PNWD-3464 WTP-RPT-106 Rev. 0

## Vitrification and Product Testing of AZ-101 Pretreated LAW Envelope B Glass

H. D. Smith R. J. Bates P. R. Bredt J. V. Crum P. R. Hrma M. J. Schweiger

June 2004

Prepared for Bechtel National Inc. under Contract 24590-101-TSA-W000-00004

#### LEGAL NOTICE

This report was prepared by Battelle Memorial Institute (Battelle) as an account of sponsored research activities. Neither Client nor Battelle nor any person acting on behalf of either:

MAKES ANY WARRANTY OR REPRESENTATION, EXPRESS OR IMPLIED, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, process, or composition disclosed in this report may not infringe privately owned rights; or

Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, process, or composition disclosed in this report.

References herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by Battelle. The views and opinions of authors expressed herein do not necessarily state or reflect those of Battelle.

## Vitrification and Product Testing of AZ-101 Pretreated LAW Envelope B Glass

H. D. Smith R. J. Bates P. R. Bredt J. V. Crum P. R. Hrma M. J. Schweiger

June 2004

6/ m/04 for W.L. Tamose

# ACCEPTED FOR Project USE

Test Specification: 24590-LAW-TSP-RT-02-004, Rev 0 Test Plan: TP-RPP-WTP-177, Rev 0 R&T Focus Area: Waste Form Qualification Test Scoping Statement(s): B-13 Test Exceptions: 24590-WTP-TEF-RT-03-025

Battelle—Pacific Northwest Division Richland, Washington 99352

#### COMPLETENESS OF TESTING

This report describes the results of work and testing specified by Test Specification 24590-PTF-RSP-RT-02-004, Rev 0, Test Exception 24590-WTP-TEF-RT-03-025, and Test Plan TP-RPP-WTP-177, 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:

Gorgon H. Beeman, Manager GHB 6-11-04 Date

WTP R&T Support Project

Abbr	reviat	tions and Acronyms	ix	
Refe	rence	28	xi	
Testi	ing S	ummary	xiii	
	Obj	ectives	xiii	
	Test	xiii		
	Res	ults and Performance Against Success Criteria	xiv	
	Qua	lity Requirements		
	R&	xvii		
	Disc	crepancies and Follow-on Tests	xxi	
1.0	Intro	oduction		
2.0	Quality Assurance Requirements.			
	2.1	Application of RPP-WTP Quality Assurance Requirements		
	2.2	Conduct of Experimental and Analytical Work		
	2.3	Internal Data Verification and Validation		
3.0	Obi	ectives		
4.0				
5.0	Europimental Mathed			
5.0	Experimental Method			
	5.1	Glass Fabrication		
		5.1.2 RPP-WTP Mineral Additives	5 2	
		5.1.3 Batch Recipe		
		5.1.4 Melter Feed Preparation		
		5.1.5 Glass Melting.		
		5.1.6 Container-Centerline Cooling		
	5.2	Glass Analyses and Testing		
		5.2.1 Chemical Composition		
		5.2.2 Radiochemical Composition		
		5.2.3 Crystalline and Non-Crystalline Phase Determination		
		5.2.4 TCLP		
		5.2.5 PCT		
6.0	Res	ults	6.1	
	6.1	LAW AZ-101 Waste Components Content	6.1	
	6.2	LAW Glass AZ-101 Chemical Composition		
	6.3	LAW Glass AZ-101 Radiochemical Composition		
		6.3.1 Data Comparison with Requirements		

		6.3.2	Measured Dose Rates from LAW Glasses	6.12		
	6.4	Crystalline and Noncrystalline Phases				
	6.5	РСТ		6.18		
	6.6	TCLP		6.21		
	6.7	Propert	y Comparison of Actual and Simulated AZ-101 Waste, Melter Feed and Glass	6.22		
7.0	Con	clusions.		7.1		
App	endix	A: Radio	ochemistry Summary for AZ-101 Glass	A.1		
App	Appendix B: ICP Mass Spectrometry Summary for AZ-101 Pretreated WasteB.1					
Appendix C: ICP Mass Spectrometry Summary for AZ-101 Glass						
App	Appendix D: VSL Batch Sheet for AZ-101(B) Waste Glass LAWB83D.1					
App	Appendix E: TCLP Results for AZ-101 Envelope B Glass					

# **List of Figures**

Figure 5.1. Steel	Photograph of AZ-101 Molten Glass being Quenched by Pouring the Melt on a Plate	5.8
Figure 5.2. Plotte	Measured CCC Heat Treatment Temperature Profile for AZ-101 Envelope B Glass d Against Target Temperature Control Points	5.9
Figure 5.3. nickel	Desensitized Type 304L Stainless Steel, 22 mL, PCT Vessel and Lid (Teflon gasket, -plated brass compression fittings are also shown)	5.15
Figure 6.1.	Analyzed Versus Target Mass Fractions of AZ-101 LAW Glass Components	6.6
Figure 6.2. (excep	Analyzed Versus Target Mass Fractions of AZ-101 LAW Glass Components of SiO <sub>2</sub> ) with Mass Fractions >0.005	6.7
Figure 6.3. Comp	Individual Versus All-Average Analyzed Mass Fractions of AZ-101 LAW Glass onents	6.8
Figure 6.4. Subje	Optical Images (multicolored in polarized light) of Crystals in AZ-101 LAW Glass cted to CCC Heat Treatment	6.14
Figure 6.5.	SEM Micrographs of AZ-101 LAW Melt Subjected to CCC Heat Treatment	6.15
Figure 6.6.	XRD Pattern of AZ-101 LAW Glass Subjected to CCC Heat Treatment	6.16
Figure 6.7.	Normalized PCT Releases Versus Crystallinity Fraction in AZ-101 LAW Glass	6.21

## List of Tables

Table S.1.	Summary of Test Objectives and Results	.xiii
Table S.2.	Test Exceptions	. xiv
Table S.3.	Success Criteria	. xiv
Table S.4.	R&T Test Conditions	xvii
Table S.5.	Target and Measured (Best Analytical Estimate) AZ-101 LAW Glass Composition	. xix
Table S.6.	Analytical Results for TCLP Inorganic Constituents of Potential Concern	xx
Table 5.1.	Chemical Composition of AZ-101 LAW Pretreated Waste: Inorganic Analytes in mg/L	. 5.1
Table 5.2. and (	Chemical Composition of AZ-101 Pretreated Waste (in mg/L): Ion Chromatography Dxidation Analysis	. 5.1
Table 5.3.	Radionuclide Activity of AZ-101 Pretreated Waste in µCi/mL	. 5.2
Table 5.4.	Solution Properties of AZ-101 Pretreated LAW	. 5.2

Table 5.5. Glass Forming Minerals and Chemicals	5.3
Table 5.6. Glass Forming Minerals to Make 425 g of AZ-101 LAW Glass	5.4
Table 5.7. Composition of Glass Forming Minerals and Pretreated AZ-101 (B) in Mass%	5.5
Table 5.8. Mass Fractions of Glass Components in AZ-101 Pretreated LAW Waste, Glass-Former         Mineral Mix, and AZ-101 Glass	5.6
Table 5.9. Quantities of Raw Minerals to Prepare Additive Mix for AZ-101 LAW Glass	5.7
Table 5.10. CCC Schedule for Crucible Testing	5.9
Table 5.11. Summary of Analytical Methods	5.12
Table 5.12. TCLP Inorganic Constituents of Potential Concern (CoPC)	5.14
Table 6.1. Solids and Oxide Content of AZ-101 Pretreated LAW Solution	6.1
Table 6.2. Best Analytical Estimates for AZ-101 LAW Glass Composition in Mass Fractions	6.5
Table 6.3. Values of $10^4 \sigma_A$ for Best Analytical Estimates for AZ-101 LAW Glass Composition	6.6
Table 6.4. Averaged Best Analytical Estimates for AZ-101 LAW Glass Composition in Mass         Fractions Sorted by Target	6.7
Table 6.5. Waste Loading as Dilution Factor for AZ-101 LAW Waste Glass Constituents	6.9
Table 6.6. Radioisotope Activity in AZ-101 Glass in µCi/g (including dates of analysis)	6.10
Table 6.7. Expected and Measured Radionuclide Content in µCi/g of AZ-101 Glass	6.11
Table 6.8. Measured Dose Rates of ILAW Glasses at Contact	6.12
Table 6.9. EDS Composition (in atomic fractions) of Spinel Crystals in AZ-101 LAW Melt         Subjected to CCC Heat Treatment	6.16
Table 6.10. EDS Composition (in atomic fractions of spinel-forming cations) of Spinel Crystals         in AZ-101 LAW Melt Subjected to CCC Heat Treatment	6.16
Table 6.11. EDS Composition (in atomic fractions of cations) of Augite Crystals in AZ-101 LAW         Melt Subjected to CCC Heat Treatment.	6.17
Table 6.12. EDS Composition (in atomic fractions) of Glass Matrix in AZ-101 LAW Melt         Subjected to CCC Heat Treatment	6.17
Table 6.13. EDS Composition of Bulk Glass Matrix in AZ-101 LAW Melt Subjected to CCC         Heat Treatment	6.17
Table 6.14.       7-Day PCT Solution Analysis of AZ-101 LAW Glass Subjected to CCC Heat         Treatment	6.19
Table 6.15. Normalized 7-Day PCT Releases of AZ-101 LAW Glass Subjected to CCC Heat         Treatment	6.20

Table 6.16. Calculated Compositions of Amorphous Matrices and PCT Releases for AZ-101LAW Glass as Functions of Mass Fraction of Pyroxene Crystals (Vienna et al. 2002)	. 6.20
Table 6.17. Concentrations of TCLP Inorganic Constituents of Potential Concern (CoPC)	. 6.22
Table 6.18. Properties of Actual and Simulant AZ-101 Waste at 2.75M Na	. 6.23
Table 6.19. Properties of Actual and Simulant AZ-101 Melter Feed at 2.75M Na	. 6.24
Table 6.20. Properties of Actual and Simulant AZ-101 LAW Glass	. 6.24
Table 6.21. Comparison of PCT Normalized Releases (in g/m²) Between Actual and Simulant         AZ-101 CCC-Treated Glass	. 6.24
Table 6.22. Comparison of Average 7-Day 90°C PCT Normalized Mass Loss Data Between VSL Non-Radioactive Simulant Glasses and Actual Radioactive LAW Glass Counterparts from this Study.	. 6.25
Table 6.23. Durability of the LRM Glass Shown for the Two Different Studies	. 6.25
Table 7.1. Summary of Radiochemical Results Showing Contract Compliance for Waste Glass	7.2

# Abbreviations and Acronyms

AEA	alpha energy analysis
AES	atomic emission spectroscopy
ALO	Analytical Laboratory Operations
ARG-1	Analytical Reference Glass-1
ASO	Analytical Service Operations
ASTM	American Society for Testing and Materials
BNI	Bechtel National Inc.
CAS	Chemical Abstract Service
CCC	container centerline cooling
CFR	U.S. Code of Federal Regulations
СМС	Chemical Management Center
CoPC	Constituents of Potential Concern
CRM	Certified Reference Material
CUA	Catholic University of America
CVAA	cold vapor atomic absorption spectroscopy
DIW	deionized water
DOE	U.S. Department of Energy
EDS	energy dispersive spectroscopy
EPA	U.S. Environmental Protection Agency
EQL	estimated quantification limit
GEA	gamma energy analysis
HLW	high-level waste
IC	ion chromatography
ICP	inductively coupled plasma
ICP-AES	inductively coupled plasma-atomic emission spectroscopy
ICP-MS	inductively coupled plasma-mass spectroscopy
ILAW	immobilized low-activity waste
ISE	ion-specific electrode
KPA	kinetic phosphorescence analysis
LAW	low-activity waste
LCS	laboratory control standard
LDR	Land Disposal Restrictions
LFCM	liquid-fed ceramic melter
LRM	low-activity test reference material
mass%	mass percent

MDL	method detection limit
MS	mass spectrometry
M&TE	measuring and test equipment
ND	non detect
NSBG	near-surface burial ground
ORP	Office of River Protection
РСТ	Product Consistency Test
PNWD	Battelle—Pacific Northwest Division
QA	quality assurance
QAPjP	quality assurance project plan
QC	quality control
RCRA	Resource Conservation Recovery Act
RPD	relative percent deviation
RPL	Radiochemical Processing Laboratory
RPP-WTP	River Protection Project-Waste Treatment Plant
RSD	relative standard deviation
SEM	scanning electron microscopy
TCLP	Toxicity Characteristic Leaching Procedure
TDS	total dissolved solids
TIC	total inorganic carbon
TOC	total organic carbon
TRU	transuranic
UTS	Universal Treatment Standards
vol%	volume percent
VSL	Vitreous State Laboratory
WAC	Washington Administrative Code
WTP	Hanford Waste Treatment and Immobilization Plant
WTPSP	Waste Treatment Plant Support Project
XRD	x-ray diffraction

## References

40 CFR 268. U.S. Environmental Protection Agency, "Land Disposal Restrictions," U.S. Code of *Federal Regulations*. Washington, D. C.

49 CFR 172.101, Table 2. U.S. Department of Transportation, "Radionuclides," U.S. Code of Federal Regulations. Washington, D. C.

American Society for Testing and Materials (ASTM). 1997. ASTM C1285-97, *Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses: The Product Consistency Test (PCT)*. West Conshohoken, PA.

Brackenbury P. 2001. *Interface Control Document for Waste Treatability Samples*. Bechtel Document Number ICD-24590-01-00023, Rev 0A, Bechtel National, Inc. Richland, WA.

Burgeson IE. 2002. Small Column Testing of SuperLig® 639 for Removing <sup>99</sup>Tc from Hanford Tank Waste Envelope A (Tank 241-AZ-101). PNWD-3222, Battelle Pacific Northwest Division., Richland, WA.

Ebert WL and SF Wolf. 1999. *Round-Robin Testing of a Reference Glass for Low-Activity Waste Forms*. ANL-99/22, Argonne National Laboratory, Argonne, IL.

Fiskum SK. 2002. Small Column Ion Exchange Testing of SuperLig<sup>®</sup> 644 for Removal of <sup>137</sup>Cs from Hanford Waste Tank 241-AZ-101 Diluted Feed (Envelope A). PNWD-3198, Battelle Pacific Northwest Division, Richland, WA.

Goheen SC, PR Bredt, OT Farmer, SK Fiskum, KA Gaither, LR Greenwood, LK Jagoda, AP Poloski, RD Scheele, CZ Soderquist, RG Swoboda, MP Thomas, MW Urie, and JJ Wagner. 2002. *Chemical Analyses and Physical Property Testing of Diluted 241-AZ-101 Tank Waste*. PNWD-3174, Battelle Pacific Northwest Division, Richland, WA.

Hansen EK, and RF Schumacher. 2003. *Characterization of HLW and LAW Glass Formers – Final Report*. SRT-RPP-2002-00146 Rev. 1, Westinghouse Savannah River Company, Aiken, SC.

Hrma P, P Izak, JD Vienna, GM Irwin, and M-L Thomas. 2002. "Partial Molar Liquidus Temperatures of Multivalent Elements in Multicomponent Borosilicate Glass." *Phys. Chem. Glasses* 43(2):128-136.

Muller, I. S., A. C. Buechelle, and I. L. Pegg. 2001. *Glass Formulation and Testing with RPP-WTP LAW Simulants*, VSL-01R3560-2, Vitreous State Laboratory, Washington, D. C.

Muller, Isabelle S., and Ian L. Pegg. 2003. "*LAW Glass Formulation to Support AZ-101 Actual Waste Testing*". VSL-03R3470-3. Vitreous State Laboratory, *The* Catholic University of America *for* Duratek, Inc. and *Bechtel* National, Inc.

Poloski AP, PR Bredt, RG Swoboda, and DE Wallace. 2003. *Rheological and Physical Properties of AZ-101 LAW Pretreated Waste and Melter Feed*. PNWD-3367, Battelle Pacific Northwest Division, Richland, WA.

Russell RL. 2002. *AZ-101 Diluted Batch (Envelope B) Simulant Development Report*. PNWD-3248, Battelle Pacific Northwest Division, Richland, WA.

Sidibe A. 2002. *AZ-101 (Envelope B) LAW Vitrification, Product Testing, and Regulatory Analyses.* 24590-LAW-TSP-RT-02-004, Rev. 0. Bechtel National, Inc. Richland, WA.

Smith GL. 1993. *Characterization of Analytical Reference Glass-1 (ARG-1)*. PNL-8992, Pacific Northwest National Laboratory, Richland, WA.

Smith, G. L., Greenwood, L. R., Piepel, G. F., Schweiger, M. J., Smith, H. D., Urie, M.W., and Wagner, J. J. 2000. *Vitrification and Product Testing of AW-101 and AN-107 Pretreated Waste*. PNNL-13372, Pacific Northwest National Laboratory, Richland, WA.

Smith, H. D., R. J. Bates, P. R. Bredt, L. R. Greenwood, M. J. Schweiger, M. W. Urie, and D. R. Weier. 2004. *Vitrification and Initial Product Testing of AP-101 Pretreated LAW Envelope A Glass.* WTP-RPT-092. Rev. 0, Pacific Northwest National Laboratory, Richland, WA.

U.S. Environmental Protection Agency (EPA). 1992. "Toxicity Characteristic Leaching Procedure (TCLP)." SW-846, Method 1311, Rev. 0. In: *Test Methods for Evaluating Solid Waste*, Volume 1C: Laboratory Manual Physical/Chemical Methods, Office of Solid Waste and Emergency Response, Washington, D.C.

U.S. Department of Energy, Office of River Protection (DOE-ORP). 2000. *Contract between DOE Office of River Protection and Bechtel National, Inc. for the Design and Construction of the Hanford Tank Waste Treatment and Immobilization Plant*. DE-AC27-01RV14136, Richland, WA

U.S. Nuclear Regulatory Commission (NRC). 1998. Instructions for Completing NRC's Uniform Low-Level Radioactive Waste Manifest. NUREG/BR-0204, Washington, D.C.

Vienna JD, D-S Kim, and P Hrma. 2002. *Database and Interim Glass Property Models for Hanford HLW and LAW Glasses*. PNNL-14060, Pacific Northwest National Laboratory, Richland, WA.

Washington Administrative Code (WAC). 2000. "Dangerous Waste Regulations, as amended." WAC 173-303, Olympia, WA.

Weier DR, and GF Piepel. 2002. *Methodology for Adjusting and Normalizing Analyzed Glass Compositions*. WTP-RPT-049, Battelle Pacific Northwest Division, Richland, WA.

## **Testing Summary**

This document describes work performed under Battelle—Pacific Northwest Division (PNWD) Test Plan TP-RPP-WTP-177, Rev 0, "AZ-101 (Envelope B) LAW Vitrification, Product Testing, and Regulatory Analyses" by S. K. Fiskum, 2002. The U.S. Department of Energy (DOE) Office of River Protection (ORP) has contracted with Bechtel National Inc. (BNI) to design, construct, and demonstrate a waste treatment plant (WTP) (DOE-ORP 2000). The River Protection Project-Waste Treatment Plant (RPP-WTP) will separate waste into low-activity waste (LAW) and high-level waste (HLW) and will separately vitrify these wastes into borosilicate glasses.

## **Objectives**

The primary objective for vitrifying the LAW sample is to generate glass for subsequent product testing. The work presented in this report includes seven work elements: 1) glass fabrication, 2) chemicalcomposition analyses, 3) radiochemical composition analyses, 4) waste loading, 5) determination of crystalline and noncrystalline phases, 6) waste-form leachability, and 7) demonstrating that the waste form can meet requirements for land disposal under the State of Washington Dangerous Waste Regulations, WAC 173-303 (WAC 2000), and Resource Conservation and Recovery Act (RCRA) Land Disposal Restrictions (LDR) in 40 CFR 268 (The Toxicity Characteristic Leaching Procedure [TCLP] [EPA 1992] for hazardous inorganics was applied to show that the waste form met the UTS limits). Crystalline and noncrystalline phase determination and the Product Consistency Test (PCT) (waste-form leachability) are performed on the centerline-cooled glass. These work elements will help demonstrate the River Protection Project-Waste Treatment Plant (RPP-WTP) project's ability to satisfy the product requirements concerning chemical and radionuclide reporting, waste loading, identification and quantification of crystalline and noncrystalline phases, and waste-form leachability. Table S.1 gives a summary of the attained objectives.

		Objective		
	Test Objective	Met	Discussion	
1.	Glass Fabrication	yes	~425 grams of glass fabricated	
2.	Chemical Composition Analyses	yes	ICP-AES <sup>(a)</sup> – Statistically Refined	
3.	Radiochemical Composition Analyses	yes	A combination of Radiochemistry and ICP-MS <sup>(b)</sup>	
4.	Waste loading	yes	>5 Wt % of glass consists of waste Na <sub>2</sub> O	
5.	Determination of Crystalline and		A combination of XRD <sup>(c)</sup> , optical microscopy, and	
	Noncrystalline Phases	yes	SEM <sup>(d)</sup> identified a pyroxene devitrification phase.	
6.	Waste-Form Leachability (PCT)	yes	Met requirements	
7.	Dangerous Waste Limitations - the waste			
	form meets requirements for land disposal.	yes	Met UTS limits	
(a)	a) ICP-AES = inductively coupled plasma-atomic emission spectroscopy.			
(b)	) ICP-MS = inductively coupled plasma-mass spectrometry.			
(c)	XRD = X-ray diffraction.			
(d)	SEM = scanning electron microscopy.			

Table S.1.	Summary	of Test	Objectives	and	Results

### **Test Exceptions**

One test exception was issued during the course of this work, 24590-WTP-TEF-RT-03-025. This test exception resulted in four changes to the Test Plan as shown in Table S.2:

Test Exceptions	Description
1. 24590-WTP-TEF-RT-03-025	<ol> <li>Reporting of boron shall be included in the analysis of the TCLP extract. The EQL for boron shall be 0.05 mg/L</li> </ol>
	<ol> <li>Change "Method Detection Limit (MDL)" to "Estimated Quantification Limit" in paragraph 2 of section titled "Additional QA Requirements" to allow for quantitative reporting of element concentrations.</li> <li>Delete the requirement to perform cyanide analyses from the test specification and test plan.</li> <li>Replace method RPG-CMC-134 in section 3.0 with method RPG-CMC-138 or equivalent method.</li> </ol>
	Based on this test exception, an interim change notice (ICN) was issued incorporating these changes into test plan <i>TP-RPP-WTP-177</i> .

