performed for thallium only.

Mercury Analysis

Acid digestion of the TCLP extract solutions was done per procedure RPG-CMC-131 using approximately 1.5 mL of the acidified TCLP extract. The samples were analyzed per procedure RPG-CMC-201.

2.0 Quality Control Criteria

2.1 Preparation Blank (PB) and Laboratory Control Sample (LCS) Results

Table D.2. Preparation Blank (PB) and Laboratory Control Sample (LCS) Results

Analyte	PB Success Criteria: <EQL		LCS Success Criteria: 75%–125% Recovery		
	Success Criteria (EQL) (mg/L)	Prep Blank Results (mg/L)	Expected Spike Cone (mg/L)	LCS/BS Results (mg/L)	Recovery[(a)] (%)
Analytes of Interest:					
Antimony	0.659	0.039 U	2.22	2.28	103
Arsenic	3.08	0.052 U	3.11	3.25	104
Barium	100	0.21 J	2.22	2.50 J	103
Beryllium	1.22	0.00021 U	1.11	1.14 J	103
Cadmium	0.48	0.0047 U	1.11	1.11	100
Chromium	5.0	0.0065 U	2.22	2.28 J	102
Copper	29,200	0.025U	2.22	2.37 J	106
Lead	5.0	0.044 U	1.33	1.27 J	95
Mercury	0.2	0.000023 U	0.00259	0.00239 J	92
Nickel	11	0.015 U	4.44	4.65 J	105
Selenium	1.0	0.045 U	1.78	1.79	101
Silver	3.07	0.0076 U	0.667	0.680 J	102
Thallium	0.20	0.000041 J	3.11	3.28	105
Vanadium	16.9	0.0053 U	2.22	2.27 J	102
Zinc	225	0.11 U	4.44	4.67 J	105
Opportunistic Analytes:					
Aluminum	N/A	0.059	N/A	N/A	N/A
Boron	0.05	1.2	N/A	N/A	N/A
Calcium	N/A	0.73	N/A	N/A	N/A
Phosphorous	N/A	0.047 U	N/A	N/A	N/A
Potassium	N/A	1.34 U	N/A	N/A	N/A
Sodium	N/A	1500	N/A	N/A	N/A

U = Undetected. Analyte was analyzed but not detected (e.g., no measurable instrument response) or response was less than the MDL.
J = Estimated value. Value is below EQL and above MDL.
Underlined values are ≥ MDL but have no EQL established for the current method.

(a) LCS/BS recoveries have been corrected for contribution of analyte concentration in the preparation blank.
Note: Recovery values are calculated using more significant figures than shown in the table.

Process Blank:

ICPAES (Metals, except Hg and Tl)

A process blank was prepared for each digestion option from a portion of the acidified TCLP extraction blank. The concentration of all analytes of interest in the process blanks was within the acceptance criteria of <EQL or ≤ 5% of the concentration in the samples.

Mercury Analysis

A process blank was prepared from a portion of the TCLP extraction blank. The concentration of mercury in the process blank was within the acceptance criteria of <EQL or ≤ 5% of the concentration in the samples.

ICP-MS (Tl only)

A process blank was prepared from a portion of the TCLP extraction blank. The concentration of thallium in the process blank was within the acceptance criteria of <EQL or ≤ 5% of the concentration in the samples.

Laboratory Control Sample (i.e., Blank Spike):

Two blank spikes were prepared (one for each digestion option) by addition of 0.2 mL of multi-element spike solution INT-QC-TCLP-A (containing all analytes of interest except B, Cu, Sb, and Hg) combined with 0.2 mL each of separate spike solutions containing boron, copper, antimony, and thallium (Tl analyzed by ICP-MS). A mercury spike solution was added to only one of the blank spike preparations.

ICP-AES (metals, except Hg and Tl)

The recovery values for both digestions were within the success criterion for all analytes.

Mercury Analysis

The blank spike mercury recovery was within the success criterion defined by the QA Plan; the test plan defined no success criterion for mercury. An additional laboratory control sample (NIST SRM 1641d) digested and analyzed with the TCLP extract samples, but not prepared from the TCLP blank extract, demonstrated excellent recovery at 97%.

ICP-MS (Tl only)

The recovery value for the digestion was within the success criteria.