 Table S.2. Test Exceptions

## **Results and Performance Against Success Criteria**

The primary objective for vitrifying the LAW sample was to generate a glass product and conduct product testing. Table S.3 summarizes the Success Criteria as well as the results. Testing sought to demonstrate the RPP-WTP project's ability to satisfy the product requirements.

	Success Criteria	How the Criteria were Met		
1.	Chemical constituents present in the glass at concentrations greater than 0.5 wt% are identified and quantified.	Met. The AZ-101 LAW glass contains 12 constituent oxides with concentration >0.5 mass%. These oxides are (with best analytical estimates in mass%): SiO <sub>2</sub> (48.70), B <sub>2</sub> O <sub>3</sub> (10.04), CaO (6.79), Al <sub>2</sub> O <sub>3</sub> (6.21), Na <sub>2</sub> O (5.35), Fe <sub>2</sub> O <sub>3</sub> (5.29), ZnO (4.85), Li <sub>2</sub> O (4.31), ZrO <sub>2</sub> (3.17), MgO (2.99), TiO <sub>2</sub> (1.40), and SO <sub>3</sub> (0.51).		
2.	The radionuclides determined as significant per NUREG/BR-0204 (NRC 1998) and 49 CFR 172.101 Table 2 in Appendix A (current and indexed to December 31, 2002) are identified and quantified.	Met. Identification and quantification of those radionuclides identified as significant in NUREG/BR-0204 and 49 CFR 172.101. The date of analysis is given Table 6.6 and allows the values reported to be indexed to any date desired. Technetium-99 is considered significant at concentrations >3.0E-3 Ci/m <sup>3</sup> . Assuming that the		

Table S.3. Success Criteria

	Success Criteria	How the Criteria were Met		
		density of the glass is 2.7 g/mL, the AZ-101 glass contains a maximum of 9.29E-4 Ci/m <sup>3</sup> of <sup>99</sup> Tc. Hence, this glass does not contain a significant quantity of <sup>99</sup> Tc.		
3.	The concentrations of <sup>137</sup> Cs, <sup>90</sup> Sr, <sup>99</sup> Tc and transuranic (TRU) radionuclides in the ILAW product are less than 0.3 Ci/m <sup>3</sup> , 20 Ci/m <sup>3</sup> , 0.1 Ci/m <sup>3</sup> , and 100 nCi/g, respectively. In another section, the contractual requirement indicates that <sup>137</sup> Cs will be less than 3 Ci/m <sup>3</sup> of glass. Note that the glass meets the most stringent limit. See Section 4.0 for contract reference.	Met. The AZ-101 LAW glass contains ${}^{90}$ Sr, ${}^{99}$ Tc, ${}^{137}$ Cs, and TRU at levels considerably below the contract limits as shown in the table. $^{90}$ Sr (Ci/m <sup>3</sup> ) 0.347 ${}^{99}$ Tc (Ci/m <sup>3</sup> ) 7.16E-2 ${}^{137}$ Cs (Ci/m <sup>3</sup> ) 3.43E-2 TRU (nCi/g) 0.046 Met. The physical sector is shown		
4.	The mass fraction of $Na_2O$ from LAW for Envelope B in the LAW glass is >5 wt%.	AZ-101 LAW glass is 5.58 mass%. Hence, the AZ-101 LAW glass meets the task specification concentration.		
5.	Crystalline and non-crystalline phases are identified and quantified.	Met. The AZ-101 LAW glass subjected to CCC contained sporadic crystals of spinel (mainly zincochromite) and augite of a similar composition to the glass. The total amount is less than ~0.8 wt%.		
6.	The normalized mass loss of sodium, silicon, and boron, is $<2.0 \text{ g/m}^2$ measured with a 7-day Product Consistency Test (PCT) at 90°C as defined in C1285-97 (ASTM 1997).	Met. The measured normalized PCT releases from the AZ-101 LAW glass are 0.26 g/m <sup>2</sup> for B, 0.11 g/m <sup>2</sup> for Si, and 0.25 g/m <sup>2</sup> for Na. These values are well below the limit of 2.0 g/m <sup>2</sup> . The precipitation of crystals on cooling apparently does not affect glass leachability.		
7.	The glass meets the Land Disposal Restrictions (LDR) of Washington Dangerous Waste Regulations, WAC 173-303 (WAC 2000), and Resource Conservation Recovery Act (RCRA) LDR in 40 CFR 268 (TCLP for hazardous inorganics) or the TCLP response of the LDR components meet the UTS limits.	Met. The TCLP leachate from the AZ-101 LAW glass had inorganic hazardous constituent concentrations below the UTS limits of the LDR regulations for Washington state and RCRA.		

## **Quality Requirements**

## **Application of RPP-WTP Quality Assurance Requirements**

PNWD implements the 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, and NQA-2a-1990, Part 2.7. These quality requirements are implemented through PNWD's Waste Treatment Plant Support Project (WTPSP) *Quality Assurance Requirements and Description Manual*. The work reported in Sections 5.1.1, 5.1.4, 5.1.5, and 6.1 and all analytical data collection pertaining to the pretreated AZ-101 LAW were conducted in the summer of 2002 accordance with PNWD's *Conducting Analytical Work in Support of Regulatory Programs*. The work pertaining to the vitrification of pretreated AZ-101 LAW and glass testing reported in Sections 5.2.1 - 5.2.5 and 6.2 - 6.7 and all analytical data collections were performed in the fall of 2003 and winter of 2004 and met the analytical requirements as 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 and 2a requirements with the PNWD's procedures for this work is given in Test Plan TP-RPP-WTP-177, Rev 0, Table 5. 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" assuring that sufficient data were taken with properly calibrated measuring and test equipment (M&TE) to obtain quality results.

As specified in Test Specification, 24590-LAW-TSP-RT-02-004, 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-177, Rev 0, Table 3.

The ICP-AES analysis of the AZ-101 ILAW (glass) was carried out by dissolving the powdered glass in a molten salt using both KOH, KNO<sub>3</sub> in a Ni crucible and Na<sub>2</sub>O<sub>2</sub>-NaOH in a Zr crucible. Then the fusion buttons are dissolved in nitric acid and aliquots of these solutions are analyzed. The only QC issue with the analysis using the KOH, KNO<sub>3</sub> – Ni crucible fusion was a low recovery for manganese with one of the laboratory control standards. For the Na<sub>2</sub>O<sub>2</sub>-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 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 quantification. So these results should be considered acceptable.

TCLP Results for AZ-101 Envelope B Glass are summarized in Appendix E.

#### **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 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 lists the required R&T test requirements and briefly summarizes the successful outcome of these tests.

	<b>R&amp;T</b> Test Conditions	Test Conditions Followed? Results
1.	Pretreated LAW active sample will be combined with a glass former mixture prescribed by the WTP project and melted in a 90% platinum/ 10% rhodium crucible.	Yes. Pretreated LAW active sample was combined with a glass former mixture prescribed by the WTP project and melted in a 90% platinum/ 10% rhodium crucible. The melter feed was dried in stages to 350°C, calcined at 600°C to 732°C and melted at 1150°C.
2.	Elemental Composition of the glass.	Yes. The primary components with concentrations above 0.5 wt% and RCRA metals were determined. See Section 6.2
3.	Radiochemical Composition of the glass.	Yes. Radiochemical analyses for listed fission products, uranium isotopes, and transuranics completed. See Section 6.3
4.	Determination and Quantification of Crystalline and non-crystalline phases.	Yes. Pyroxene and spinel phases identified in glass. Amount less than 0.8 wt%.
5.	A 7-day Product Consistency Test (PCT) at 90°C as defined in C1285-97 (ASTM 1997).	Yes. The measured normalized PCT releases from the AZ-101 LAW glass are 0.26 g/m <sup>2</sup> for B, 0.11 g/m <sup>2</sup> for Si, and 0.25 g/m <sup>2</sup> for Na. These values are well below the limit of 2.0 g/m <sup>2</sup> . The precipitation of crystals on cooling apparently does not affect glass leachability. The normalized mass loss of sodium, silicon, and boron, is <2.0 g/m <sup>2</sup> .
6.	Performed the Toxic Characteristic Leaching Procedure on glass samples.	Yes. The TCLP leachate from the AZ-101 LAW glass had inorganic hazardous constituent concentrations below the UTS limits of the LDR regulations for Washington state and RCRA.

 Table S.4.
 R&T Test Conditions

#### **Glass Fabrication**

A pretreated tank supernatant, LAW originating from Hanford Tank 241-AZ-101 (AZ-101) was prepared as melter feed for vitrification. The analyzed composition of the pretreated AZ-101 LAW was used by Catholic University of America's (CUA's) Vitreous State Laboratory (VSL) to formulate the target glass composition (LAWB83).

The supernatant tank samples from AZ-101 were received by PNWD in glass jars transferred from Hanford's 222-S facility. These jars contained only tank supernatant liquid with no visible solids. The materials in the jars were composited, homogenized, and characterized (Goheen et al. 2002). The composite was then processed through pretreatment chemical separation processes, including the following unit operations to simulate the RPP-WTP project flowsheet: 1) dilution of the batch, 2) removal of <sup>137</sup>Cs by ion exchange, and 3) removal of <sup>99</sup>Tc by ion exchange.

Project-approved glass-former additives were added to the pretreated LAW to produce a melter feed. These additives are kyanite ( $Al_2SiO_5$ ), boric acid ( $H_3BO_3$ ), wollastonite ( $CaSiO_3$ ), iron III oxide ( $Fe_2O_3$ ), lithium carbonate ( $Li_2CO_3$ ), olivine ( $Mg_2SiO_4$ ), silica ( $SiO_2$ ), rutile ( $TiO_2$ ), zinc oxide (ZnO), and zircon ( $ZrSiO_4$ ). The AZ-101 melter feed was dried at 200°C, calcined to 732°C, and melted at 1150°C for 1 hour. The melt was then poured onto a stainless steel plate, cooled, crushed to a fine powder in a tungsten carbide mill, mixed, added back into the crucible, and melted for an additional hour at 1150°C to assure the homogenization of the glass melt.

The product-quality-related properties of the glass, which are the focus of this study, are determined by the composition and temperature history of the glass. The preparation of glass in this project roughly reproduced the three phases of feed-to-glass conversion in the large-scale melter (drying, calcining, and melting). Except the impact of gas atmosphere on the redox states of multivalent oxides, any other differences between crucible and melter vitrification conditions are virtually inconsequential for the properties of the final product. To bracket the effects of temperature histories on product quality, both steel quenching and simulated container centerline cooling were performed on glass samples used for testing.

#### **Analytical Results**

The measured chemical composition of AZ-101 LAW glass is close to its target composition (VSL glass composition designated "LAWB83," see table in Appendix D). Per the RPP-WTP project LAW glass Task Specification 24590-LAW-TSP-RT-02-004, Rev 0, "AZ-101 (Envelope B) LAW Vitrification, Product Testing, and Regulatory Analyses," the concentration of the waste sodium oxide shall be greater than 3 mass%. The target mass fraction of Na<sub>2</sub>O for AZ-101 LAW was 5.35, and the measured mass fraction of Na<sub>2</sub>O was 5.58 mass%. These low values are necessitated by the following constraint: the product of Na<sub>2</sub>O and SO<sub>3</sub> mass fractions in glass must be no greater than  $5 \times 10^{-4}$  for the melt to be processable in WTP melters. The actual value of this product, based on the best analytical estimates for Na<sub>2</sub>O and SO<sub>3</sub> fractions, is  $3.1 \times 10^{-4}$ . As all of the Na<sub>2</sub>O content for the AZ-101 glass originated from the initial tank waste, the AZ-101 LAW glass has a waste Na<sub>2</sub>O content compatible with the contract limits.

The target and measured total content of LAW components in glass (the waste loading) was 6.67 mass% and 6.68 mass%, respectively. The difference between the actual and target composition of

the AZ-101 LAW glass was calculated as  $\sqrt{[\Sigma(g_{Ai}-g_{Ti})^2]}$ , where  $g_{Ai}$  is the measured *i*-th component mass fraction, and  $g_{Ti}$  is the targeted *i*-th component mass fraction. This difference is 0.0056, showing excellent agreement between the actual and target composition of AZ-101 LAW glass. Table S.5 compares the target mass fraction with the measured values for major glass components (those with more than 0.5 mass% in glass). The less accurate energy dispersive spectroscopy (EDS) estimates are also included; the SEM-EDS composition analysis agreed with both the inductively coupled plasma (ICP) analysis and the target composition of the AZ-101 glass. The percent difference in the analyzed values for AZ-101 compared with the targeted values are +4.4% for Al<sub>2</sub>O<sub>3</sub>, +0.0% for B<sub>2</sub>O<sub>3</sub>, 3.6% for CaO, -0.6% for Fe<sub>2</sub>O<sub>3</sub>, 0.7% for Li<sub>2</sub>O, +0.8% for MgO, +4.4% for Na<sub>2</sub>O, +0.4% for SiO<sub>2</sub>, +8.6% for TiO<sub>2</sub>, -0.5% for ZnO, and -7.3% for ZrO<sub>2</sub>.

	Target	<b>Final Estimate</b>	$10^4 \sigma^{(a)}$	EDS Estimate	
SiO <sub>2</sub>	0.4870	0.4890	5.48	0.493	
B <sub>2</sub> O <sub>3</sub>	0.1004	0.1004	10.29	n/a	
CaO	0.0679	0.0655	0.03	0.069	
Al <sub>2</sub> O <sub>3</sub>	0.0621	0.0593	0.06	0.056	
Na <sub>2</sub> O	0.0535	0.0558	7.67	0.049	
Fe <sub>2</sub> O <sub>3</sub>	0.0529	0.0526	0.13	0.054	
ZnO	0.0485	0.0483	0.01	0.053	
Li <sub>2</sub> O	0.0431	0.0434	3.78	n/a	
ZrO <sub>2</sub>	0.0317	0.0294	1.44	n/a	
MgO	0.0299	0.0301	5.85	0.026	
TiO <sub>2</sub>	0.0140	0.0152	3.98	0.016	
SO <sub>3</sub> <sup>(b)</sup>	0.0055	0.0055	n/a	0.0051	
(a) $\sigma$ is the average standard deviation based on duplicate measurements with three sample preparation methods. (b) SO <sub>3</sub> content is not measured by ICP-AES but was measured instead by EDS (energy dispersion spectrometry)					

Table S.5. Target and Measured (Best Analytical Estimate) AZ-101 LAW Glass Composition

Based on identification and quantification of radionuclides found in the pretreated wastes and a comparison with radionuclides identified as significant in RPP-WTP project LAW glass Task Specification 24590-LAW-TSP-RT-02-004, "AZ-101 (Envelope B) LAW Vitrification, Product Testing, and Regulatory Analyses," and 49 CFR 172.101, the radionuclides of interest in the AZ-101 glass were determined and analytically measured specific to the task specification. The activity of <sup>90</sup>Sr, <sup>99</sup>Tc, <sup>137</sup>Cs, and transuranic (TRU) radionuclides is less than 20 Ci/m<sup>3</sup>, 0.1 Ci/m<sup>3</sup>, 0.3 Ci/m<sup>3</sup>, and 100 nCi/g, respectively. As summarized in Table S.3 above, the glass easily meets each of these criteria.

Identification and quantification of crystalline and noncrystalline phases were performed on glass subjected to a simulated cooling profile for glass at the centerline of an LAW container. Using XRD, optical microscopy, and SEM-EDS, the AZ-101 LAW glass contained sporadic crystals. Based on visual inspection and XRD, the crystalline content of the glass was less than 0.8% and probably less than 0.5%. Spinel crystals formed at a higher temperature and slowly reacted with the surrounding melt to form the pyroxene as the temperature decreased. Spinel was mainly zincochromite (ZnCr<sub>2</sub>O<sub>4</sub>) in solid solution with spinel (MgAl<sub>2</sub>O<sub>4</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>). Augite dendrites of the average composition Na<sub>0.08</sub>Ca<sub>0.81</sub>Mg<sub>0.49</sub>Zn<sub>0.07</sub>Al<sub>0.08</sub>Fe<sub>0.35</sub>Cr<sub>0.01</sub>Si<sub>1.92</sub>Ti<sub>0.08</sub>O<sub>6</sub> nucleated on and branched from bubbles and spinel.

The release of sodium, silicon, and boron from crushed AZ-101 glass into water was measured with a 7-day PCT at 90°C as defined in ASTM C1285-97. The normalized mass loss is required to be less than  $2.0 \text{ g/m}^2$ . The measured normalized PCT releases of the AZ-101 LAW glass (measured in triplicate) were  $0.26 \text{ g/m}^2$  for B,  $0.25 \text{ g/m}^2$  for Na, and  $0.11 \text{ g/m}^2$  for Si. These values are well below the limit of 2.0 g/m<sup>2</sup>. Because the composition of the crystalline phase (augite) that precipitates from the glass on cooling is close to that of the glass, the impact of crystallization on PCT is virtually zero.

Dangerous-waste limitations testing (the TCLP test [EPA 1992]) was completed on 10 g of quenched AZ-101 LAW glass. As shown in Table S.6., AZ-101 LAW glass passes this test and qualifies for land disposal.

		UTS <sup>(a)</sup>	Required	Measured			
Elemen	t	(mg/L-TCLP)	for LDR	(mg/L-TCLP)			
Antimony	Sb	1.15	Х	0.028 U			
Arsenic	As	5.0	VIT	0.045 U			
Barium	Ba	21	VIT	0.24 J			
Beryllium	Be	1.22	Х	0.0002 U			
Boron <sup>(b)</sup>	В	n/a	n/a	0.428			
Cadmium	Cd	0.11	VIT	0.006 U			
Chromium	Cr	0.6	VIT	0.008 J			
Lead	Pb	0.75	VIT	0.035 U			
Mercury	Hg	0.025	VIT	0.000049 J			
Nickel	Nickel Ni 11			0.014 U			
Selenium	Se	5.7	VIT	0.042 U			
Silver	Silver Ag 0.14			0.005 U			
Thallium	Tl	0.20	Х	0.00011J			
Vanadium	V	1.6	n/a	0.003 U			
Zinc	Zn	4.3	n/a	0.79 J			
(a) UTS = $U$	Jnive	ersal treatment standar	rd, 40 CFR 268				
(b) Boron i	s inc	cluded for informati	on only and is r	ot a Constituent of			
Potentia	al Co	oncern.					
X = Require	X = Required for LDR						
VIT = vitrification has been recognized as the best available technology							
for immobilizing these elements per 40 CFR 268.40.							
n/a = not ap	n/a = not applicable						
U = Undetected. Analyte was analyzed but not detected (e.g., no measurable							
instrument response), or response was less than the MDL.							
J = Estimate	J = Estimated value. Value is below EQL and above MDL.						

Table S.6. Analytical Results for TCLP Inorganic Constituents of Potential Concern

#### Simulant Use

Simulant produced by VSL and characterized by them was shown to produce a melter feed with physical properties like those of the AZ-101 (B) actual melter feed and produced a glass with similar properties too. See Section 6.7.

## **Discrepancies and Follow-on Tests**

None

## **1.0 Introduction**

The U.S. Department of Energy (DOE) Office of River Protection (ORP) has contracted with Bechtel National Inc. (BNI) to design, construct, and demonstrate a waste treatment plant (WTP) (DOE-ORP 2000). The River Protection Project-Waste Treatment Plant (RPP-WTP) will separate Hanford tank waste into low-activity waste (LAW) and high-level waste (HLW) and will separately vitrify them into borosilicate glasses. Battelle—Pacific Northwest Division, hereafter referred to as PNWD, has been contracted to produce and test a vitrified immobilized low-activity waste (ILAW) form from the AZ-101 Envelope B LAW samples previously supplied to the RPP-WTP project by DOE.

DOE currently has radioactive waste stored in underground storage tanks at the Hanford site in southeastern Washington State. A supernatant sample was taken from Tank AZ-101. Before the vitrification testing reported here, most of the radioactivity was removed from the supernatant sample through pretreatment chemical-separation processes (Burgeson 2002). The decontaminated supernatant was then processed into LAW glass. The AZ-101 supernatant sample was processed through the following unit operations to simulate the RPP-WTP project flowsheet: 1) dilute the batch, 2) remove <sup>137</sup>Cs by ion exchange (Fiskum 2002), and 3) remove <sup>99</sup>Tc by ion exchange.

The primary objective for vitrifying the Tank AZ-101 (Envelope B) pretreated waste sample was to characterize the glass produced from the crucible melt. [24590-LAW-TSP-RT-02-004, Rev. 0, *AZ-101 (Envelope B) LAW Vitrification, Product Testing, and Regulatory Analyses,* by A. Sidibe]. The objective of this testing is to demonstrate compliance with the RPP-WTP contractual requirements, such as chemical and radionuclide reporting, product loading, and dangerous-waste limitations and to validate the use of simulants for estimation of glass properties. The work scope reported here is divided into 7 work elements: 1) glass fabrication, 2) chemical composition analyses, 3) radiochemical composition analyses, 4) waste loading, 5) identification of crystalline and noncrystalline phases, 6) waste-form leachability, and 7) Toxicity Characteristic Leaching Procedure (U.S. Environmental Protection Agency (EPA). 1992). The various properties of the glass are then compared to those of a simulant glass fabricated to the same target composition and characterized by VSL (Muller and Pegg 2003). These work elements will help demonstrate the River Protection Project-Waste Treatment Plant (RPP-WTP) project's ability to satisfy the product requirements concerning chemical and radionuclide reporting, waste loading, identification and quantification of crystalline phases, and waste-form leachability.

## 2.0 Quality Assurance Requirements

## 2.1 Application of RPP-WTP Quality Assurance Requirements

PNWD implements the 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, and NQA-2a-1990, Part 2.7. 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 and 2a requirements with the PNWD's procedures for this work is given in test plan TP-RPP-WTP-177, Rev 0, Table 5. (Applicable Quality Assurance Procedures) It includes justification for those requirements not implemented.

## 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-LAW-TSP-RT-02-004, Rev 0, *AZ-101 (Envelope B) LAW 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 5 in Test Plan TP-RPP-WTP-177, Rev 0 (Quality Control Parameters for ILAW Analysis).

The ICP-AES analysis of the AZ-101 ILAW (glass) was carried out using both a KOH,  $KNO_3$  - Ni crucible fusion and a  $Na_2O_2$  - NaOH - Zr crucible fusion. 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 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 quantification. So these results should be considered acceptable.

TCLP Results and QA data for AZ-101 Envelope B Glass are completely summarized in Appendix E.

## 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*. Third-party independent validation is beyond the scope of this report.

## 3.0 Objectives

This work addresses RPP-WTP contract requirements to demonstrate the contractor's ability to satisfy the ILAW product requirements (Specification 2 of the *Contract between DOE Office of River Protection and Bechtel National, Inc. for the Design and Construction of the Hanford Tank Waste Treatment and Immobilization Plant.* (DOE-ORP 2000)) with samples of LAW. See 24590-LAW-TSP-RT-02-004, Rev. 0, *AZ-101 (Envelope B) LAW Vitrification, Product Testing, and Regulatory Analyses* and TP-RPP-WTP-177, Rev 0, *AZ-101 (Envelope B) LAW 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 B) LAW sample (see Brackenbury 2001) was to generate a glass product for subsequent testing to demonstrate the Waste Treatment Plant (WTP) project's ability to satisfy the product requirements concerning:

- chemical and radionuclide reporting
- waste loading
- identification and quantification of crystalline and non-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 2 of the RPP-WTP project contract (24590-LAW-TSP-RT-02-004, Rev. 0, *AZ-101 (Envelope B) LAW Vitrification, Product Testing, and Regulatory Analyses*). All work was performed to the test plan which was approved by BNI. (TP-RPP-WTP-177, Rev 0, *AZ-101 (Envelope B) LAW Vitrification, Product Testing, and Regulatory Analyses*).

These criteria are:

- Chemical constituents present in the glass at concentrations greater than 0.5 wt% are identified and quantified.
- The radionuclides determined as significant per NUREG/BR-0204 (NRC 1998) and 49 CFR 172.101 Table 2 in Appendix A (current and indexed to December 31, 2002) are identified and quantified.
- The concentrations of <sup>137</sup>Cs, <sup>90</sup>Sr, <sup>99</sup>Tc and transuranic (TRU) radionuclides in the ILAW product are less than 3 Ci/m<sup>3</sup>, 20 Ci/m<sup>3</sup>, 0.1 Ci/m<sup>3</sup>, and 100 nCi/g, respectively. [2.2.2.8 <u>Radionuclide</u> <u>Concentration Limitations clause Section C from WTP Contract- DE-AC27-01RV1413 Modification No. M033</u>] Note <u>Waste Treatment and Immobilization Plant Unit Operation iii Cs Removal:</u> This operation removes <sup>137</sup>Cs from the filtered supernatant to allow for production of an ILAW waste product that meets the Specification 2.2.2.8, *Radionuclide Concentration Limitations*. In addition, <sup>137</sup>Cs will be further removed, to achieve a 0.3 Ci/m<sup>3</sup> in the ILAW product, to facilitate the maintenance concept established for the ILAW melter system. Hence our target is actually 0.3 Ci/m<sup>3</sup> in the ILAW product.
- The mass fraction of Na<sub>2</sub>O from LAW for Envelope B in the LAW glass is >5 wt%. Note that at the time the Test Specification and BNI approved Test Plan were written the contract limit was >5 wt%.
- Crystalline and non-crystalline phases are identified and quantified.
- The normalized mass loss of sodium, silicon, and boron, is <2.0 g/m<sup>2</sup> measured with a 7-day Product Consistency Test (PCT) at 90°C as defined in C1285-97 (ASTM 1997).
- The glass meets the Land Disposal Restrictions (LDR) of Washington Dangerous Waste Regulations, WAC 173-303 (WAC 2000), and Resource Conservation Recovery Act (RCRA) LDR in 40 CFR 268 (TCLP for hazardous inorganics) or the TCLP response of the LDR components meet the UTS limits.

## 5.0 Experimental Method

## 5.1 Glass Fabrication

A pretreated tank supernatant LAW (AZ-101) was prepared as a melter feed for vitrification. The analyzed composition of the pretreated AZ-101 wastes was used by Catholic University of America (CUA) Vitreous State Laboratory (VSL) to formulate the target glass composition (LAWB83)( Muller and Pegg. 2003). The recipe was forwarded to PNWD to prepare the waste glass.

#### 5.1.1 Pretreated AZ-101 Waste

The pretreated AZ-101 waste was blended with glass-forming chemicals. Before preparing the melter feed, the mass of the pretreated LAW solutions was checked to determine any weight change between the pretreatment process and the initiation of vitrification processing. The composition and properties of the pretreated AZ-101 waste are given in Table 5.1 through Table 5.4(Burgeson 2002, Goheen et al. 2002, Fiskum 2002).

# Table 5.1. Chemical Composition of AZ-101LAW Pretreated Waste: InorganicAnalytes in mg/L

Analyte	mg/L
Al	5280
As	13.5
В	7.75
Cr	569.5
Hg	0.0116
Κ	3800
Мо	85.3
Na	99000
Р	482
Pb	6.65
Si	52.5
Sn	44
Ti	2.55
V	1.35
W	51
Zn	1.65
Zr	1.95

#### Table 5.2. Chemical Composition of AZ-101 Pretreated Waste (in mg/L): Ion Chromatography and Oxidation Analysis

Analyte	mg/L	
Br	685	
F <sup>-</sup>	1900	
NO <sub>2</sub> <sup>-</sup>	61900	
NO <sub>3</sub> <sup>-</sup>	52950	
$C_2O_4^{-2}$	1000	
$PO_4^{-3}$	1600	
$SO_4^{-2}$	16500	
TIC <sup>(a)</sup>	6380	
TOC <sup>(b)</sup>	345	
NH <sub>3</sub>	4.11	
(a) TIC = total inorganic carbon		
(b) $TOC = total organic carbon$		

Isotope	μCi/mL	Reference	Isotope	μCi/mL	Reference	Isotope	μCi/mL	Reference
		Date			Date			Date
<sup>3</sup> H	3.24×10 <sup>-2</sup>	9/12/02	<sup>113</sup> Sn	<7×10 <sup>-5</sup>	10/30/02	<sup>232</sup> Th	<8×10 <sup>-5</sup>	10/30/02
<sup>14</sup> C	1.92×10 <sup>-3</sup>	n/a	<sup>106</sup> RuRh	<3×10 <sup>-4</sup>	10/30/02	<sup>236</sup> Pu	<6×10 <sup>-8</sup>	9/12/02
<sup>51</sup> Cr	<4×10 <sup>-4</sup>	10/30/02	<sup>125</sup> Sb	9.98×10 <sup>-3</sup>	10/30/02	<sup>238</sup> Pu	1.07×10 <sup>-6</sup>	9/12/02
<sup>54</sup> Mn <sup>(a)</sup>	nr	n/a	<sup>126</sup> SnSb	2.23×10 <sup>-3</sup>	10/30/02	<sup>239</sup> Pu	9.25×10 <sup>-6</sup>	9/12/02
<sup>59</sup> Fe	<2×10 <sup>-5</sup>	10/30/02	<sup>134</sup> Cs	<2×10 <sup>-5</sup>	10/30/02	<sup>242</sup> Pu	<2×10 <sup>-7</sup>	9/18/02
<sup>60</sup> Co	1.68×10 <sup>-5</sup>	10/30/02	<sup>137</sup> Cs	3.56×10 <sup>-2</sup>	10/30/02	<sup>241</sup> Pu	5.24×10 <sup>-5</sup>	n/a
<sup>79</sup> Se	1.40×10 <sup>-4</sup>	8/8/02	<sup>144</sup> Ce	<3×10 <sup>-4</sup>	10/30/02	<sup>241</sup> Am	6.75×10 <sup>-7</sup>	9/12/02
<sup>88</sup> Y	<1×10 <sup>-5</sup>	10/30/02	<sup>151</sup> Sm	6.04×10 <sup>-5</sup>	n/a	<sup>243</sup> Am	<2×10 <sup>-7</sup>	9/18/02
<sup>90</sup> Sr	1.60×10 <sup>-1</sup>	9/12/02	<sup>152</sup> Eu	<2×10 <sup>-5</sup>	10/30/02	<sup>242</sup> Cm	<5×10 <sup>-8</sup>	9/12/02
$^{99}{\rm Tc}^{(b)}$	9.33×10 <sup>-4</sup>	9/12/02	<sup>154</sup> Eu	<2×10 <sup>-5</sup>	10/30/02	$^{243}Cm + ^{244}Cm$	<1×10 <sup>-7</sup>	9/12/02
<sup>103</sup> Ru	<5×10 <sup>-5</sup>	10/30/02	<sup>155</sup> Eu	<2×10 <sup>-4</sup>	10/30/02		not used	
(a) Nondet	(a) Nondetect – interference							
b) Partachastata is reported since the complexies analyzed under evidining conditions								

Table 5.3. Radionuclide Activity of AZ-101 Pretreated Waste in µCi/mL

(b) Pertechnetate is reported since the sample was analyzed under oxidizing conditions.

nr = not reported

n/a = not available

Property	Units	Value		
Solution Density,	g/mL	1.224		
Fraction of Solids <sup>(a)</sup>	Mass %	26.68		
Fraction of Oxides <sup>(b)</sup>	Mass %	14.79		
(a) Dried to constant weight at 105°C.				
(b) Fired to constant weight at 1050°C.				

#### 5.1.2 **RPP-WTP Mineral Additives**

Table 5.5 lists the project-approved glass-former minerals (Hansen and Schumacher 2003) for the target glass composition. The chemicals were received from each vendor in the condition that would be used by the vitrification plant at Hanford.

#### 5.1.3 Batch Recipe

The batch composition used to batch the AZ-101 glass was designed by VSL (See the table in Appendix D) (Muller and Pegg, 2003). The VSL batch is made up on the basis of incorporating 2.75 moles of waste sodium and is projected to make 1586 g of glass. For the product testing carried out for this report, it was determined that 425 g of glass would be sufficient. The batch amounts given in Table 5.6 were calculated by multiplying the VSL numbers by 425/1586 = 0.268, so for kyanite, we find  $156.19 \times 0.268 = 41.85$ . Notice that the weight of the raw minerals used in the batch were greater than 425 g because they contained some H<sub>2</sub>O and CO<sub>2</sub>. Also from the VSL formulation, it is indicated that the glass contained 6.68 wt% waste oxides, so the total waste oxides in the 425 g of glass will be  $425 \times 0.0668 = 28.39$  g. Since the waste solution is 14.79 wt% waste oxides, the weight of the waste solution needed will be 28.39/0.1479 = 191.95 g.

Oxide	Mineral	Grade	Company	Telephone No.
Al <sub>2</sub> O <sub>3</sub>	Kyanite Al <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub>	Raw -325	Kyanite Mining Corp Dillwyn, VA, 23936 www.kyanite.com	804-983-2043 Carrol Kay VP
B <sub>2</sub> O <sub>3</sub>	Boric Acid H <sub>3</sub> BO <sub>3</sub>	Technical Grade-Granular	U.S. Borax Valencia, CA, 91355-1847 www.borax.com	805-287-5400
CaO	Wollastonite CaSiO <sub>3</sub>	NYADM325 NWest Mexico	NYCO Wilsboro, NY www.nycominerals.com	518-963-4262
Fe <sub>2</sub> O <sub>3</sub>	Hematite Fe <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub> 5001	Prince Mfg. Co. Quincey, IL 62306 www.princemfg.com	217-222-8854
Li <sub>2</sub> O	Li <sub>2</sub> CO <sub>3</sub>	Technical Grade	Chemettal-Foote Kings Mt, NC www.chemetalllithium.com	704-734-2501 704-734-2670
MgO	Olivine	#180 Hamilton, WA	Unimin Corp qualityceramics@unimin.com	800-243-9004
SiO <sub>2</sub>	SiO <sub>2</sub>	SCS-75 Mill Creek OK	U.S. Silica Berkeley Springs WV www.u-s-silica.com	800-243-7500 304-258-2500 FAX304-258-8295
TiO <sub>2</sub>	Rutile (Air floated) TiO <sub>2</sub> /Fe <sub>2</sub> O <sub>3</sub>	Air Float Rutile 94 Phil. PA	Chemalloy Co. Bryn Mawr, PA www.chemalloy.com	610-527-3700
ZnO	ZnO	Kadox 920 Camden, NJ	Zinc Corp Amer. Monaca, PA horseheadinc.com	800-962-7500 724-774-1020
ZrO <sub>2</sub>	ZrSiO <sub>4</sub>	Zircon Flour	Amer. Miner. Inc. Monaca, PA 19406 www.americanminerals.net	610-652-3301

Table 5.5. Glass Forming Minerals and Chemicals

Additives	$m_j$ (g)
Kyanite (Al <sub>2</sub> SiO <sub>5</sub> ) 325 mesh	41.85
H <sub>3</sub> BO <sub>3</sub> (technical - granular)	75.80
Wollastonite NYAD 325 mesh	63.37
Fe <sub>2</sub> O <sub>3</sub> (iron III oxide, Prince Mgt.)	20.34
Li <sub>2</sub> CO <sub>3</sub> (Chemetall Foote Co. tech. gr.)	45.72
Olivine (Mg <sub>2</sub> SiO <sub>4</sub> ) 325 mesh (#180)	25.61
$SiO_2$ (Sil-co-Sil 75)	138.73
TiO <sub>2</sub> (rutile - airfloated)	6.33
ZnO (K-920)	20.62
Zircon ZrSiO <sub>4</sub> (flour) 325 mesh	20.34
Total	458.71

Table 5.6. Glass Forming Minerals to Make 425 g of AZ-101 LAW Glass

PNWD confirmed the VSL formulation using a linear algebra approach as follows. The component mass balance requires that

$$\sum_{j=1}^{J} m_j x_{ij} = M_G g_i \qquad (i = 1, 2, ..., K)$$
(1)

where  $M_G$  = mass of glass to be produced

 $g_i = i$ -th oxide (including chlorine and fluorine) mass fraction in the glass (i.e., the target glass composition)

 $m_i = j$ -th batch component (i.e., the waste and glass forming mineral mass)

 $x_{ij} = i$ -th oxide mass fraction in the glass in the *j*-th batch component.

The recipe to attain the target glass composition is obtained by solving the set of Equation 1 for  $m_j$ . The  $x_{ij}$  values for the glass forming minerals used are in Table 5.7. The  $m_j$  values determined for  $M_G = 425$  g are in Table 5.6 and the bottom row of Table 5.7.

	Kyanite	<b>Boric Acid</b>	Wollastonite	Iron Oxide	Li <sub>2</sub> CO <sub>3</sub>	Olivine	Silica	Rutile	Zinc Oxide	Zircon	AZ-101	AZ-101-
• 1											(B)	
oxide			t		i	x <sub>ij</sub>	i		i	1		$g_i \times M_G$
$Al_2O_3$	0.5703	0.000	0.002	0.015	0.000	0.0019	0.00135	0.005	0.000	0.0025	0.0598	26.32
$B_2O_3$	0.000	0.5652	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	42.84
CaO	0.0003	0.000	0.475	0.0004	0.00001	0.0002	0.00008	0.000	0.000	0.000	0.000	30.14
Cr <sub>2</sub> O <sub>3</sub>	0.000	0.000	0.000	0.000	0.000	0.0013	0.000	0.0016	0.000	0.000	0.0050	0.19
Fe <sub>2</sub> O <sub>3</sub>	0.0078	0.00001	0.004	0.97	0.0004	0.0768	0.00016	0.007	0.001	0.00075	0.000	22.38
Li <sub>2</sub> O	0.000	0.000	0.000	0.000	0.4012	0.000	0.000	0.000	0.000	0.000	0.000	18.34
MgO	0.0001	0.000	0.001	0.001	0.00099	0.4801	0.00008	0.000	0.000	0.000	0.000	12.44
Nb <sub>2</sub> O <sub>5</sub>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0040	0.000	0.000	0.000	0.03
NiO	0.000	0.000	0.000	0.000	0.000	0.0037	0.000	0.000	0.000	0.000	0.000	0.09
$P_2O_5$	0.000	0.000	0.000	0.00275	0.000	0.000	0.000	0.000	0.000	0.000	0.0072	0.26
PbO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00001	0.000	0.000	0.00
R <sub>2</sub> O <sup>a</sup>	0.0042	0.000	0.001	0.000	4E-06	0.0003	0.00019	0.000	0.000	0.000	0.8275	23.70
SiO <sub>2</sub>	0.4067	0.000	0.51	0.0135	0.000	0.4252	0.997	0.022	0.000	0.3225	0.0007	205.54
SO <sub>3</sub>	0.000	0.00029	0.000	0.00075	0.00003	0.000	0.000	0.000	0.000	0.000	0.0825	2.38
TiO <sub>2</sub>	0.0079	0.000	0.0002	0.000	0.000	0.000	0.00008	0.932	0.000	0.001	0.000	6.27
U+Th	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.00004	0.000	0.00
V <sub>2</sub> O <sub>5</sub>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.0045	0.000	0.000	0.000	0.03
ZnO	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.999	0.000	0.000	20.60
ZrO <sub>2</sub>	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.019	0.000	0.66	0.000	13.54
$m_j(g)$	41.85	75.80	63.37	20.34	45.72	25.61	138.73	6.33	20.62	20.34	28.39	$SUM(g_i \times$
												$M_G$ ) =
												425.09
<sup>a</sup> R <sub>2</sub> O includes Na <sub>2</sub> O, K <sub>2</sub> O, and H <sub>2</sub> O												

 Table 5.7. Composition of Glass Forming Minerals and Pretreated AZ-101 (B) in Mass%.

Note that the relationship between  $g_i$ ,  $m_j$ , and  $x_{ij}$  is shown in the table below where the matrix (shaded area) of  $x_{ij}$  relate the oxide amounts for a given quantity of glass ( $g_i \times M_G$  column) to the batch component amounts ( $m_j$ ) to make the glass when melted together.

The batch composition was determined using the analyzed composition of AZ-101 LAW (Table 5.1 through Table 5.3) with the waste loading of 0.0668 g (oxides + halogens) from the waste per g of glass. The compositions of the glass forming minerals and the target glass composition ( $g_i$ ) were provided by the VSL (LAWB83) (see Appendix D). Table 5.8 lists the compositions of the AZ-101 LAW, the glass forming minerals mix, and the glass in terms of oxide mass fractions. The relationship between these three compositions is subjected to the mass-balance equation (Equation 1), so, for example, as illustrated in Table 5.7 the total SiO<sub>2</sub> in the glass is 205.54 g (=  $g_{SiO2} \times M_G$ ) = 41.85 g × 0.4067 + 63.37 g × 0.51 + ---+ 138.73 g × 0.997 + ---- + 20.34 g × 0.3225 + 28.39 g × 0.0007 and so forth for each oxide in the glass.

<b>Glass Comp</b>	w <sub>i</sub>	$a_i$	$g_i$
$Al_2O_3$	0.0598	0.0622	0.0620
As <sub>2</sub> O <sub>3</sub>	0.0001	n/a	0.0000
$B_2O_3$	0.0001	0.1076	0.1004
Br	0.0041	n/a	0.0003
CaO	0.0000	0.0727	0.0678
Cr <sub>2</sub> O <sub>3</sub>	0.0050	n/a	0.0003
F-	0.0114	n/a	0.0008
Fe <sub>2</sub> O <sub>3</sub>	0.0000	0.0567	0.0529
K <sub>2</sub> O	0.0274	n/a	0.0018
Li <sub>2</sub> O	0.0000	0.0462	0.0431
MgO	0.0000	0.0320	0.0299
MoO <sub>3</sub>	0.0008	n/a	0.0001
Na <sub>2</sub> O	0.8001	n/a	0.0534
$P_2O_5$	0.0072	n/a	0.0005
$SO_3$	0.0825	n/a	0.0055
SiO <sub>2</sub>	0.0007	0.5216	0.4868
SnO <sub>2</sub>	0.0003	n/a	0.0000
TiO <sub>2</sub>	0.0000	0.0150	0.0140
$V_2O_5$	0.0000	n/a	0.0000
WO <sub>3</sub>	0.0004	n/a	0.0000
ZnO	0.0000	0.0520	0.0485
ZrO <sub>2</sub>	0.0000	0.0340	0.0317
SUM	1.0000	1.0000	1.0000

# Table 5.8. Mass Fractions of Glass Components in AZ-101 PretreatedLAW Waste, Glass Former Mineral Mix, and AZ-101 Glass

#### 5.1.4 Melter Feed Preparation

To prepare the AZ-101 LAW melter feed, the glass former minerals were mixed with the waste to make a melter feed that was dried, calcined, and melted. The following paragraphs describe this process in greater detail.

The mass of the AZ-101 pretreated LAW available was 460 g. The solution density was checked and found to be within the limits of the reported density, 1.224±0.030 g/mL (Table 5.9), confirming that

negligible evaporation of the LAW sample occurred during storage. Based on the solution density and the waste loading, it was determined that 192 g of the LAW solution was needed to make 425 g of glass.

The quantities of glass former minerals given in Table 5.9 are 10% higher than those needed for making 425 g of glass (Table 5.6). This was done so that any material loss during mixing would not impact the final amount of glass produced. The measured total mass of the mix was 504.45 g; this was considered a satisfactory agreement with the projected mass, 504.58 g (=  $458.71 \times 1.1$ ). The minerals were well mixed, first in a plastic bag and then for 4 minutes in a 500-mL agate mill. The mass of the mix after milling was 503.99 g.