2.2 Matrix Spike (MS) Results

Table D.3. Matrix Spike (MS) Results

Matrix Spike Success Criteria: 75%–125%				
Analyte	**Expected Spike Conc. (mg/L)**	**Original Sample Results (mg/L)**	**Matrix Spike (mg/L)**	**Recovery (%)**
Antimony	1.11	0.039 U	1.12	101
Arsenic	1.56	0.052 U	1.65 J	106
Barium	1.11	0.19 J	1.35 J	105
Beryllium	0.556	0.00021 U	0.573 J	103
Cadmium	0.556	0.065 J	0.631	102
Chromium	1.11	0.0065 U	1.15 J	103
Copper	1.11	0.025 U	1.18 J	107
Lead	0.667	0.045 U	0.622 J	93
Mercury	0.00131	0.000023 U	0.00116	89
Nickel	2.22	0.015 U	2.38 J	106
Selenium	0.889	0.045 U	0.893 J	100
Silver	0.333	0.0076 U	0.30 J	90
Thallium	1.56	0.000027 J	1.62	104
Vanadium	1.11	0.0053 U	1.14 J	102
Zinc	2.22	0.35 J	2.65 J	104

U = Undetected. Analyte was analyzed but not detected (e.g., no measurable instrument response) or response was less than the MDL.
J = Estimated value. Value is below EQL and above MDL.

Note: Recovery values are calculated using more significant figures than shown in the table.

Two matrix spikes were prepared for the AZ-101 sample (one matrix spike for each sample for each digestion option) in the same manner as the blank spike except that 0.1 mL of each spike component was used. Again, a mercury-spike solution was added to only one matrix-spike preparation for each sample.

ICP-AES (metals, except Hg and Tl)

Recovery values were within the success criterion for all analytes measured by ICP-AES.

Mercury Analysis

The matrix-spike mercury recovery was within the success criterion defined by the QA Plan; the test plan defined no success criterion for mercury.

ICP-MS (Tl only)

The recovery value for thallium was within the success criteria.

2.3 Post-Spike Results

Table D.4. Post-Spike Results

Post-Spike Success Criteria: 75%–125%				
Analyte	**Expected Spike Conc (mg/L)**	**Sample[(a)] (mg/L)**	**Post Spike (mg/L)**	**Recovery (%)[(b)]**
Antimony	1.25	0.039 U	1.37	109
Arsenic	1.25	0.052 U	1.37 J	109
Barium	0.25	0.034 J	0.28 J	105
Beryllium	0.05	0.00020 U	0.05 J	103
Cadmium	0.25	0.013 J	0.27 J	104
Chromium	0.50	0.0063 U	0.53 J	106
Copper	0.50	0.024 U	0.52 J	104
Mercury	n/a			
Lead	1.25	0.043 U	1.28 J	102
Nickel	0.50	0.015 U	0.54 J	108
Selenium	1.25	0.043 U	1.32	106
Silver	0.25	0.0076 U	0.258 J	103
Thallium	0.0052	0.000027 J	0.0048	92
Vanadium	0.50	0.0051 U	0.52 J	104
Zinc	0.75	0.11 U	0.84 J	112

U = Undetected. Analyte was analyzed but not detected (e.g., no measurable instrument response) or response was less than the MDL.
J = Estimated value. Value is below EQL and above MDL.

(a) Sample Results in this column are presented as "observed at instrument" and do not include the process factor.
(b) PS recoveries have been corrected for contribution of analyte concentration in the preparation blank.
Note: Recovery values are calculated using more significant figures than shown in the table.

Post-Spike Results Narrative:

ICP-AES (metals, except Hg and Tl)

A post spike (containing all ICP-AES analytes of interest) was conducted on both samples for each digestion. Recovery values are listed for all analytes in the spike that had a concentration ≥ 25% of that in the sample. The recovery values were within the success criterion for all analytes of interest.

Mercury Analysis

No post spike performed.

ICP-MS (Tl only)

The post-spike recovery was within the success criteria.

Serial Dilution Results (ICP-AES Only):

For both sample digestions (nitric/Hal or nitric only), no analyte of interest had concentrations that exceeded 100 times the concentration in the process blank. Therefore, per Bechtel QAPP, PL-24590-QA00001, Rev 0, serial dilution was not required. Matrix effects were evaluated from the respective post-spike data.

3.0 Modifications to Procedures

No modifications were made to the test plan.

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