Additives	Mass (g)
Kyanite (Al <sub>2</sub> SiO <sub>5</sub> ) 325 mesh	46.04
H <sub>3</sub> BO <sub>3</sub> (technical - granular)	83.38
Wollastonite NYAD 325 mesh	69.71
Fe <sub>2</sub> O <sub>3</sub> (iron III oxide, Prince Mgt.)	22.37
Li <sub>2</sub> CO <sub>3</sub> (Chemetall Foote Co. tech. gr.)	50.29
Olivine (Mg <sub>2</sub> SiO <sub>4</sub> ) 325 mesh (#180)	28.17
SiO <sub>2</sub> (Sil-co-Sil 75)	152.60
TiO <sub>2</sub> (rutile - airfloated)	6.96
ZnO (K-920)	22.68
Zircon ZrSiO <sub>4</sub> (flour) 325 mesh	22.37
Total	504.58

Table 5.9. Quantities of Raw Minerals to Prepare Additive Mix for AZ-101 LAW Glass

The LAW solution (192 g) was preheated at 97°C in a shatter-resistant beaker. The amount of 458.71 g of the additive mix was stirred into the LAW solution, adding about 20 g of the mix at a time while the solution was agitated with a magnetic stirrer, keeping all solids completely dispersed.

Melter-feed heating and stirring was maintained until it began to thicken, forming rounded clumps. The stir bar was then removed, and the dried feed was transferred to a Pt-Rh melting crucible and placed into an oven at 200°C for 1 hour. The temperature was gradually increased to 350°C. Then the crucible was transferred to a melting furnace preheated at 600°C. To prepare calcine, the temperature was slowly (in 1 hour) increased to 732°C.

#### 5.1.5 Glass Melting

After calcination was complete, the crucible was removed from the furnace. The furnace temperature was then raised to 1150°C, and the crucible was placed back into the furnace. When the melting reactions were complete (after about 20 minutes), the crucible was covered with a lid and heated at 1150°C for an additional 1 hour.

The melt was quenched by pouring onto a clean stainless steel plate. On cooling to ambient temperature, the poured glass broke into a number of shards. These shards of the quenched glass were milled in a 100-mL tungsten-carbide disc mill for 5 minutes. This glass powder was remelted at 1150°C for 1 hour and quenched again on a stainless steel plate see Figure 5.1.

The total amount of glass thus made was 422.64 g of which 338.10 g were shards and 82.97 g remained in the crucible. After the residual glass was removed from the crucible, 1.57 g of glass adhered to crucible walls. Hence, the experiment yielded 421.07 g of usable glass. Quenched glass was used for chemical and radiochemical composition analysis (~1 g for each) and TCLP (22 g). For PCT (~20 g) and crystalline phase identification (~10 g for SEM-EDS and ~1 g for XRD), the glass was subjected to container-centerline cooling (CCC).



Figure 5.1. Photograph of AZ-101 Molten Glass being Quenched by Pouring the Melt on a Steel Plate

### 5.1.6 Container-Centerline Cooling

The CCC schedule given in Table 5.10 was provided by BNI in the form of a letter.<sup>(a)</sup> The CCC schedule was derived from measurements on an LAW container of glass at a position at 2/5 of the melt height from the bottom of the full container. The calculated CCC time-temperature history was approximated by a series of seven linear time-temperature segments duplicated with a programmable furnace. The eighth segment was a natural cooling down of the sample left in the furnace. This segment occurs below  $T_g$  where the cooling rate does not affect crystallinity and does not cause any permanent stresses. (T<sub>g</sub> - the glass transformation temperature below which the glass is considered a true solid)

For the CCC heat treatment, 29.3 g of glass was added to a Pt/Rh rectangular mold  $(25 \times 25 \times 25 \text{ mm})$  with a tight-fitting cover. The mold was placed in the furnace at 1150°C for 30 minutes before the CCC treatment was initiated according to the CCC procedure. Figure 5.2 shows the CCC curve that was

<sup>(</sup>a) L. Petkus to C. Musick. October 16, 2003. "LAW Container Centerline Cooling Data." CCN 074181, Contract No. DE-AC27-01RV14136.
achieved, which was very close to the target curve. The CCC monolith of glass was cut diagonally with a low-speed, diamond, wafering saw to prepare a polished thin-section of glass for SEM-EDS evaluation.

Segment	Time (min)	Interval (min)	Temperature (°C)	Rate (°C/min)
1	0	16	1114	-7.125
2	16	57	1000	-1.754
3	73	122	900	-0.369
4	195	160	855	-0.500
5	355	285	775	-0.175
6	640	960	725	-0.130
7	1600	2110	600	-0.095
8	3710	n/a	400	n/a

Table 5.10. CCC Schedule for Crucible Testing



Figure 5.2. Measured CCC Heat Treatment Temperature Profile for AZ-101 Envelope B Glass Plotted Against Target Temperature Control Points

#### 5.2 Glass Analyses and Testing

The product quality is defined in terms of glass properties. Glass properties depend on glass composition and temperature history. The AZ-101 LAW glass was subjected to two different temperature histories: rapid cooling by quenching on a steel plate and slower cooling following a simulated container centerline cooling curve. These two histories roughly bracket the temperature histories that LAW glass will experience during large-scale production. The chemical and radiochemical composition of the glass is discussed in the following two subsections. The remainder of this section is concerned with the phase characterization of the CCC glass and the measurement of its key properties, i.e., PCT.

## 5.2.1 Chemical Composition

For chemical and radiochemical analyses, a representative powdered sample of about 2 g of the quenched glass was produced by grinding in a tungsten carbide disc mill for 2 minutes. Approximately <sup>1</sup>/<sub>4</sub> g quantities were dissolved in a Sodium peroxide (Na<sub>2</sub>O<sub>2</sub>-NaOH) fusion conducted in a zirconium crucible according to procedure PNL-ALO-114 and in a potassium hydroxide (KOH) fusion conducted in a nickel crucible according to procedure PNL-ALO-115. The same fusions were made for the low-activity reference material (LRM) and analytical reference ARG-1 powdered glass standards described below. All sample material appeared to go into solution (no apparent residue remained in fusion crucibles or as precipitate in final solution) after the fusion procedures. Analytical dilutions of 5×, 10×, and 50× were prepared for each fusion preparation. Table 5.11 provides a summary of the preparation and analysis methods performed.

Cation analysis was performed using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Before ICP-AES analysis, a small amount (0.1 mL) of hydrofluoric acid was added to the prepared samples. Portions of the samples fused with sodium peroxide were submitted for radiochemical analysis and inductively coupled plasma-mass spectrometry (ICP-MS). Specifically, thallium was measured by ICP-MS. No hydrofluoric acid was added to the aliquots submitted for radiochemistry or ICP-MS analysis.

The chemical composition of the glass was measured in duplicate along with low-activity reference material (LRM) and analytical reference ARG-1 powdered glass standards (Ebert and Wolf 1999; Smith 1993). The ARG-1 and LRM glasses are compositionally well characterized and provide an excellent independent check of the analytical processes and results.

Cation analysis of the TCLP leachate solutions for all elements except for thallium was completed using a Thermo Jarrell-Ash, Model 61 inductively coupled argon plasma spectrometer according to procedure PNL-ALO-211. Thallium was measured with mass spectrometry per 329-OP-SC01.

Corrections to the waste-glass analysis were applied using a procedure developed by Weier and Piepel (2002).

#### 5.2.2 Radiochemical Composition

About 0.1 g of the powdered quenched glass prepared under section 5.2.1 was solubilized with a  $Na_2O_2$ -NaOH fusion in a Zr crucible according to procedure PNL-ALO-114. The material fused was dissolved in HNO<sub>3</sub> and diluted to 100 mL with deionized water.

Radiochemical analyses included <sup>99</sup>Tc, <sup>129</sup>I, <sup>237</sup>Np, <sup>233</sup>U, <sup>234</sup>U, <sup>235</sup>U, <sup>236</sup>U, <sup>238</sup>U, <sup>239</sup>Pu, <sup>240</sup>Pu, <sup>241</sup>Pu, <sup>241</sup>Am, and <sup>242</sup>Pu by ICP-MS; <sup>63</sup>Ni, <sup>79</sup>Se, <sup>90</sup>Sr, <sup>151</sup>Sm, and <sup>241</sup>Pu with separation and  $\beta$ -counting; <sup>236</sup>Pu, <sup>238</sup>Pu, <sup>239</sup>Pu, <sup>239</sup>Pu, <sup>239</sup>Pu, <sup>241</sup>Am, <sup>243</sup>Am, <sup>242</sup>Cm, <sup>242</sup>Pu, and <sup>243/244</sup>Cm with separation and  $\alpha$  energy analysis (AEA); and <sup>60</sup>Co, <sup>95</sup>Nb, <sup>113</sup>Sn, <sup>125</sup>Sb, <sup>126</sup>Sn/Sb, <sup>134</sup>Cs, <sup>137</sup>Cs, <sup>144</sup>Ce, <sup>152</sup>Eu, <sup>154</sup>Eu, <sup>155</sup>Eu, and <sup>232</sup>Th with extended counting time  $\gamma$  energy analysis (GEA). Concentration values or less-than values of other  $\gamma$  emitters, e.g., <sup>51</sup>Cr, <sup>59</sup>Fe, <sup>88</sup>Y, <sup>95</sup>Zr, <sup>103</sup>Ru, and <sup>106</sup>Ru, were obtained with GEA, depending on concentrations and detection limits.

For Pu, Am, Cm, and Sr analyses, a 10-mL aliquot of dissolved material was evaporated to dryness to remove HCl and then brought back to 10-mL volume with 2 molar HNO<sub>3</sub> and filtered through a 0.45-micron filter. Where appropriate, larger samples were taken for analysis in the case of responses that were close to the detection limits. The fused sample material in 10-mL aliquots was directly  $\gamma$  counted for 14 hours on high-efficiency Ge detectors according to procedure PNL-ALO-450.

The Pu and Am/Cm separations were performed on a 4-mL fusion aliquot according to procedure PNL-ALO-417. The separated fractions were precipitation plated according to PNL-ALO-496, and the samples were counted by  $\alpha$  spectrometry according to PNL-ALO-422. Plutonium recovery was traced with <sup>242</sup>Pu. The curium is known to follow the americium, and both these isotopes were traced with <sup>243</sup>Am.

The Sr separation was performed according to PNL-ALO-476, and radiochemical yields were traced with <sup>85</sup>Sr. The separated fractions were then  $\beta$ -counted according to RPG-CMC-408 and  $\gamma$ -counted according to PNL-ALO-450 (for <sup>85</sup>Sr determination and <sup>137</sup>Cs impurity assessment).

Samples of the AZ-101 glass were analyzed with a ICP-MS for <sup>99</sup>Tc, <sup>237</sup>Np, <sup>239</sup>Pu, and <sup>240</sup>Pu according to 329-OP-SC01 using a machine set up to handle radioactive materials. Dilutions of isotope product standards for <sup>237</sup>Np and <sup>239</sup>Pu and an Amersham <sup>99</sup>Tc standard were used to generate calibration curves. The 1% high-purity nitric acid solution was used to dilute the standards and samples, and also as a reagent blank.

Analysis	Preparative Method	Analysis Method	
Density	Direct	PNL-ALO-501	
Mass% Total Solids/TDS <sup>(a)</sup>	Direct	PNL-ALO-501	
ICP-AES <sup>(b)</sup> (metals)	PNL-ALO-128	RPG-CMC-211 Rev. 0	
ICP-MS <sup>(c)</sup> (except iodine)	PNL-ALO-128	329-OP-SC01 Rev. 0	
ICP-MS (iodine)	Direct	329-OP-SC01 Rev. 0	
KPA <sup>(d)</sup> (uranium)	PNL-ALO-128	RPG-CMC-4014	
IC <sup>(e)</sup> -Inorg (inorganic anions)	Direct	PNL-ALO-212	
IC-F <sup>(f)</sup> (F only)	Direct	TP-RPP-WTP-212	
IC-Org (organic acids/anions)	TP-RPP-WTP-049	TP-RPP-WTP-046	
$TOC^{(g)}/TIC^{(h)}$ – furnace	Direct	PNL-ALO-380	
TOC/TIC - hot persulfate	Direct	PNL-ALO-381	
CN <sup>(i)</sup>	PNL-ALO-287	PNL-ALO-289	
Нg	RPG-CMC-131	RPG-CMC-201 Rev. 0	
OH <sup>(j)</sup>	Direct	PNL-ALO-228	
ISE <sup>(k)</sup> (ammonia)	Direct	RPG-CMC-226	
GEA <sup>(1)</sup>	PNL-ALO-128	PNL-ALO-450	
Tatal a		RPG-CMC-4001,	
Total a	PNL-ALO-128	RPG-CMC-408	
Total B	DNI ALO 128	RPG-CMC-4001,	
rotar p	TINL-ALO-128	RPG-CMC-408	
<sup>90</sup> Sr	PNL-ALO-128,	RPG-CMC-408,	
51	PNL-ALO-476	PNL-ALO-450	
$^{99}\text{Tc}^{+7}$	PNL-ALO-432 <sup>(m)</sup>	RPG-CMC-474	
<sup>3</sup> H	PNL-ALO-418	RPG-CMC-474	
<sup>14</sup> C	PNL-ALO-482	RPG-CMC-474	
<sup>79</sup> Se	PNL-ALO-128,	RPG-CMC-474	
	PNL-ALO-440		
	PNL-ALO-128,		
Pu, Am, Cm	PNL-ALO-417,	RPG-CMC-422	
	PNL-ALO-496		
	RPG-CMC-110 Rev. 1	RPG-CMC-211 Rev 0	
Toxic Characteristic Leaching Procedure (TCLP)	RPG-CMC-139 Rev. 0	RPG-CMC-201 Rev 0	
	RPG-CMC-101 Rev. 0		
(a) $TDS = total dissolved solids$	(g) $TOC = total organic carbon$	n	
(b) ICP-AES = inductively coupled plasma-	(h) TIC = total inorganic carbon		
(a) ICD MS = inductively courled releases	(i) $CN = cyanide$		
(c) ICP-IVIS – inductively coupled plasma-	(j) $OH = hydroxide$		
	(k) $ISE = ion specific electrode$		
(a) $KI = KII = K$	(l) GEA = gamma energy analysis		
(f) $F = $ fluorine	(m) Without sodium dichromate added.		

## Table 5.11. Summary of Analytical Methods

## 5.2.3 Crystalline and Non-Crystalline Phase Determination

Crystalline and noncrystalline phases in the CCC glass were identified with X-ray diffraction (XRD), optical microscopy, and scanning electron microscope (SEM). Glass samples were cut and polished with Buhler diamond saw and polishing equipment. Crystalline material content was estimated from the XRD results and visual observations.

Optical examination was conducted both with a metallurgical microscope (magnification from  $10 \times$  to  $70 \times$ ) and a transmitting polarized light Meiji Techno microscope (magnification at  $100 \times$  to  $250 \times$ ).

XRD was performed with a SCINTAG model PAD V Powder X-ray diffractometer using Cu K $\forall$  radiation (1.54056) having a scan 2 $\theta$  increment of 0.05°, a dwell time of 6 seconds, and a 2 $\theta$  range of 5 to 70°. The glass was powdered, spiked with 5 wt% of CaF<sub>2</sub> standard, and mixed in a tungsten carbide grinding chamber using a disc mill. An approximately 100-mg sample of glass was mounted on a plastic XRD sample mount, leveled to the X-ray beam height, encapsulated in Mylar film, transported to an XRD facility, and analyzed.

A SEM (model VG elemental shielded PQ2) with energy dispersive spectroscopy (EDS) capabilities analyzed crystals and chemical inhomogeneities. A thin section of the LAW glass sample, approximately  $1 \text{ cm}^2$  in area and 4 mm thick, was polished and mounted on an aluminum SEM specimen holder. The glass sample was polished to a minimum of #600 grit. The mount was coated with a transparent conducting film and examined both at low magnification (15× and 100×) and higher magnifications (500× through 20,000×).

#### 5.2.4 TCLP

A TCLP test was performed on two quench-cooled AZ-101 LAW glass samples. Leachates were analyzed with inductively coupled plasma-atomic emission spectroscopy (ICP-AES) for Sb, As, Ba, Be, B, Cd, Cr, Pb, Ni, Se, Ag, V, and Zn and with cold vapor atomic absorption spectroscopy (CVAA) for Hg. ICP-MS was used for Tl. Table 5.12 presents the universal treatment standard (UTS) limits for the concentrations of these elements in the TCLP solution. The testing was conducted per SW-846, Method 1311 (EPA 1992).

The amount of ~25 g of quenched glass was sieved to pass through a 9.5-mm (USA 3/8 inch Mesh) sieve. Larger pieces were broken with a hammer in a plastic bag. Per procedure RPG-CMC-110, a 10-g sample was placed into an extractor vessel with 200 mL of extraction fluid #1. The sample was rotated head-over-heel at 30 rpm for 18 hours at 23°C ( $\pm$ 2°C). The extract was acidified by adding concentrated nitric acid, and then aliquots were taken for subsequent acid digestion per procedure RPG-CMC-139 using from 40 to 45 mL of the acidified TCLP extract. Two digests were conducted, one using nitric and hydrochloric acids, and the other using nitric acid alone.

CAS#	Constituent	Symbol	UTS <sup>(a)</sup> mg/L TCLP
7440-36-0	Antimony	Sb	1.15
7440-38-2	Arsenic	As	5.0
7440-39-3	Barium	Ba	21
7440-41-7	Beryllium	Be	1.22
7440-42-8	Boron	В	0.05
7440-43-9	Cadmium	Cd	0.11
18540-29-9	Chromium	Cr	0.6 Total
7439-92-1	Lead	Pb	0.75
7439-97-6	Mercury	Hg	0.025
7440-02-0	Nickel	Ni	11
7782-49-2	Selenium	Se	1
7440-22-4	Silver	Ag	0.14
7440-28-0	Thallium	Tl	0.20
7440-62-2	Vanadium	V	1.6
7440-66-6	Zinc	Zn	4.3
(a) UTS = Univ	versal Treatment Standard	l, 40 CFR 268	3.

 Table 5.12. TCLP Inorganic Constituents of Potential Concern (CoPC)

#### 5.2.5 PCT

The PCT is conducted in accordance to the ASTM procedure C 1285-97, "Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses: The Product Consistency Test (PCT)" (ASTM 1997). The test was conducted on both AZ-101 LAW glass subjected to CCC cooling and the LRM glass. The glass was ground in a tungsten-carbide disc mill and then sieved through 75 and 150 µm (-100 to +200 mesh) stainless steel sieves. The glass particles were cleaned by washing in deionized water (DIW) and ethanol with an ultrasonic cleaner and dried in an oven at 90°C. Approximately 1.5 g of glass were placed into a 22-mL desensitized type 304L stainless steel container filled with approximately 15 mL of DIW. The glass was precisely weighed and the leachate volume precisely controlled to achieve a solution volume-to-glass mass ratio of 10 mL/g glass. The container and its contents were held (without agitation) at 90°C temperature for 7 days. The initial and final pH values of the solution were taken. Aliquots of the solution were filtered through a 0.45-µm filter and analyzed using ICP.

The ratio of the surface area of the sample to solution volume is estimated to be 2000 m<sup>-1</sup>. This estimate is based on the assumption that spherical particles with Gaussian size distribution range from 74  $\mu$ m to 149  $\mu$ m in diameter. This estimated particle-size distribution closely approximates the observed distribution for the -100 to +200 mesh sieve fraction—see Appendix 11 of ASTM C 1285-97. Assuming that particles are cubic or tabular results in ~1% difference in the specific surface area. Therefore, no significant error is introduced when the release of elements (sodium, silicon, and boron) from the glass is expressed per exposed glass surface area thus estimated.

Triplicate samples were prepared and tested for each glass. The LRM standard glass was included in these tests to provide a reliable baseline of results by which to judge the quality of the PCT results for the

AZ-101 LAW glass. Two vessels were tested as blanks by filling the container with 15 mL of DIW and following the PCT procedure, except that no glass sample was added to the vessel. Each container and its contents were held (without agitation) at 90°C for 7 days for each PCT conducted with each glass sample.

The leach vessels used were 22-mL screw-cap containers fabricated from desensitized 304L stainless steel (Figure 5.3). The vessels, including the lids and Teflon gaskets, were cleaned following the ASTM C 1285-97 procedure. DIW used for cleaning and leachate was taken from a Barnstead, NANOpure Ultra Water System, Model D4741, with resistivity of the water measured at 18.1 M $\Omega$ ·cm.

The initial and final pH values of the solution were taken with an Orion Research Ion Analyzer, Model 720A. The pH meter was calibrated before use with VWR brand buffer solutions of pH = 4.00, 7.00, and 10.00. Aliquots of the solution were filtered through a 0.45-µm filter, acidified to 1 vol% HNO<sub>3</sub>, and analyzed with a Thermo Jarrell-Ash, Model 61 inductively coupled argon plasma atomic emission spectrometer according to procedure PNL-ALO-211. Results were reported as normalized elemental mass releases in grams of glass per square meter of calculated surface area.



Figure 5.3. Desensitized Type 304L Stainless Steel, 22 mL, PCT Vessel and Lid (Teflon gasket, nickel-plated brass compression fittings are also shown)

## 6.0 Results

The AZ-101 LAW glass melter feed was successfully processed and melted into an LAW glass that was prepared for chemical and radiochemical composition determination and for property testing (TCLP and PCT); glass was also archived for future testing. Material was also used for phase characterization. Approximately 421 g of usable glass was recovered from the targeted 425 g LAW and mineral additives batch that was melted.

The preparation of glass in this work roughly reproduced the three phases of feed-to-glass conversion in the liquid-fed ceramic melter (LFCM) (dry, calcine, and melt). Except the impact of gas atmosphere on the redox states of multivalent oxides, any other differences between crucible and melter vitrification conditions are virtually inconsequential for the properties of the final product (cf. Hrma et al. 2002). The crucible lid kept the batch gases in the crucible.

## 6.1 LAW AZ-101 Waste Components Content

The content of the dried and calcined waste in the as-received AZ-101 LAW solution was checked by taking an ~4-g aliquot of the solution that was first dried in a porcelain crucible for 24 hours at 105°C and then calcined for 130 minutes at 1050°C. The measurement was performed in duplicate. The test was then modified by adding 14 to 16 g of silica to the LAW before drying. On calcination, the silica reacts with the LAW, reducing its hydroscopic nature and assisting the decomposition reactions of inorganic salts. This test was also performed in duplicate. A blank test was performed with silica alone. The mass loss on drying (0.01%) and on calcining (0.13%) of the silica was used to correct the values listed in Table 6.1, which compares the measured and reported values. The fraction of dry solids (26.1 mass% with silica addition and 26.5 mass% without silica addition) is slightly lower than a previously determined value of 26.7 mass%. The measured fraction of glass components (oxides, halides, and sulfates), both 14.8 mass% with and without silica addition, is in excellent agreement with the reported fraction of 14.8 mass%. From these results, it was concluded that the waste solution had not changed significantly in concentration since the time it had been sampled to perform chemical analysis.

	Reported (mass %) (Goheen et al., 2002)	Measured Without Silica (mass %)	Measured with Silica (mass %)
Fraction of solids <sup>(a)</sup>	26.68	26.52	26.09
Fraction of refractory components <sup>(b)</sup>	14.79	14.79	14.83
<ul><li>(a) Dried to constant weight at 105°C.</li><li>(b) Fired to constant weight at 1050°C.</li></ul>			

Table 6.1. Solids and Oxide Content of AZ-101 Pretreated LAW Solution

## 6.2 LAW Glass AZ-101 Chemical Composition

Three different sample-preparation methods were used on the glasses: Na<sub>2</sub>O<sub>2</sub>-NaOH fusion in a Zr crucible (PNL-ALO-114), KOH-KNO<sub>3</sub> fusion in a Ni crucible (PNL-ALO-115), and acid digestion

(PNL-ALO-138). For each method, ICP-AES analyses was performed for a batch containing a blank, two Certified Reference Material (CRM) glasses, ARG-1 (Smith 1993) and LRM (Ebert and Wolf 1999), and duplicate samples of the AZ-101 LAW glass. Inclusion of the standard glasses allowed a way to screen out matrix effects when doing analyses with the ICP-AES technique when a large number of elements are analyzed simultaneously. However, the instrument cannot be set up to optimize each of a large number of elements. Therefore, the analytical values obtained by the ICP-AES technique were corrected using analyses of standard glasses with well-established compositions, such as ARG-1 and LRM and sound statistical principles. This section describes the procedure for corrections made to the waste glass analysis based on standard glass analyses (Weier and Piepel 2002). This correction was used to extract the most likely composition of the glass indicated by the ICP-AES data.

As outlined by Weier and Piepel (2002), the following steps were performed to obtain a single "best" estimate from individual AZ-101 LAW glass sample analytical results:

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

Unlike the analysis reported by Weier and Piepel (2002), the sampling variability ( $\sigma_s$ ) did not need to be addressed in this project. The current project performed multiple CRMs in a batch instead of multiple analyses of a CRM in a batch as assumed by Weier and Piepel (2002). Multiple unknown glass replicates in each batch were handled identically. Concentrations of some constituents were not reported because of the nature of analytical methods used: Na and Zr concentrations were not obtained from the analysis using Na<sub>2</sub>O<sub>2</sub>-NaOH fusion, K and Ni concentrations were not obtained from the analysis using KOH-KNO<sub>3</sub> fusion, and Si concentration was not obtained from the analysis using acid digestion. Also, concentrations of F and SO<sub>3</sub> were not obtained by the analytical methods used for most of the elements, but SO<sub>3</sub> was determined in the glass by SEM-EDS at 0.51 Wt% consistent with the expected of 0.55 Wt% based on its concentration in the pretreated waste. Some known minor waste LAW constituents (As and W) were not detected in the glass. Unlike in Weier and Piepel (2002), all adjustments to the analytical data were done in the original analytical units. Conversions to mass fractions were done after adjustment and before normalization.

Several analytes were not detected in any of the AZ-101-LAW glasses: Ag, As, Ce, Dy, Eu, Nd, Pd, Ru, Sb, Se, Te, Th, Tl, U, W, and Y; because no adjustments or corrections could be performed on these analytes, they were removed from the list of constituents. Further, because of the large differences in detection limits between the acid-digestion method and the fusion-preparation methods, Be, Cd, Co, La, and Mo, analytes that were detected in the acid-digestion results but not detected in either of the fusion preparation methods, were also removed from the list of constituents. Of all of these removed analytes, only As, Mo, and W were listed in the AZ-101 LAW target composition as minor components; their calculated fractions in the glass were less than 0.01 mass%. Concentrations of these non-detect (ND) constituents were assumed 0 in blanks and 1/2 method detection limit (MDL) in AZ-101 LAW; for CRMs, the ND's concentration was assumed 1/2 MDL for elements in the recipe; 0 concentration was

used when it could be assumed that the element was absent in blanks and in CRM (elements not in their recipe).

A pair of AZ-101 LAW replicate measurements was available for each digestion method. This gave three pairs of measurements for a direct estimate of analytical uncertainty with the exception of only two pairs for Na, Zr, K, Ni, and Si. Na and Zr were not reported for Na<sub>2</sub>O<sub>2</sub>-NaOH fusion, K and Ni were not reported for KOH-KNO<sub>3</sub> fusion, and Si was not reported for acid digestion. Relative percent deviations (RPDs) were computed for each of the available pairs. If both of the paired values were NDs, the pair was not included in the relative standard deviation (RSD) estimation. From the RPDs available for each analyte, a pooled estimate was obtained by squaring the RPDs, averaging their squares, and taking the square root. This value was then divided by  $\sqrt{2}$  to obtain an estimate of the RSD ( $\rho_A$ ) and standard deviation (Std) values (RSD = Std/Concentration). It was assumed that the Std for the blank ( $\rho_B$ ) was 15%. Further,  $\rho_A$ , the RSD for glass analysis, was estimated from replicated AZ-101 analyses, and  $\sigma_T$ , the Std for the CRM target value, was obtained from CRM reports. Thus,  $\sigma_B = B\rho_B$ ,  $\sigma_A = X\rho_A$  or  $C\rho_A$ , and  $\rho_T = \sigma_T/T$ , where, *B*, *X*, *C*, and *T* denote the concentration of the blank, unknown glass analysis, CRM analysis, and CRM target value, respectively.

For each sample-preparation batch, the blank concentrations were subtracted from each of the four glass measurements (one such subtraction resulted in a negative value, which was set to 0). In most cases, the blank corrections had little effect, as expected, but there was an especially noticeable improvement in the repeatability for Ca and also some improvement for Sn and Sr. Analytical results that have not been blank corrected retained their uncertainty of  $\sigma_A$  (see Weier and Piepel 2002, Equation 3.9) while those that have been blank corrected (*X* - *B* or *C* - *B*) had an uncertainty of  $\sqrt{\sigma_A^2 + \sigma_B^2}$  (see Weier and Piepel 2002, Equation 3.7).

The AZ-101 analytical results were corrected for analytical bias using the CRM target values. The bias correction is better for those constituents for which the unknown glass and the CRM glass concentrations are closer. For a given constituent bias correction, that CRM was chosen in which that constituent concentration was closer than in the AZ-101 LAW glass. The minor constituent analytes not represented in either CRM were Bi, Rh, Sn, and V; their concentrations could not be bias adjusted. For Ba, K, Mn, Ni, Pb, and Zr, only one of the CRMs contained a particular analyte. These analytes were subject to bias correction. The majority of detected analytes are subject to bias correction by ARG-1; they include Al, B, Ca, Cr, Cu, Fe, Li, Mg, Na, P, Si, Sr, Ti, and Zn.

Accordingly, the selected target CRM value was compared to the measured CRM concentration for each analyte. The difference was compared to the appropriate function of the estimated uncertainty of the measured result and an uncertainty associated with the actual target values. Bias correction was performed only if the difference was statistically significant relative to these uncertainties (>1.96).

When the correction was required, it was performed by multiplying the concentration value for the AZ-101 LAW glass by the ratio of the CRM target values to the CRM measured value. The uncertainty of the bias-corrected value for the AZ-101 LAW glass was increased since it then also included the influence of the uncertainties of the CRM target and the CRM measured result.

At the completion of these data-adjustment steps, element concentrations were converted to glass constituent (mainly oxide) mass fraction. Values for unanalyzed, undetected, or unreported glass

constituents were substituted before performing normalization. Two expected but unanalyzed components (F and SO<sub>3</sub>) and three expected but undetected constituents (As, Mo, and W) were given their calculated values (based on the compositions of LAW and mineral additives); these values have no quantifiable uncertainty. Unreported components in any method (Na, Zr, K, Ni, and Si) were substituted with inverse-variance weighted means of the results from the other two methods.

The final adjusted normalized results for each of the two replicates in each of the three digestions are summarized in Table 6.2. Table 6.3 lists the standard deviations for each analysis and each constituent. Table 6.4 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, the  $\Sigma \sigma_A^2$  for all constituents listed in the target composition; the  $\Sigma \sigma_A^2$  is smallest for the acid-digestion preparation method ( $\Sigma \sigma_A^2 = 8.1 \times 10^{-6}$ ) and largest for the Na<sub>2</sub>O<sub>2</sub>-NaOH fusion preparation method ( $\Sigma \sigma_A^2 = 4.3 \times 10^{-5}$ ). The squared error,  $\Sigma (A-T)^2$ , was highest for the KOH-KNO<sub>3</sub> fusion preparation method [ $\Sigma (A-T)^2 = 3.1 \times 10^{-5}$ ] and lowest for the average value for all three methods [ $\Sigma (A-T)^2 = 3.1 \times 10^{-5}$ ]. Thus, it can be concluded that the actual and target compositions differ by  $\sqrt{[\Sigma (A-T)^2]} = 0.0056$ . This 0.56 mass% difference qualifies as excellent agreement between the actual and target composition of AZ-101 LAW glass.

The mass-fraction values from Table 6.4 are graphically displayed in Figure 6.1 through Figure 6.3. Figure 6.1 compares the analytical values (the best estimates averaged for the two measured duplicate samples) with the target values, showing excellent agreement for components with mass fractions higher than 0.005. For components with mass fractions lower than 0.005, the relative deviation from the target generally increases, and the mass fraction of constituents decreases. For these constituents, the analyses tend to provide exaggerated concentration values.

Identification and quantification 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 for all components with mass fractions higher than 0.005, except SiO<sub>2</sub>, which was not included in the plot because of its high mass fraction. Finally, Figure 6.3 compares best estimates for the individual sample preparation method with the overall averages, showing good agreement.

At the time this work was initiated, the RPP-WTP contract ILAW specification (DOE-ORP 2000) required a waste loading of 5 weight percent based on Na<sub>2</sub>O for Envelope B wastes, The requirement was subsequently changed to 3.0 weight percent based upon Na2O for Envelope B wastes, which include AZ-101. The target and measured mass fractions of Na<sub>2</sub>O for AZ-101 LAW are 5.35 and 5.58 mass%, respectively. This low concentration of Na<sub>2</sub>O and SO<sub>3</sub> mass fractions in glass was necessitated by an additional constraint that the product of Na<sub>2</sub>O and SO<sub>3</sub> mass fractions in glass must be no greater than  $5 \times 10^{-4}$ . According to Muller et al. (2001), LAW glass segregates molten salt when processed in a Joule-heated melter if  $x_{\text{Na}_2\text{O}}x_{\text{SO}_3} > 5 \times 10^{-4}$  where  $x_{\text{Na}_2\text{O}}$  and  $x_{\text{SO}_3}$  are the mass fractions of Na<sub>2</sub>O and SO<sub>3</sub> in glass [also known as the VSL rule of five, i.e., Na<sub>2</sub>O×SO<sub>3</sub>  $\leq 5 \pmod{2}^2$  limit]. According to Muller et al. (2001), this inequality was an empirically determined based on melter processing data at a relatively fixed processing rate. The measured content of SO<sub>3</sub> in the glass was 0.51 mass% and the measured Na<sub>2</sub>O×SO<sub>3</sub> product was 2.8 (mass%)<sup>2</sup>

	Na <sub>2</sub> O <sub>2</sub> -	NaOH	KOH-	KNO3	Acid Di	Acid Digestion	
Al <sub>2</sub> O <sub>3</sub>	0.0593	0.0589	0.0588	0.0591	0.0600	0.0592	
B <sub>2</sub> O <sub>3</sub>	0.1019	0.1009	0.1018	0.1013	0.0974	0.0983	
BaO	0.0000	0.0000	0.0001	0.0001	0.0001	0.0001	
Bi <sub>2</sub> O <sub>3</sub>	0.0002	0.0002	0.0002	0.0002	0.0001	0.0001	
CaO	0.0649	0.0645	0.0643	0.0643	0.0671	0.0671	
Cr <sub>2</sub> O <sub>3</sub>	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	
CuO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
Fe <sub>2</sub> O <sub>3</sub>	0.0520	0.0512	0.0507	0.0507	0.0552	0.0555	
K <sub>2</sub> O	0.0037	0.0040	0.0019	0.0019	0.0018	0.0017	
Li <sub>2</sub> O	0.0422	0.0416	0.0434	0.0432	0.0454	0.0444	
MgO	0.0308	0.0302	0.0301	0.0301	0.0293	0.0298	
MnO	0.0004	0.0004	0.0002	0.0002	0.0004	0.0004	
Na <sub>2</sub> O	0.0551	0.0551	0.0554	0.0558	0.0569	0.0562	
NiO	0.0004	0.0003	0.0002	0.0002	0.0002	0.0002	
$P_2O_5$	0.0011	0.0011	0.0008	0.0008	0.0007	0.0007	
PbO	0.0002	0.0002	0.0002	0.0002	0.0000	0.0000	
Rh <sub>2</sub> O <sub>3</sub>	0.0007	0.0007	0.0003	0.0003	0.0001	0.0001	
SiO <sub>2</sub>	0.4864	0.4906	0.4929	0.4930	0.4827	0.4834	
SnO <sub>2</sub>	0.0004	0.0005	0.0005	0.0005	0.0002	0.0001	
SrO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	
TiO <sub>2</sub>	0.0154	0.0151	0.0151	0.0151	0.0153	0.0152	
V <sub>2</sub> O <sub>5</sub>	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	
ZnO	0.0483	0.0477	0.0465	0.0462	0.0504	0.0502	
ZrO <sub>2</sub>	0.0293	0.0293	0.0292	0.0293	0.0295	0.0297	
As <sub>2</sub> O <sub>3</sub>	7.E-06	7.E-06	7.E-06	7.E-06	7.E-06	7.E-06	
F	0.0008	0.0008	0.0008	0.0008	0.0008	0.0008	
MoO <sub>3</sub>	5.E-05	5.E-05	5.E-05	5.E-05	5.E-05	5.E-05	
SO <sub>3</sub>	0.0055	0.0055	0.0055	0.0055	0.0055	0.0055	
WO <sub>3</sub>	3.E-05	3.E-05	3.E-05	3.E-05	3.E-05	3.E-05	
<ul> <li>Notes:</li> <li>(1) Two analyses were performed for each sample preparation method (i.e., Na<sub>2</sub>O<sub>2</sub>-NaOH, KOH-KNO<sub>3</sub>, and acid digestion).</li> <li>(2) As<sub>2</sub>O<sub>3</sub>, F, MoO<sub>3</sub>, SO<sub>3</sub>, and WO<sub>3</sub> concentrations were calculated from the Mass balance equation.</li> </ul>							

Table 6.2. Best Analytical Estimates for AZ-101 LAW Glass Composition in Mass Fractions

(3) Na and Zr concentrations were not obtained from the analysis using Na<sub>2</sub>O<sub>2</sub>-NaOH fusion, K and Ni concentrations were not obtained from the analysis using KOH-KNO<sub>3</sub> 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.

	Na <sub>2</sub> O <sub>2</sub> -	NaOH	KOH-	KNO <sub>3</sub>	Acid digestion	
$Al_2O_3$	6.30	6.23	6.21	6.23	3.98	3.93
$B_2O_3$	10.93	10.78	10.51	10.44	9.50	9.56
BaO	0.04	0.04	0.01	0.01	0.03	0.03
Bi <sub>2</sub> O <sub>3</sub>	0.08	0.07	0.07	0.07	0.03	0.03
CaO	13.31	13.28	6.00	5.99	3.71	3.71
Cr <sub>2</sub> O <sub>3</sub>	0.12	0.12	0.14	0.14	0.13	0.14
CuO	0.01	0.01	0.03	0.03	0.00	0.00
Fe <sub>2</sub> O <sub>3</sub>	3.80	3.74	3.74	3.74	3.81	3.83
K <sub>2</sub> O	2.69	2.91	0.61	0.61	0.94	0.88
Li <sub>2</sub> O	5.07	5.00	7.33	7.29	5.25	5.13
MgO	3.78	3.72	3.55	3.55	4.59	4.66
MnO	0.06	0.06	0.98	1.00	0.06	0.06
Na <sub>2</sub> O	3.02	3.02	7.45	7.45	5.12	5.06
NiO	0.88	0.72	0.15	0.15	0.23	0.23
$P_2O_5$	0.73	0.73	0.42	0.42	0.36	0.37
PbO	0.14	0.15	0.17	0.18	0.02	0.02
Rh <sub>2</sub> O <sub>3</sub>	0.18	0.19	0.08	0.07	0.03	0.03
SiO <sub>2</sub>	19.87	19.73	16.95	16.89	13.01	13.01
SnO <sub>2</sub>	2.64	2.71	0.45	0.44	0.15	0.13
SrO	0.14	0.14	0.00	0.00	0.00	0.00
TiO <sub>2</sub>	1.66	1.64	1.62	1.62	0.96	0.96
$V_2O_5$	0.00	0.00	0.00	0.00	0.00	0.00
ZnO	2.81	2.77	2.69	2.68	2.90	2.89
ZrO <sub>2</sub>	1.11	1.11	2.21	2.21	2.22	2.23

Table 6.3. Values of  $10^4 \sigma_A$  for Best Analytical Estimates for AZ-101 LAW Glass Composition (see Table 6.2)



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

	Na <sub>2</sub> O <sub>2</sub> -NaOH	KOH-KNO <sub>3</sub>	Acid Digestion	Average	Target
SiO <sub>2</sub>	0.4896	0.4937	0.4836	0.4890	0.4870
$B_2O_3$	0.1016	0.1017	0.0980	0.1004	0.1004
CaO	0.0648	0.0644	0.0671	0.0655	0.0679
Al <sub>2</sub> O <sub>3</sub>	0.0592	0.0591	0.0596	0.0593	0.0621
Na <sub>2</sub> O	0.0552	0.0557	0.0566	0.0558	0.0535
Fe <sub>2</sub> O <sub>3</sub>	0.0517	0.0507	0.0554	0.0526	0.0529
ZnO	0.0481	0.0464	0.0504	0.0483	0.0485
Li <sub>2</sub> O	0.0420	0.0433	0.0450	0.0434	0.0431
ZrO <sub>2</sub>	0.0293	0.0293	0.0296	0.0294	0.0317
MgO	0.0305	0.0302	0.0296	0.0301	0.0299
TiO <sub>2</sub>	0.0153	0.0151	0.0153	0.0152	0.0140
SO <sub>3</sub>	0.0055	0.0055	0.0055	0.0055	0.0055
K <sub>2</sub> O	0.0038	0.0019	0.0018	0.0025	0.0018
F-	0.0008	0.0008	0.0008	0.0008	0.0008
$P_2O_5$	0.0011	0.0008	0.0007	0.0009	0.0005
Cr <sub>2</sub> O <sub>3</sub>	0.0008	0.0008	0.0008	0.0008	0.0003
MoO <sub>3</sub>	0.0001	0.0001	0.0001	0.0001	0.0001
SnO <sub>2</sub>	5.E-04	5.E-04	2.E-04	0.0004	2.E-05
As <sub>2</sub> O <sub>3</sub>	n/a	n/a	n/a	n/a	7.E-06
$10^4 \Sigma \sigma_A^2$	0.427	0.196	0.081	n/a	n/a
$10^4 \Sigma (A-T)^2$	0.437	0.897	0.527	0.311	n/a

Table 6.4. Averaged Best Analytical Estimates for AZ-101 LAW GlassComposition in Mass Fractions Sorted by Target



Figure 6.2. Analyzed Versus Target Mass Fractions of AZ-101 LAW Glass Components (except SiO<sub>2</sub>) with Mass Fractions >0.005



#### Figure 6.3. Individual Versus All-Average Analyzed Mass Fractions of AZ-101 LAW Glass Components

The waste-loading fraction in the glass can be obtained based on the dilution of major waste components in the glass. This calculation constitutes an independent check that the glass was formulated according to plan. The dilution factor D was calculated as

$$D_i = \frac{g_i - a_i}{w_i - a_i} \tag{2}$$

where the subscript i at D signifies that  $D_i$  can vary with the component selected.

Table 6.5 summarizes the values of  $D_i$  for 7 of 8 most abundant components of the AZ-101 LAW glass. One major component, Al<sub>2</sub>O<sub>3</sub>, was not included because the waste, the additive mix, and the glass all contain ~6 mass% Al<sub>2</sub>O<sub>3</sub>; by Equation (4),  $D_{Al2O3}$  would be an indeterminate. The last column in Table 6.5 shows the relative difference between  $D_i$  values and the target waste loading, i.e., the expression  $(D_i - D)/D$ , where D = 0.0668. As Table 6.3 shows, the value of  $D_{B2O3}$  is exactly on target. The values of  $D_i$  for SiO<sub>2</sub>, Na<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, and ZnO do not deviate more than 10 relative % from the target. The 3 mass% (49 relative %) deviation in D based on the CaO fraction is caused by a minor difference of 0.24 mass% in the analyzed and targeted fraction of CaO (Table 6.4) that could be caused by the uncertainty of the CaO content in the mineral additives used, but also by an analytical error (see the large Std values listed for CaO in Table 6.3).

The overall measured waste loading  $(D_a)$  can be defined either as an average value, i.e.,

$$D_{a} = m^{-1} \sum_{i=1}^{m} D_{i}$$
(3)

or as a weighted average  $(D_{Wa})$  defined as

$$D_{Wa} = \frac{\sum_{i=1}^{m} D_i g_{iA}}{\sum_{i=1}^{m} g_{iA}}$$
(4)

where m = 7 is the number of abundant components listed in Table 6.5. These values are listed in Table 6.5, showing that the weighted average is 6.73 mass%, a value higher than the targeted 6.68 mass%. The difference between the actual and targeted values is 0.05 mass% (1 relative %). Summarizing, the waste fraction of AZ-101 LAW glass is very close to and slightly exceeds the target.

Glass Comp	Wi	$a_i$	$g_i^{(a)}$	$D_i^{(b)}$	RP		
SiO <sub>2</sub>	0.0007	0.5216	0.4890	0.0627	-0.06		
$B_2O_3$	0.0001	0.1076	0.1004	0.0666	0.00		
CaO	n/a	0.0727	0.0655	0.0997	0.49		
Na <sub>2</sub> O	0.8001	n/a	0.0558	0.0698	0.04		
Fe <sub>2</sub> O <sub>3</sub>	n/a	0.0567	0.0526	0.0718	0.07		
ZnO	n/a	0.052	0.0483	0.0712	0.07		
Li <sub>2</sub> O	n/a	0.0462	0.0434	0.0598	-0.10		
Average				0.0717	0.07		
Weighted aver	rage			0.0673	0.01		
(a) The averaged best analytical estimate for AZ-101 LAW glass.							
(b) The waste loading (W) was calculated from Equation 4, where							
$w_i$ , $a_i$ , and $g_i$ are the measured <i>i</i> -th component mass fractions in waste,							
additive m	ix, and AZ-10	1 LAW glass	5.		-		
RP = Relative n	ercent	e					

Table 6.5. Waste Loading as Dilution Factor for AZ-101 LAW Waste Glass Constituents

## 6.3 LAW Glass AZ-101 Radiochemical Composition

Table 6.6 summarizes the radioisotope analysis results for the quenched AZ-101 glass. The dates of analysis allow the analytical values to be indexed to any date. Note that all of the isotopes reported were determined radiochemically, except for <sup>99</sup>Tc, <sup>241</sup>Pu, and Uranium. The <sup>241</sup>Pu activity based on the less-than mass spectrometry number is very high and effectively almost meaningless, because of the high activity of <sup>241</sup>Pu. The expected value in the glass based on the radiochemical measurement of <sup>241</sup>Pu in the AZ-101(B) waste solution will be used in the computation of the TRU loading of the glass because that <sup>241</sup>Pu concentration is based on a measured quantity. The uranium in the glass is almost all due to uranium in the zircon added as a glass forming chemical. If the zircon is 200-ppm uranium, the uranium contributed to the glass will be (20.34/425) × 200 ppm = 9.6 ppm, where 20.34 is the mass of the zircon in the batch producing 425 g of glass. This is quite close to the 10.67 ppm reported for the glass.

Isotope	Activity μCi/g	Date	Isotope	Activity μCi/g	Date
<sup>60</sup> Co	<5E-6	5/19/2003	<sup>151</sup> Sm	<8E-4	3/15/2004
<sup>63</sup> Ni	2.59E-3	11/21/2003	<sup>152</sup> Eu	<2E-5	5/19/2003
<sup>79</sup> Se	<3.3E-3	3/1/2004	<sup>154</sup> Eu	<2E-5	5/19/2003
<sup>90</sup> Sr	1.285E-1	9/25/2003	<sup>155</sup> Eu	<8E-5	5/19/2003
<sup>95</sup> Nb	<5E-6	5/19/2003	<sup>232</sup> Th	<4E-5	5/19/2003
<sup>99</sup> Tc <sup>(a)</sup>	<2.65E-2	3/16/2004	<sup>238</sup> Pu	<8E-5	2/24/2004
<sup>113</sup> Sn	<3E-5	5/19/2003	<sup>239+240</sup> Pu	<9E-5	2/24/2004
<sup>125</sup> Sb	3.02E-3	5/19/2003	$^{241}Pu^{(a)}$	<8E-0	3/16/2004
<sup>126</sup> SnSb	7.73E-4	5/19/2003	<sup>241</sup> Am	<2E-5	2/24/2004
<sup>134</sup> Cs	<7E-6	5/19/2003	<sup>242</sup> Cm	<7.0E-6	2/24/2004
<sup>137</sup> Cs	1.27E-2	5/19/2003	<sup>243+244</sup> Cm	<7.5E-6	2/24/2004
<sup>144</sup> Ce	<2E-4	5/19/2003	$U(\mu g/g)^{(a)}$	10.67	n/a
(a) ICP-N	1S				

Table 6.6. Radioisotope Activity in AZ-101 Glass in µCi/g (including dates of analysis)

#### 6.3.1 Data Comparison with Requirements

Table 6.7 gives the analysis for AZ-101 glass determined by radiochemistry or ICP-MS for radioisotopes that could be measured in the AZ-101 waste solution given in Table 5.3. Appendices A, B, and C provide additional analysis information. The expected loading ( $\mu$ Ci/g glass) was calculated from the radiochemical analysis of the waste by taking those analytical values (Table 5.3) that are in  $\mu$ Ci/mL, converting to  $\mu$ Ci/g dried solids by dividing by the density (1.224 g/mL), and then by the weight fraction of dried solids (0.2668), and converting that value to  $\mu$ Ci/g waste oxides by dividing by the calcination factor (14.79/26.68 = 0.554 weight fraction of oxide in dried solids). The  $\mu$ Ci/g waste oxides are then multiplied by the waste loading factor (0.0668) to give  $\mu$ Ci/g glass. All of these operations can be combined into one factor (0.369), which multiplies the original waste analytical value (Table 5.3) to give the expected radionuclide content of the glass. Note for the elements in Table 6.7 for which definite values are available for both the expected and measured categories that their ratio is close to one, as expected, if the glass contained all of the waste radionuclides.

The activity of <sup>90</sup>Sr is present in the glass at 1.285E-1  $\mu$ Ci/g of glass. The factor of two difference between the measured and expected value for <sup>90</sup>Sr is not explained at present. Assuming conservatively that the density of the glass is 2.7 g/cc, there are 3.47E-1 Ci of <sup>90</sup>Sr in a cubic meter of glass. The requirement is that <sup>90</sup>Sr be present in a quantity that is less than 20 Ci/m<sup>3</sup>. Hence, the concentration of <sup>90</sup>Sr in the AZ-101 glass easily meets the requirement because it is about 58 times less concentrated.

Less than 1.56  $\mu$ g/g <sup>99</sup>Tc was measured by ICP-MS in the AZ-101 glass or less than 4.212 g/m<sup>3</sup>, assuming a density of 2.7 g/cc for the glass. This is equivalent to less than 7.16E-2 Ci/m<sup>3</sup>. The requirement is that the glass contains less than 1.0E-1 Ci/m<sup>3 99</sup>Tc. The requirement is easily met being only 70% of the limit at the maximum.

	Expected <sup>(a)</sup>	<b>Measured</b> <sup>(b)</sup>				
Isotope	μCi/g	μCi/g	Ratio <sup>(c)</sup>			
<sup>60</sup> Co	6.20E-6	<5E-6	n/a			
<sup>63</sup> Ni	4.5E-5	<3E-3	n/a			
<sup>90</sup> Sr	5.91E-2	1.285E-1	2.17			
<sup>99</sup> Tc	3.44E-4	<2.65E-2	n/a			
<sup>125</sup> Sb	3.68E-3	3.02E-3	0.821			
<sup>126</sup> SnSb	8.23E-4	7.73E-4	0.939			
<sup>137</sup> Cs	1.314E-2	1.27E-2	0.967			
<sup>151</sup> Sm	1.247E-5	<8.E-4	n/a			
<sup>238</sup> Pu	3.95E-7	<8E-5	n/a			
<sup>239</sup> Pu	3.42E-6	<9E-5	n/a			
<sup>241</sup> Pu	1.93E-5	<8.21E+0	n/a			
<sup>241</sup> Am	2.49E-7	<2.E-5	n/a			
Total U (µg/g)	<4.3E-3	$10.67^{(d)}$	n/a			
(a) This is the amount of activity expected to be included in the final glass						
based on the waste content.						
(b) This is the measured concentration in the final glass.						
(c) This is the measured	ured divided by the exp	ected, which ideally s	hould be one.			
(d) This uranium is	believed to originate fro	om the zircon batch m	ineral.			

Table 6.7. Expected and Measured Radionuclide Content in µCi/g of AZ-101 Glass

The activity of <sup>137</sup>Cs measured in the glass is 1.27E-2  $\mu$ Ci/g of glass. This measured value is slightly less than the expected value, which is based on the contribution made by the AZ-101(B) LAW. Using the same conservative density (2.7 g/cc), AZ-101 glass contains 3.43E-2 Ci/m<sup>3</sup> of <sup>137</sup>Cs, which is about 87 times less than the maximum requirement of 3 Ci/m<sup>3</sup>.

The TRU activity in the glass is required be less than 0.10  $\mu$ Ci/g (100 nCi/g). The sum total given in Table 6.8 is <4.6 ×10<sup>-4</sup>  $\mu$ Ci/g or <0.046 nCi/g. Hence, the requirement is met by a wide margin. Note that to estimate the total activity of all of the radioisotopes, those that are reported as "less than" in Table 6.8 were included at their "less than" value, so the 0.046 nCi/g total TRU is expected to be greater than the actual total for the glass.

TRU Isotope	Activity µCi/g AZ-101				
<sup>236</sup> Pu	nd				
<sup>237</sup> Np	<2.2E-4				
<sup>238</sup> Pu	<8E-5				
$^{239}$ Pu + $^{240}$ Pu	<9E-5				
<sup>241</sup> Pu	1.93E-5				
<sup>242</sup> Pu	<3.3E-6				
<sup>244</sup> Pu	nd				
<sup>241</sup> Am	<2.E-5				
<sup>242</sup> Cm	<8.0E-6				
<sup>243</sup> Am	<7.5E-6				
$^{243}$ Cm + $^{244}$ Cm	<8.0E-6				
Maximum Total TRU Activity <sup>(a)</sup>	<4.6E-4				
<sup>(a)</sup> The values are based on mass spectrometry or direct radiological					
determination. MS values were used when radiological data were no					
available. Where the data gave only an upper limit, that value was					
used as the measured amount.					
nd = non-detect					

Table 6.8. Measured or Calculated Activity (in µCi/g) of TRU Isotopes in the AZ-101 Glass<sup>(a)</sup>

#### 6.3.2 Measured Dose Rates from LAW Glasses

The dose rates were measured on LAW glass fragments weighing from 2 to 13 grams by an RPL radiation control technician (RCT). The standard RCT instrument was used in the standard way to make these measurements. That means radiation rates were measured at about 5 and 30 cm distant from the glass fragment with the shield off and on. The shield allows gamma radiation to pass while blocking the beta component, so total and gamma radiation are measured directly and the beta component is the difference between the total and the gamma dose rates. Note that alpha radiation does not contribute to the dose rate because of its very short range and the very low content of alpha emitters in the glass.

Table 6.9 gives the uncorrected and corrected dose rates normalized to mass measured on the four LAW glasses fabricated to date. The uncorrected values are the direct instrument reading while the corrected values are calculated from the uncorrected values. The correction is done by multiplying the uncorrected values by factors which take into account the geometric configuration of the sample and detection instrument as well as the counting efficiency of the instrument, which has been previously determined.

		Uncorrected		Co	rrected		
Sample ID	Weight, g	Beta mr/g	Gamma mr/g	Beta mr/g	Gamma mr/g		
AP-101 <sup>(a)</sup>	1.949	0.77	-	69	-		
AZ-101 <sup>(b)</sup>	13.392	0.48	0.04	17	1.05		
AN-107 <sup>(C)</sup>	10.922	0.15	0.07	1	0.29		
AW-101 <sup>(d)</sup>	11.208	0.56	0.06	30	1.07		
(a) AP-101 is	described in	RPP-WTP-092	2.				
(b) AZ-101 is	(b) AZ-101 is described in RPP-WTP-106 (this report).						
(c) AN-107 is described in WTP-RPT -003.							
(d) AW-101	is described in	WTP-RPT -0	03.				

Table 6.9. Measured Dose Rates of ILAW Glasses at Contact

## 6.4 Crystalline and Noncrystalline Phases

Optical microscopy revealed transparent monoclinic crystals of augite (Figure 6.4). SEM micrographs (Figure 6.5) show that the dendrites of augite (the light gray crystals) nucleated on and branched from bubbles and spinel (the bright crystals). Spinel crystals formed at a higher temperature. As temperature decreased, spinel was slowly reacting with the surrounding melt to form pyroxene. Based on these visual inspections and XRD, the crystalline content of the glass was estimated to be less than 0.8 wt% and probably less than 0.5 wt%. The uncertainty in the amount arises from the heterogeneous distribution of the crystals as shown in Figures 6.4 and 6.5.

Table 6.10 lists the compositions of spinel crystals as determined with EDS. Based on the average atomic fractions of the spinel-forming cations (Table 6.11), the following formula was obtained:

 $(Mg_{0.11}Fe_{0.19}Zn_{0.70})O \cdot (Al_{0.05}Cr_{0.79}Fe_{0.19})_2O_3$ 

It can also be written as

$$Mg_{0.11}Fe_{0.19}Zn_{0.70}Al_{0.09}Cr_{1.53}Fe_{0.38}O_4.$$

Hence, the bright crystals are mainly zincochromite  $(ZnCr_2O_4)$  in solid solution with spinel  $(MgAl_2O_4)$  and magnetite  $(Fe_3O_4)$ .

Table 6.12 lists the compositions of augite crystals as determined with EDS. Based on the average atomic fractions of cations, the following formula was obtained:

 $0.08 Na_2 O \cdot 1.37 (Mg_{0.49} Ca_{0.81} Zn_{0.07}) O \cdot 0.21 (Al_{0.04} Cr_{0.005} Fe_{0.17})_2 O_3 \cdot 2 Si_{0.96} Ti_{0.04} O_2.$ 

It can also be written as

$$Na_{0.08}Ca_{0.81}Mg_{0.49}Zn_{0.07}Al_{0.08}Fe_{0.35}Cr_{0.01}Si_{1.92}Ti_{0.08}O_6.$$

Hence, the light gray crystals are mainly augite  $(Ca_{0.9}Na_{0.1}Mg_{0.9}Fe^{2+}_{0.2}Al_{0.4}Ti_{0.1}Si_{1.9}O_6)$  in solid solution with other pyroxenes.

Because the fraction of crystalline phase in the CCC-treated AZ-101 sample was very low, the XRD analysis (see Figure 6.6) did not result in a sufficiently distinct pattern. Therefore, the suggested structures of minerals in the sample are subjected to a high uncertainty. A good fit was found for protoenstatite (MgSiO<sub>3</sub>) and aenigmatite (Na<sub>2</sub>Fe<sub>5</sub>TiSi<sub>6</sub>O<sub>20</sub>), a mineral rich in sodium (7.16 mass% Na<sub>2</sub>O). Its Na fraction of cations is 0.143 compared to 0.020 from EDS. Though sodium is an element that is usually underestimated in EDS analysis by approximately 10%, this possible error cannot account for the large difference in the Na<sub>2</sub>O content between stoichiometric aenigmatite and the crystals measured with EDS, which are most likely pyroxene.



Figure 6.4. Optical Images (multicolored in polarized light) of Crystals in AZ-101 LAW Glass Subjected to CCC Heat Treatment. Note that two nucleation sites are observed; on the wall where the melt contacted the container and free floating in the melt where nucleation may have occurred on a bubble, on a insoluble particle, or directly from the melt.



Figure 6.5. SEM Micrographs of AZ-101 LAW Melt Subjected to CCC Heat Treatment

Label	0	Na	Mg	Al	Si	Ca	Ti	Cr	Fe	Zn
AZ-101eds01	0.535	0.006	0.017	0.015	0.001	0.001	0.001	0.224	0.107	0.093
AZ-101eds17	0.498	0.015	0.016	0.018	0.081	0.013	0.003	0.195	0.069	0.093
AZ-101eds19	0.537	0.007	0.015	0.007	0.002	0.004	0.001	0.243	0.069	0.116

 Table 6.10. EDS Composition (in atomic fractions) of Spinel Crystals in AZ-101

 LAW Melt Subjected to CCC Heat Treatment

 Table 6.11. EDS Composition (in atomic fractions of spinel-forming cations) of Spinel

 Crystals in AZ-101 LAW Melt Subjected to CCC Heat Treatment

	Mg	Al	Cr	Fe	Zn
AZ-101eds01	0.04	0.03	0.49	0.24	0.20
AZ-101eds17	0.04	0.05	0.50	0.18	0.24
AZ-101eds19	0.03	0.01	0.54	0.15	0.26
Average	0.04	0.03	0.51	0.19	0.23



Figure 6.6. XRD Pattern of AZ-101 LAW Glass Subjected to CCC Heat Treatment

Table 6.13 presents EDS data of the glass-matrix composition in the AZ-101 sample subjected to CCC heat treatment. Data numbered 23 to 30 were taken from the bulk glass (far from crystals); the rest of the data relate to glass near crystals. Bulk glass data are averaged and compared with the target composition in Table 6.14; for fair comparison, the EDS data were normalized to the sum of the mass fractions of the target components. Table 6.14 indicates that fractions of low-atomic-mass elements tend to be underestimated by EDS, whereas fractions of high-atomic-mass elements tend to be overestimated.

	Na	Mg	Al	Si	Ca	Ti	Cr	Fe	Zn
AZ-101eds11	0.021	0.126	0.026	0.488	0.217	0.019	0.001	0.085	0.017
AZ-101eds18	0.017	0.124	0.019	0.487	0.214	0.025	0.001	0.093	0.018
AZ-101eds10	0.017	0.124	0.023	0.494	0.215	0.022	0.000	0.087	0.016
AZ-101eds16	0.019	0.122	0.019	0.490	0.210	0.025	0.002	0.092	0.019
AZ-101eds06	0.021	0.129	0.021	0.500	0.207	0.020	0.001	0.086	0.014
AZ-101eds05	0.020	0.127	0.018	0.507	0.207	0.019	0.002	0.082	0.017
AZ-101eds02	0.024	0.127	0.018	0.500	0.207	0.021	0.002	0.084	0.017
AZ-101eds03	0.018	0.126	0.018	0.504	0.205	0.021	0.002	0.088	0.018
Average	0.020	0.126	0.021	0.496	0.210	0.022	0.001	0.087	0.017

 Table 6.12. EDS Composition (in atomic fractions of cations) of Augite Crystals in AZ-101 LAW

 Melt Subjected to CCC Heat Treatment

Table 6.13. EDS Composition (in atomic fractions) of Glass Matrix in AZ-101 LAW MeltSubjected to CCC Heat Treatment

Label	0	Na	Mg	Al	Si	S	Ca	Ti	Cr	Fe	Zn
AZ-101eds09	0.635	0.032	0.015	0.027	0.211	n/a	0.034	0.006	0.0003	0.022	0.019
AZ-101eds15	0.622	0.030	0.015	0.029	0.220	n/a	0.036	0.006	0.0003	0.021	0.020
AZ-101eds04	0.632	0.045	0.003	0.043	0.222	n/a	0.023	0.004	0.0003	0.010	0.019
AZ-101eds12	0.620	0.034	0.012	0.030	0.224	n/a	0.032	0.006	0.0001	0.019	0.024
AZ-101eds23	0.615	0.043	0.017	0.030	0.219	0.14	0.033	0.005	n/a	0.018	0.018
AZ-101eds24	0.613	0.042	0.017	0.030	0.221	0.16	0.033	0.005	n/a	0.018	0.018
AZ-101eds25	0.612	0.043	0.017	0.030	0.221	0.14	0.033	0.005	n/a	0.018	0.018
AZ-101eds26	0.614	0.043	0.018	0.030	0.220	0.12	0.033	0.006	n/a	0.018	0.017
AZ-101eds27	0.615	0.042	0.017	0.029	0.220	0.12	0.033	0.005	n/a	0.018	0.017
AZ-101eds28	0.607	0.043	0.017	0.031	0.224	0.14	0.034	0.005	n/a	0.018	0.018
AZ-101eds29	0.600	0.042	0.018	0.031	0.228	0.18	0.034	0.006	n/a	0.019	0.018
AZ-101eds30	0.599	0.043	0.017	0.031	0.230	0.14	0.034	0.005	n/a	0.019	0.018

Table 6.14. EDS Composition of Bulk Glass Matrix in AZ-101LAW Melt Subjected to CCC Heat Treatment

	Mass Fractio	ons of Oxides							
	Target	EDS	Δ	$\Delta_{rel}$					
Na <sub>2</sub> O	0.054	0.049	-0.005	-0.087					
MgO	0.030	0.026	-0.004	-0.144					
Al <sub>2</sub> O <sub>3</sub>	0.062	0.056	-0.006	-0.094					
SiO <sub>2</sub>	0.487	0.493	0.006	0.013					
SO <sub>3</sub>	0.0055	0.0051	-0.0004	-0.073					
CaO	0.068	0.069	0.001	0.013					
TiO <sub>2</sub>	0.014	0.016	0.002	0.132					
Fe <sub>2</sub> O <sub>3</sub>	0.053	0.054	0.001	0.019					
ZnO	0.049	0.053	0.005	0.099					
$\Delta$ the dif	$\Delta$ the difference between EDS and target mass fraction of an oxide								
$\Delta_{\rm rel}$ the r	elative difference	$(\Delta_{\rm rel} = (x_i({\rm EDS})/$	$x_i(\text{target})) - 1$	1)					

## 6.5 PCT

Results of the analyses of 7-day PCT solutions from testing the CCC-treated AZ-101 glass are summarized in Table 6.15. Concentrations of elements were measured for AZ-101 LAW glass and for LRM standard glass, both in triplicate. Normalized elemental releases for the key elements are listed in Table 6.16. The measured normalized releases of the standard glass are in good agreement with reported values, except for lithium. The large error in the normalized Li release from the LRM glass is caused by its small content of Li, only 0.1 mass% compared to 4.3 mass% of Li in AZ-101 LAW glass. As expected, normalized boron, sodium, and lithium releases from AZ-101 LAW glass are close: 0.26 g/m<sup>2</sup> for B, 0.11 g/m<sup>2</sup> for Si, and 0.25 g/m<sup>2</sup> for Na; all these values are well below the limit of 2.0 g/m<sup>2</sup>.

One reason for performing the PCT on glasses that have partially crystallized is that the growth of the crystals can modify the composition of the glass in the neighborhood of the crystal and the modified glass composition can be less durable. Precipitation of the pyroxene crystals of the composition listed in Table 6.12 is an example where this phenomena has very little impact on the PCT release from the glass matrix. The impact is virtually zero because the composition of the crystalline phase is close to that of the glass. The calculated PCT normalized releases based on the model developed by Vienna et al. (2002) are listed in Table 6.17 for glasses with mass fractions of pyroxene crystals of the composition found in the glass and in the range from 0 to 15 mass%. The calculated release is plotted as a function of percent crystallinity in Figure 6.7 illustrating the fact that the pyroxene crystallization during the CCC heat treatment has not significantly affected the AZ-101 glass durability.

	AZ	Z-101-C-9	D <sup>(a)</sup>	LAW-	<b>FP121-LR</b>	M-90 <sup>(a)</sup>
Element		(mg/L)			(mg/L)	
В	16.7	15.7	15.8	26.1	26.4	25.8
Li	12.1	11.5	11.7	0.088	0.088	0.088
Na	21.2	20.0	20.2	163.0	165.0	162.0
Si	52.2	49.8	50.3	85.2	86.1	85.2
Ag	n/a	0.007	n/a	n/a	n/a	n/a
Al	1.37	1.38	1.45	15.4	15.6	15.5
Ва	0.001	0.001	0.001	0.001	n/a	n/a
Са	2.25	2.36	2.28	0.40	0.16	0.37
Со	0.005	0.007	n/a	0.009	0.008	0.009
Cr	0.062	0.059	0.071	0.378	0.379	0.386
Cu	0.010	0.013	0.011	0.013	0.012	0.013
Fe	0.283	0.362	0.391	2.910	2.860	2.930
K	1.2	1.7	1.5	4.0	3.9	3.6
Mg	0.180	0.290	0.300	0.120	0.110	0.094
Mn	0.007	0.008	0.009	0.157	0.145	0.149
Мо	0.033	0.040	0.032	0.253	0.257	0.247
Nd	n/a	0.047	n/a	n/a	n/a	n/a
Ni	0.067	0.070	0.070	0.561	0.567	0.558
Р	0.150	0.150	0.160	0.759	0.780	0.745
Pb	0.037	0.050	0.042	0.216	0.209	0.200
Rh	n/a	0.051	n/a	n/a	n/a	n/a
Ru	n/a	0.024	n/a	n/a	n/a	n/a
Sb	0.045	0.050	0.056	0.045	0.040	0.040
Se	n/a	0.036	0.045	n/a	n/a	n/a
Sn	n/a	0.170	n/a	n/a	n/a	n/a
Sr	n/a	0.002	n/a	0.002	n/a	n/a
Те	n/a	0.052	n/a	n/a	n/a	n/a
Ti	0.007	0.011	0.012	0.156	0.157	0.158
Tl	0.022	0.023	n/a	n/a	n/a	n/a
V	0.041	0.040	0.039	0.007	0.006	0.006
W	0.083	0.098	0.090	n/a	n/a	n/a
Zn	0.287	0.388	0.430	0.049	0.066	0.048
Zr	n/a	0.006	0.007	1.720	1.750	1.730
(a) Analys	es were perf	formed in tri	plicate.			

Table 6.15.7-Day PCT Solution Analysis of AZ-101LAW Glass Subjected to CCC Heat Treatment and LRM Glass.

Element		AZ- (g	·101 <sup>(a)</sup> /m <sup>2</sup> )			LAW-TP121-LRM-90 <sup>(a)</sup> (g/m <sup>2</sup> )				
	1	2	3	Average	1	2	3	Average	Reported <sup>(b)</sup>	$\Delta_{\rm rel}^{(c)}$
В	0.27	0.25	0.25	0.26	0.52	0.53	0.52	0.52	0.59	-0.11
Li	0.30	0.29	0.29	0.29	0.07	0.07	0.07	0.07	0.21	-0.65
Na	0.26	0.25	0.25	0.25	0.55	0.55	0.54	0.55	0.57	-0.04
Si	0.11	0.11	0.11	0.11	0.17	0.17	0.17	0.17	0.17	0.01
(a) Analyses were performed in triplicate. (b) Values reported in WSRC-TR-99-00095. (c) $\Delta_{rel} = Average/Reported - 1$ , note for LRM glass only.										

Table 6.16. Normalized 7-Day PCT Releases of AZ-101LAW Glass Subjected to CCC Heat Treatment

Table 6.17. Calculated Compositions of Amorphous Matrices and PCT Releases for AZ-101 LAW
Glass as Functions of Mass Fraction of Pyroxene Crystals (Vienna et al. 2002)

				Glass	with Cr	ystals					
<b>C</b> <sup>(a)</sup>	Crystal	0.000	0.020	0.040	0.060	0.080	0.100	0.150	$b_{B,i}$	$b_{Li,i}$	$\boldsymbol{b}_{Na,i}$
Al <sub>2</sub> O <sub>3</sub>	0.011	0.090	0.091	0.093	0.095	0.097	0.099	0.104	-28.48	-28.87	-27.37
B <sub>2</sub> O <sub>3</sub>		0.099	0.101	0.103	0.106	0.108	0.110	0.117	13.75	11.09	8.98
CaO	0.225	0.054	0.051	0.047	0.043	0.039	0.035	0.024	-11.54	-7.37	-4.04
F		0.000	0.000	0.000	0.000	0.000	0.000	0.000	15.96	24.63	11.99
Fe <sub>2</sub> O <sub>3</sub>	0.047	0.120	0.122	0.123	0.125	0.126	0.128	0.133	-9.69	-10.01	-11.60
K <sub>2</sub> O		0.002	0.003	0.003	0.003	0.003	0.003	0.003	8.06	2.93	11.81
Li <sub>2</sub> O		0.018	0.019	0.019	0.019	0.020	0.020	0.022	9.06	9.00	7.18
MgO	0.135	0.017	0.015	0.012	0.010	0.007	0.004	0.000	7.03	5.32	9.06
Na <sub>2</sub> O	0.011	0.047	0.048	0.049	0.049	0.050	0.051	0.054	11.51	12.62	15.19
$P_2O_5$		0.001	0.001	0.001	0.001	0.001	0.001	0.001	-24.52	-8.03	-19.35
SiO <sub>2</sub>	0.530	0.416	0.413	0.411	0.408	0.406	0.403	0.395	-4.35	-3.94	-4.67
$SO_3$		0.006	0.006	0.007	0.007	0.007	0.007	0.007	75.52	n/a	49.95
TiO <sub>2</sub>	0.023	0.016	0.016	0.016	0.015	0.015	0.015	0.015	-27.16	-20.20	-30.91
ZnO	0.018	0.056	0.057	0.058	0.059	0.059	0.060	0.063	-3.51	14.49	-21.49
ZrO <sub>2</sub>		0.056	0.057	0.058	0.059	0.060	0.062	0.065	-19.61	-18.66	-17.05
Others	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	1.91	0.64	-1.99
$r_B$ , g/m <sup>2</sup>	0.005	0.005	0.006	0.006	0.006	0.006	0.006	0.006	n/a	n/a	n/a
$r_{Li}$ , g/m <sup>2</sup>	0.021	0.012	0.012	0.012	0.012	0.011	0.011	0.011	n/a	n/a	n/a
$r_{Na}$ , g/m <sup>2</sup>	0.019	0.002	0.002	0.001	0.001	0.001	0.001	0.001	n/a	n/a	n/a
(a) C is th	ne mass frac	tion of cr	ystals in g	glass ; $r_B$ ,	$r_{Li}$ , and $r_{Li}$	<sub>Na</sub> are nor	malized I	PCT relea	uses of B, I	Li, and Na	;
$b_{B,i}, b_I$	$L_{i,i}$ , and $b_{Na,i}$	are partia	ıl molar n	ormalized	d PCT rel	eases of I	3, Li, and	Na.			



Figure 6.7. Normalized PCT Releases Versus Crystallinity Fraction in AZ-101 LAW Glass

## 6.6 TCLP

Leachates from the TCLP test were analyzed for Sb, As, Ba, Be, B, Cd, Cr, Pb, Hg, Ni, Se, Ag, Tl, V, and Zn. The only elements detected in the TCLP leachates were Ba, B, Cr, Hg, and Zn. The CoPCs (Ba, Cr, Hg, and Zn) were all significantly below the UTS limit (Table 6.18). Thallium was detected by ICP-MS at 0.000113 mg/L while the MDL was stated to be 0.000013 mg/L, so this element is also present significantly below its UTS as shown in Table 6.18. Note that the elements that need to be beneath the UTS to meet Land Disposal Restrictions are indicated with an "×" in Table 6.18. All those elements meet the LDR.

The blank-spike recovery values were within the acceptance criterion of 80% to 120% for all analytes. Both matrix-spike and post-spike recovery values were within the acceptance criterion of 75% to 125% for all analytes.

			Required	ICP-AES <sup>(a)</sup>	MDL <sup>(b)</sup>	EQL <sup>(c)</sup>
CAS#	Element	Symbol	for LDR	(mg/L TCLP)	(mg/L)	(mg/L)
7440-36-0	Antimony	Sb	Х	0.028 U	0.028	1.15
7440-38-2	Arsenic	As	VIT	0.045 U	0.045	5.0
7440-39-3	Barium	Ва	VIT	0.24 J	0.002	21
7440-41-7	Beryllium	Be	Х	0.0002 U	0.0002	1.22
7440-42-8	Boron <sup>(d)</sup>	В	n/a	0.428	0.012	0.05
7440-43-9	Cadmium	Cd	VIT	0.006 U	0.006	0.11
18540-29-9	Chromium	Cr	VIT	0.008 J	0.004	0.6
7439-92-1	Lead	Pb	VIT	0.035 U	0.034	0.75
7439-97-6	Mercury	Hg	VIT	0.000049 J	0.000045	0.025
7440-02-0	Nickel	Ni	Х	0.014 U	0.014	11
7782-49-2	Selenium	Se	VIT	0.042 U	0.042	1.0
7440-22-4	Silver	Ag	VIT	0.005 U	0.004	0.14
7440-28-0	Thallium	Tl	Х	0.00011J	0.000013	0.20
7440-62-2	Vanadium	V	n/a	0.003 U	0.003	1.6
7440-66-6	Zinc	Zn	n/a	0.79 J	0.005	4.3

 Table 6.18. Concentrations of TCLP Inorganic Constituents of Potential Concern (CoPC)

(a) Average of sample and duplicate; Hg was measured with CVAA; Tl was measured with ICP-MS; U (undetected), analyte had no measurable instrument response, or response was <MDL.

(b) MDLs were determined with dilute acidified water (2% HNO<sub>3</sub>) per ASO-QAP-001 and adjusted by the average sample processing factor (~1.01).

(c) Estimated quantitation limits (EQLs) were set equal to the Universal Treatment Standards (UTS); no specific EQLs have been established for TCLP solutions; the EQL for B was specified in the ASR.

<sup>(d)</sup> Boron is included for information only and is not a Constituent of Potential Concern.

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.

X = Required for LDR

VIT = vitrification has been recognized as the best available technology for immobilizing these elements per 40 CFR 268.40.

n/a = not applicable

## 6.7 Property Comparison of Actual and Simulated AZ-101 Waste, Melter

#### Feed and Glass

Table 6.19 through Table 6.23 list physical, chemical, and rheological properties for actual and simulated AZ-101 waste, melter feed, and glass. As Table 6.19 and Table 6.20 show, the actual and simulated wastes have similar pH values, the actual and simulated melter feed have similar bulk densities and the actual and simulated melter feed have similar Bingham model yield stresses. The shear-strength results indicate that the settled solids for the actual melter feed slurries can form a very cohesive layer that is difficult to shear. The 2.75 M Na sample possessed a shear strength that exceeded the scale of the viscometer with the  $1.6 \times 1.6$  cm ( $0.63 \times 0.63$  in.) shear vane is approximately 11,600 Pa (Poloski et al. 2003). Note that yield stress is a model fit parameter for a system undergoing shearing while shear strength is a direct measurement of the stress required to initiate shearing

and as indicated in Table 6.18 they can differ by several orders of magnitude. VSL data is from Muller and Pegg, 2003.

Table 6.22 compares the PCT results for PNWD actual and VSL simulant AZ-101 ILAW. Both the PNWD actual and VSL simulant AZ-101 ILAW received a CCC heat treatment as described in Section 5.1.6. Variation of the normalized release rates between the VSL simulant AZ-101LAW glass and the PNWD actual AZ-101 LAW glass is within  $0.03g/m^2$  for PCT method A. This degree of variation is only slightly higher than the experimental error ( $0.02 g/m^2$ ) observed between the triplicate samples of AZ-101 LAW glass by PNWD. Smith et al. (2000) provides similar test results for Envelope A and Envelope C glasses. First, it should be noted that the LRM glass gave close to the same leaching result in both sets of tests at 90°C indicating test conditions have been closely reproduced (Table 6.24).

Table 6.25 compares the TCLP results for PNWD actual and VSL simulant AZ-101 LAW glasses. The PNWD actual AZ-101 LAW glass was quenched from melt while the VSL simulant AZ-101 LAW glass was given a CCC heat treatment. The TCLP results for the simulant AZ-101 LAW CCC glass and actual AZ-101 LAW quenched waste glass are very similar with the exception of Zn, which is approximately twice as high for the simulant AZ-101 LAW CCC waste glass.

Property	Actual (PNWD)	Simulant (VSL)					
pН	13.4 at 25°C	13.21 <sup>(a)</sup>					
Density, g/mL	1.15	1.12					
(a) Temperature not specified; it is assumed that the values							
were obtaine	d at room temperature						

Table 6.19. Properties of Actual and Simulant AZ-101 Waste at 2.75M Na

	Actual (PNWD)						
Property	at 25°C	Simulant (VSL) <sup>(a)</sup>					
pH	7.5	7.38					
Median volume PS (µm)	13.3	n/a					
95% volume PSD, D <sub>95</sub> (μm)	74	n/a					
Bulk density (g/mL)	1.736	1.71					
Supernatant liquid density (g/mL)	1.171	n/a					
Settled solids (vol%)	73.8	n/a					
Centrifuged solids density (g/mL)	1.939	n/a					
Centrifuged solids (vol%)	73.7	n/a					
Centrifuged solids (mass%	82.4	n/a					
Total solid (mass%)	62.7	n/a					
Undissolved solids (mass%)	54.0	n/a					
Newtonian viscosity at 25°C (cP)	80	n/a					
Newtonian viscosity at 40°C (cP)	33	n/a					
Yield stress at 25° (Pa)	5.3	5.2					
Shear strength at 40°C (Pa)	>11600	n/a					
Glass components <sup>(c)</sup> (mass%)	n/a	n/a					
<ul> <li>(a) Temperature not specified (it is assumed the values were obtained at room temperature); Glass formulated to LAWB83; n/a = not available.</li> <li>(b) ND = not detected</li> </ul>							
(c) Glass components are oxides and	halogens present in the	e glass.					

Table 6.20. Properties of Actual and Simulant AZ-101 Melter Feed at 2.75M Na (Poloski et al. 2003) and (Muller and Pegg 2003)

Table 6.21. Properties of Actual and Simulant AZ-101 LAW Glass

Property	Actual (PNWD)	Simulant (VSL)		
Waste loading in glass (mass fraction)	0.0668	0.0667		
Na <sub>2</sub> O mass fraction in waste oxides	0.8037	0.8051		
Na <sub>2</sub> O mass fraction in glass	0.0557 <sup>(a)</sup>	0.0603 <sup>(b)</sup>		
Density (g/mL)	n/a	2.75 <sup>(c)</sup>		
(a) The best estimate based on Na <sub>2</sub> O <sub>2</sub> -NaOH fusion, KOH fusion, and acid digestion analyses.				
(b) X-ray fluorescence analysis.				
(c) LB83PNCC.				

Table 6.22. Comparison of PCT Normalized Releases (in g/m<sup>2</sup>) Between Actual and Simulant AZ-101 CCC-Treated Glass

	PNWD	VSL <sup>(a)</sup>	$\Delta_{\rm CCC}^{(b)}$	$\Delta_{\rm CCC, rel}^{(c)}$
В	0.26	0.23	-0.03	-0.12
Li	0.29	n/a	n/a	n/a
Na	0.25	0.23	-0.02	-0.08
Si	0.11	0.10	-0.01	-0.10
(a) Glass LB83PNCC				
(b) $\Delta_{\text{CCC}}$ is the difference between the VSL and PNWD-measured				
PCT normalized release.				
(c) $\Delta_{\text{CCC,rel}}$ is $\Delta_{\text{CCC}}$ divided by the VSL-PNWD average.				

# Table 6.23. Comparison of Average 7-Day 90°C PCT Normalized Mass Loss Data Between VSL<br/>Non-Radioactive Simulant Glasses and Actual Radioactive LAW Glass Counterparts<br/>from this Study. LRM Data are Provided for Comparison Purposes.

Average 7-DAY 90°C PCT Normalized Mass Loss (g/m <sup>2</sup> )				
Glass	Element			
	В	Na	Si	
AZ-101	0.26	0.25	0.11	
LB83PNCC	0.23	0.23	0.10	
LRM	0.506	0.504	0.165	
LAWA88 (simulant AW-101 glass)	0.434	0.426	0.171	
AW-101 (leachate pH range = $10.27 - 10.33$ )	0.569	0.589	0.196	
LAWC15 (simulant AN-107 glass) 0.329 0.335 0.161				
AN-107 (leachate pH range = $10.02 - 10.05$ ) 0.354 0.422 0.191				
Note: ORP contract requirement from Specification 2, Section 2.2.2.17.2 requires that the normalized mass loss of the LAW waste glasses produced be $< 2 \text{ g/m}^2$ .				

Table 6.24. Durability of the LRM Glass Shown for the Two Different Studies

	Standard LRM Glass (g/m <sup>2</sup> )			
	This Study Smith et al. 200			
В	0.52	0.506		
Li	0.07			
Na	0.55	0.504		
Si	0.17	0.165		

Table 6.25.	Comparison of	f TCLP Results	Between AZ-101	Actual and Simulant	Glass in mg/L
-------------	---------------	----------------	----------------	---------------------	---------------

			Actual Quenched	Simulated CCC
Element		UTS	(PNWD) (mg/L TCLP)	(VSL) (mg/L TCLP)
Antimony	Sb	1.15	< 0.043	n/a
Arsenic	As	< 0.25	< 0.045	< 0.05
Barium	Ba	21.00	0.24	<0.6
Beryllium	Be	1.22	< 0.0002	n/a
Boron	В	0.05	0.425	n/a
Cadmium	Cd	0.11	< 0.006	< 0.005
Chromium	Cr	0.60	0.008	< 0.006
Lead	Pb	0.75	< 0.034	< 0.02
Mercury	Hg	0.025	0.000085	n/a
Nickel	Ni	11	< 0.014	< 0.008
Selenium	Se	5.70	< 0.042	< 0.05
Silver	Ag	0.14	< 0.004	< 0.003
Thallium	Tl	0.20	0.000113	n/a
Vanadium	V	1.6	< 0.003	n/a
Zinc	Zn	4.30	0.79	1.64

## 7.0 **Con**clusions

The primary objective for vitrifying the AZ-101 LAW sample was to demonstrate the RPP-WTP project's ability to satisfy the ILAW product ORP contract requirements concerning chemical and radionuclide reporting, waste loading, identification and quantification of crystalline and noncrystalline phases, and waste-form PCT and TCLP leachability. A pretreated tank supernatant was prepared as a melter feed for vitrification. The analyzed composition of the pretreated AZ-101 LAW was used by CUA VSL to formulate a target glass composition LAWB83. The supernatant tank sample, i.e., AZ-101 LAW, was processed through pretreatment chemical separation processes, and the decontaminated supernatant was mixed with mineral additives to be converted to LAW glass with acceptable properties.

The primary success criteria associated with the LAW product requirements were all met:

1. Chemical constituents present in the glass at concentrations greater than 0.5 wt% are identified and quantified.

The AZ-101 LAW glass contains 12 constituent oxides with concentration >0.5 mass%. These oxides are (with best analytical estimates in mass%): SiO<sub>2</sub> (48.70), B<sub>2</sub>O<sub>3</sub> (10.04), CaO (6.79), Al<sub>2</sub>O<sub>3</sub> (6.21), Na<sub>2</sub>O (5.35), Fe<sub>2</sub>O<sub>3</sub> (5.29), ZnO (4.85), Li<sub>2</sub>O (4.31), ZrO<sub>2</sub> (3.17), MgO (2.99), TiO<sub>2</sub> (1.40), and SO<sub>3</sub> (0.51). [2.2.2.6.1 <u>Chemical Composition Qualification clause</u> *Section C* from *WTP Contract- DE-AC27-01RV1413 Modification No. M033*]

2. Key radionuclides are identified and quantified.

Identification and quantification of those radionuclides identified as significant in NUREG/BR-0204 and 49 CFR 172.101. The date of analysis is given Table 6.6 and allows the values reported to be indexed to any date desired. Technetium-99 is considered significant at concentrations >3.0E-3 Ci/m<sup>3</sup>. Assuming that the density of the glass is 2.7 g/mL, the AZ-101 glass contains a maximum of 9.29E-4 Ci/m<sup>3</sup> of <sup>99</sup>Tc. Hence, this glass does not contain a significant quantity of <sup>99</sup>Tc. [2.2.2.7 <u>Radiological Composition Documentation</u> clause Section C from WTP Contract- DE-AC27-01RV1413 Modification No. M033]

3. The activities of radionuclides in the ILAW product are: <sup>137</sup>Cs <3 Ci/m<sup>3</sup>or<0.3 Ci/m<sup>3</sup>(see note below), <sup>90</sup>Sr<20 Ci/m<sup>3</sup>, <sup>99</sup>Tc <0.1 Ci/m<sup>3</sup>, and transuranic (TRU) <100 nCi/g.

The AZ-101 LAW glass contains <sup>90</sup>Sr, <sup>99</sup>Tc, <sup>137</sup>Cs, and TRU at levels considerably below the contract limits as shown in the Table 7.1. [2.2.2.8 <u>Radionuclide Concentration Limitations clause Section C</u> from WTP Contract- DE-AC27-01RV1413 Modification No. M033]. <u>Note</u> C.7 FACILITY SPECIFICATION, <u>subheading d)Waste Treatment and Immobilization Plant Unit Operation</u> from WTP Contract- DE-AC27-01RV1413 Modification No. M033]: specifies "In addition, <sup>137</sup>Cs will be further removed, to achieve a 0.3 Ci/m<sup>3</sup> in the ILAW product, to facilitate the maintenance concept established for the ILAW melter system."

		<b>Based on Measured</b>	Ratio –Contract Limit
Radionuclide	<b>Contract Limit</b>	Value	to Measured Value
<sup>90</sup> Sr	$20 \text{ Ci/m}^3$	0.347 Ci/m <sup>3</sup>	58
<sup>99</sup> Tc	0.1 Ci/m <sup>3</sup>	7.16E-2 Ci/m <sup>3</sup>	1.4
<sup>137</sup> Cs	$3 \text{ Ci/m}^3 \text{ or } 0.3 \text{ Ci/m}^3$	3.43E-2 Ci/m <sup>3</sup>	87 or 8.7
TRU	100 nCi/g	0.046 nCi/g	2174

#### Table 7.1. Summary of Radiochemical Results Showing Contract Compliance for Waste Glass

#### 4. The fraction of $Na_2O$ from LAW for Envelope B in the glass is >5 mass%.

The measured Na2O mass fraction in the AZ-101 LAW glass is 5.58 mass%. Hence, the AZ-101 LAW glass meets the task specification concentration. [2.2.2.2 <u>Waste Loading from</u> *WTP Contract- DE-AC27-* 01RV1413 Modification No. M033]: The loading of waste sodium from Envelope A in the ILAW glass shall be greater than 14 weight percent based on Na<sub>2</sub>O. The loading of waste sodium from Envelope B in the ILAW glass shall be greater than 3.0 weight percent based on Na<sub>2</sub>O. The loading of waste sodium from Envelope C in the ILAW glass shall be greater than 10 weight percent based on Na<sub>2</sub>O. The loading of waste sodium for Na<sub>2</sub>O. The loading of waste sodium from Envelope C in the ILAW glass shall be greater than 10 weight percent based on Na<sub>2</sub>O. The loading of waste sodium for waste from double shelled tank (DST) AZ-102 shall be greater than 3.0 weight percent based upon Na<sub>2</sub>O.]

5. Crystalline and non-crystalline phases are identified and quantified.

The AZ-101 LAW glass subjected to CCC contained sporadic crystals of spinel (mainly zincochromite) and augite of a similar composition to the glass. The estimated total in the glass was <0.8 wt%. [2.2.2.6.3 <u>Crystalline Phase Identification from WTP Contract- DE-AC27-01RV1413 Modification No. M033]</u>: The ILAW Product Qualification Report (Table C.5-1.1, Deliverable 6.6) shall provide the crystalline and non-crystalline phases expected to be present and the estimated amount of each phase for the waste form and filler material.]

6. The 7-day PCT normalized mass loss of Na, Si, and  $B < 2.0 \text{ g/m}^2$  (at 90°C).

The measured normalized PCT releases from the AZ-101 LAW glass are 0.26 g/m<sup>2</sup> for B, 0.11 g/m<sup>2</sup> for Si, and 0.25 g/m<sup>2</sup> for Na. These values are well below the limit of 2.0 g/m<sup>2</sup>. The precipitation of crystals on cooling apparently does not affect glass leachability. [2.2.2.17.2 Product Consistency Test from *WTP Contract- DE-AC27-01RV1413 Modification No. M033*]: The normalized mass loss of sodium, silicon, and boron shall be measured using a seven day product consistency test run at 90°C as defined in ASTM C1285-98.]

7. The glass meets the Land Disposal Restrictions (LDR) of Washington Dangerous Waste Regulations, WAC 173-303, and RCRA LDR in 40 CFR 268 (TCLP for hazardous inorganics).

The AZ-101 LAW glass passed the TCLP test and qualifies for land disposal. [2.2.2.20 <u>Dangerous Waste</u> <u>Limitations from</u> *WTP Contract- DE-AC27-01RV1413 Modification No. M033*]: The ILAW product shall be acceptable for land disposal under the State of Washington Dangerous Waste Regulations, WAC 173-303, and RCRA LDR in 40CFR268.]

The ILAW product testing results show that the AZ-101 LAW glass meets or exceeds ORP contract specifications for waste loading, chemical composition documentation, radionuclide concentration limitations, and waste-form leachability.

## Appendix A

**Radiochemistry Summary for AZ-101 Glass**
# **Appendix A: Radiochemistry Summary for AZ-101 Glass**

		Measure	d Activity					
		μC	ci/g					
	Measured	Proc.			RSD			
Radionuclide	Radiation	Blank	Sample	±1σ(%)*	%			
<sup>60</sup> Co	γ	nr	<5E-6	nr	nr			
<sup>63</sup> Ni	β	nr	<3E-3	nr	nr			
<sup>79</sup> Se	β	nr	<3.3E-3	nr	nr			
<sup>90</sup> Sr	β	<3E-3	1.285E-1	3	3.4			
<sup>95</sup> Nb	γ	nr	<5E-6	nr	nr			
<sup>99</sup> Tc <sup>(a)</sup>	γ	nr	<2.65E-2	nr	nr			
<sup>113</sup> Sn	γ	nr	<3E-5	nr	nr			
<sup>125</sup> Sb	γ	nr	3.02E-3	3	nr			
<sup>126</sup> SnSb	γ	nr	7.73E-4	5	nr			
<sup>134</sup> Cs	γ	nr	<7E-6	nr	nr			
<sup>137</sup> Cs	γ	nr	1.27E-2	nr	nr			
<sup>144</sup> Ce	γ	nr	<2E-4	nr	nr			
<sup>151</sup> Sm	β	nr	<8E-4	nr	nr			
<sup>152</sup> Eu	γ	nr	<2E-5	nr	nr			
<sup>154</sup> Eu	γ	nr	<2E-5	nr	nr			
<sup>155</sup> Eu	γ	nr	<8E-5	nr	nr			
<sup>232</sup> Th	γ	nr	<4E-5	nr	nr			
<sup>238</sup> Pu	α	nr	<8E-5	nr	nr			
$^{239}$ Pu + $^{240}$ Pu	α	nr	<9E-5	nr	nr			
<sup>241</sup> Pu	β	nr	<8E-0	nr	nr			
<sup>241</sup> Am	α	nr	<2E-5	nr	nr			
<sup>242</sup> Cm	α	nr	<7E-6	nr	nr			
$^{243}Cm + ^{244}Cm$	α	nr	<7.5E-6	nr	nr			
Total U	ICP-AES	10.67	7μg/g					
nr = not reported	nr = not reported							
Note: Table includes only those radioisotopes for which values were reported								
* $\pm 1\sigma(\%)$ is the probability that the true value does not differ from the								
reported value b	y more than t	he given perce	ent.					

Table A.1. Radiochemistry Summary for AZ-101 Glass

# Appendix B

ICP Mass Spectrometry Summary for AZ-101 Pretreated Waste

## Appendix B: ICP Mass Spectrometry Summary for AZ-101 Pretreated Waste

	Concentration		MDL
Element	μg/g (*μCi/g)	±1 Sigma	μg/g
Tc-99	9.44E-02	4.39E-03	7.15E-03
Tc(dup)	<7.15E-02	n/a	n/a
Pd-105	4.66E00	1.95E-02	1.11E-01
Pd (dup)	4.19E00	1.22E-03	1.11E-01
Ru-101	1.89E00	1.07E-02	9.01E-03
Ru (dup)	1.83E00	6.09E-04	9.01E-03
Ru-102	8.85E-01	3.14E-03	6.77E-03
Ru (dup)	8.61E-01	5.96E-04	6.77E-03
Rh-103	2.17E00	9.67E-03	5.21E-03
Rh (dup)	2.10E00	5.66E-04	5.21E-03
I-129*	<2.94E-06	n/a	<1.03E-06
Cs-133	<2.53E-01	n/a	<2.53E-02
Cs (dup)	<2.53E-01	n/a	<2.53E-02
Pr-141	<7.09E-01	n/a	<7.09E-02
Pr (dup)	<7.09E-01	n/a	<7.09E-02
Ta-181	<4.67E-02	n/a	<4.67E-03
Ta(dup)	<4.67E-02	n/a	<4.67E-03
Pt-195	<1.22E-01	n/a	<1.22E-02
Pt (dup)	<1.22E-01	n/a	<1.22E-02
U	<1.16E-02	n/a	<1.16E-03
U (dup)	<1.16E-02	n/a	<1.16E-03
U-233	<9.56E-06	n/a	<9.56E-07
U(dup)	<9.56E-06	n/a	<9.56E-07
U-234	<2.06E-06	n/a	<2.06E-07
U(dup)	<2.06E-06	n/a	<2.06E-07
U-235	<4.07E-09	n/a	<4.07E-10
U(dup)	<4.07E-09	n/a	<4.07E-10
U-236	<1.58E-08	n/a	<1.58E-09
U(dup)	<1.58E-08	n/a	<1.58E-09
U-238	<8.12E-09	n/a	<8.12E-10
U(dup)	<8.12E-09	n/a	<8.12E-10
Pu-239	<1.62E-02	n/a	<1.62E-03
Pu(dup)	<1.62E-02	n/a	<1.62E-03
Pu-240	<1.17E-03	n/a	<1.17E-04
Pu(dup)	<1.17E-03	n/a	<1.17E-04
Pu-242	<8.42E-07	n/a	<8.42E-08
Pu(dup)	<8.42E-07	n/a	<8.42E-08
Mass241	<6.66E-04	n/a	<6.66E-05
Mass(dup)	<6.66E-04	n/a	<6.66E-05
* µCi/L			
n/a = not ap	oplicable		

 Table B1. ICP Mass Spectrometry Summary for AZ-101 Pretreated Waste

# Appendix C

**ICP Mass Spectrometry Summary for AZ-101 Glass** 

## Appendix C: ICP Mass Spectrometry Summary for AZ-101 Glass

Isotope	K Fusion	±1σ	MDL	QC Status
<sup>99</sup> Tc	<1.56E-0	n/a	1.56E-0	OK
<sup>109</sup> Ag	1.34E+1	1.7E-1	7.93E-2	OK
<sup>111</sup> Cd	3.84E+1	2.7E-1	1.7E-0	OK
<sup>121</sup> Sb	<2.20E-0	n/a	2.20E-0	OK
<sup>129</sup> I	<9.91E-0	n/a	9.91E-0	OK
<sup>205</sup> Tl	<2.59E-0	n/a	2.59E-0	OK
<sup>208</sup> Pb	<8.69E+1	n/a	8.69E+1	OK
<sup>233</sup> U	<7.98E-2	n/a	7.98E-2	OK
<sup>234</sup> U	<1.31E-1	n/a	1.31E-1	OK
<sup>235</sup> U	1.71E-1	1.3E-2	1.22E-1	OK
<sup>236</sup> U	<6. 20E-2	n/a	6.20E-2	OK
<sup>237</sup> Np	<3.11E-1	n/a	3.11E-1	OK
<sup>238</sup> U	1.05E+1	5.8E-1	1.56E-0	OK
<sup>239</sup> Pu	<2.20E-2	n/a	2.20E-2	OK
<sup>240</sup> Pu	<8.38E-4	n/a	8.38E-4	OK
<sup>241</sup> Pu/	<7.97E-2	n/a	7.97E-2	OK
<sup>241</sup> Am				
<sup>242</sup> Pu	<8.38E-4	n/a	8.38E-4	OK
n/a = no	t applicable			

Table C.1. Mass Spectrometry Results for AZ-101 Glass (µg/g)

	ICP MS	Specific Activity					
U Isotope	µg/g	μCi/μg					
<sup>233</sup> U	<7.98E-2	9.64E-3					
<sup>234</sup> U	<1.31E-1	6.225E-3					
<sup>235</sup> U	1.71E-1	1.922E-6					
<sup>236</sup> U	<6. 20E-2	6.508E-5					
<sup>238</sup> U	1.05E+1	3.36E-7					
	TRU Isot	ope					
<sup>236</sup> Pu	nr	-					
<sup>237</sup> Np	<3.11E-1	7.05E-4					
<sup>238</sup> Pu	nr	-					
<sup>239</sup> Pu	<2.20E-2	6.2E-2					
<sup>240</sup> Pu	<8.38E-4	2.27E-1					
<sup>241</sup> Pu	<7.97E-2	1.03E+2					
<sup>242</sup> Pu	<8.38E-4	3.93E-3					
<sup>244</sup> Pu	nr						
<sup>241</sup> Am	<7.97E-2	3.43E-0					
<sup>242</sup> Cm	nr	-					
<sup>243</sup> Am	nr	-					
<sup>243</sup> Cm +	nr	-					
<sup>244</sup> Cm							
nr = not repor	nr = not reported						

Table C.2. AZ-101 Glass Uranium and TRU Inventory by ICP MS

# Appendix D

## VSL Batch Sheet for AZ-101(B) Waste Glass LAWB83

Muller, Isabelle S., and Ian L. Pegg. 2003. "*LAW Glass Formulation to Support AZ-101 Actual Waste Testing*". VSL-03R3470-3. Vitreous State Laboratory, The Catholic University of America for Duratek, Inc. and Bechtel National, Inc.

# Appendix D: VSL Batch Sheet for AZ-101(B) Waste Glass LAWB83

										Recipe using AZ101 Actual PNNL Sample for	glass:		LAWB83		9-Mar-04				
Envelope		Pretreated AZ-1	GLASS	Conversion	AZ101	AZ101 wt%	Glass	LAWB83	Additives		Assay	Ratio	Target						
Constituents	calculated	RPT-WTP-02-19	Oxides	to wt%	wt%	in glass @	Former	this target	for this	Source in			Weight				other oxides		
	IVI	authorized 9/6/02	Loading	Oxides	100%	6.68%	100%	6.68%	93.32%	Additives			Additives	-	% AI2O3	% MgO	% Fe2O3	%SiO2	Vendor Inormation
Ag		<0.50	Ag2O																
AI	0.196	5280	AI2O3	3.41	6.008	0.402	6.22	6.2058	5.804	Kyanite (Al2SiO5) 325 Mesh	0.990	0.571	156.19				0.51%	42.40%	Kyanite Mining
As	0.000	13.5	As2O3	0.01	0.011	0.001		0.0007											
в	0.001	7.75	B2O3	0.01	0.015	5 0.001	10.76	10.0418	10.041	H3BO3 (Technical Granular )	1.000	0.563	282.85						US Borax
Ba		<0.20	BaO					0.0000											
Ca		<5.0	CaO				7.27	6.7841	6.784	Wollanstonite NYAD 325 Mesh	1.000	0.455	236.47		1.07%	0.82%	0.11%	52.52%	NYCO Minerals
Cr	0.011	569.5	Cr2O3	0.28	0.501	0.034		0.0335											
Fe		<0.50	Fe2O3				5.67	5.2910	5.291	Fe2O3 (Iron III oxide, Prince Mgt.)	0.996	1.000	75.90						Prince Manufacturing
к	0.097	3,800	к20	1.56	2.757	0.184		0.1843											
Li		<0.60	Li2O				4.62	4.3112	4.311	Li2CO3 (Chemetall Foote Co. Tech. gr.)	0.992	0.404	170.61						Chemetall Foote Co. Tech. gr.
Mg		<2.0	MgO				3.20	2.9861	2.986	Olivine (Mg2SiO4) 325 Mesh (#180)	0.990	0.480	95.58				7.68%	42.52%	UNIMIN Corp.
Mo	0.001	85.3	MoO3	0.04	0.077	0.005		0.0052											
Na	4.306	99,000	Na2O	45.56	80.367	5.372		5.3720											
Pb	0.000	6.65	PbO	0.00	0.004	0.000		0.0003											
Si	0.002	52.5	SiO2	0.04	0.068	0.005	52.16	48.6780	48.673	SiO2 (Sil-co-Sil 75)	0.998	1.000	517.69						US SILICA
Sr		<0.30	SrO					0.0000		· · ·							1		
Ti	0.000	2.55	TiO2	0.00	0.003	0.000	1.50	1.3999	1.400	TiO2 (Rutile Airfloated)	0.940	1.000	23.62		4.50%				Chemalloy
v	0.000	1.35	V2O5	0.00	0.001	0.000		0.0001											
w	0.000	51	WO3	0.02	0.039	0.003		0.0026											
Zn	0.000	1.65	ZnO	0.00	0.001	0.000	5.20	4.8525	4.852	ZnO (Kadox-920)	1.000	1.000	76.96				1		Zinc Corp. of America
Zr	0.000	1.95	ZrO2	0.00	0.002	0.000	3.40	3.1728	3.173	Zircon ZrSiO4 (Flour) Mesh 325	1.000	0.663	75.90		0.31%			33.35%	American Mineral
CI		<130	CI					0.0000								-		•	
F	0.100	1900	F	0.65	1.144	0.076		0.0765									_		
PO4	0.017	1,600	P2O5	0.41	0.720	0.048		0.0481		Total Sodium Moles Calculated			2.75	mole	3				
SO4	0.172	16,500	SO3	4.70	8.282	0.554		0.5536		Expected Glass yield			1586	g	_				
NO2	1.345	61,900	NO2	21.13						Sum of Additives (g)			1712	g	_		_		
NO3	0.854	52,950	NO3	18.08						Sugar as added reductant (decreased for TOC)			29.6				_		
OH	0.647	1.10E+04	OH	3.76										_			-		
CO3	0.000		CO3	0.00						Volume of AZ-101 Sample @4.3 M Na:			639	ml			1		
oxalate	0.011	1,000	С	0.34						Weight used			726.1	g			1		
formate	0.000		С	0.00						density			1.137		н				
SUM			SUM	100.00	100.000	6.684	100.00	100.00	93.32	Sodium Molarity			4.31						
NO2+NO3	2.199	3 M/I	VSI uses	12 moles Car	bon (1 mol	le sucrose/34	2.3a) per 1	6 Moles NOx in	order to mitic	ate toaming.									

# Appendix E

TCLP Results for AZ-101 Envelope B Glass

## **Appendix E: TCLP Results for AZ-101 Envelope B Glass**

Test Plan Number:	TP-RPP-WTP-177 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 (ICPAES)
	RPG-CMC-201 Rev. 0 (Mercury)
	329-OP-SC01 Rev. 0 (ICP/MS)
Leach Date:	01/14/2004-01/15/2004
Spreadsheet Author/Da	te: B.M. Oliver/2-10-04
Spreadsheet Reviewers	/Date: M.W. Urie/2-11-04, K.N Pool/3-23-04

## E.1 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 ILAW glass sample submitted under Analytical Service Request (ASR) 6889. The TCLP, using TCLP Extraction Fluid #1, was performed in the RPL Sample Receiving and Preparation Laboratory (SRPL). The TCLP batch included a Sample and Duplicate for each glass and a TCLP extraction blank. Following the TCLP extraction processing, a Laboratory Control Sample and Matrix Spikes for each glass were prepared from aliquots of the leachates prior to 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 ICPAES and ICP-MS.

All TCLP analysis results (Table 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). Conversion of solution mass to volume was done using nominal solution densities.

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

### **E.2** Sample Analysis Results

			Dunlicato		
			Duplicate		
		Sample Result	Result	MDL(1)	EQL(2)
CAS #	Constituent	(mg/L)(1)	(mg/L)(1)	(mg/L)	(mg/L)
7440-36-0	Antimony	0.028 U	0.028 U	0.028	1.15
7440-38-2	Arsenic	0.045 U	0.045 U	0.045	5.0
7440-39-3	Barium	0.24 J	0.24 J	0.002	21
7440-41-7	Beryllium	0.0002 U	0.0002 U	0.0002	1.22
7440-42-8	Boron	0.428	0.421	0.012	0.05
7440-43-9	Cadmium	0.006 U	0.006 U	0.006	0.11
18540-29-9	Chromium	0.008 J	0.007 J	0.004	0.6
7439-92-1	Lead	0.035 U	0.035 U	0.035	0.75
7439-97-6	Mercury	0.000049 J	0.00012 J	0.000045	0.025
7440-02-0	Nickel	0.014 U	0.014 U	0.014	11
7782-49-2	Selenium	0.042 U	0.042 U	0.042	1.0
7440-22-4	Silver	0.005 U	0.005 U	0.005	0.14
7440-28-0	Thallium	0.00011J	0.00010J	0.000013(3)	0.20
7440-62-2	Vanadium	0.003 U	0.003 U	0.003	1.6
7440-66-6	Zinc	0.79 J	0.79 J	0.005	4.3

#### **Table E.1. TCLP Sample Results**

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.

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

(2) As no specific EQL's 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.

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

#### **E.2.1 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). ICPAES results for Ag and Sb are from the nitric acid digests; the results for As, B, Ba, Be, Cd, Cr, Ni, Pb, Se, V, and Zn are from the combined nitric and hydrochloric acid digests. ICP-MS analysis was performed for thallium only.

### E.2.2 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.

### E.3 Quality Control Criteria

### E.3.1 Preparation Blank (PB) and Laboratory Control Sample (LCS) Results

			LCS Succ	LCS Success Criteria: 75%-125%				
ļ	PB success Ci	riteria: <eql< td=""><td colspan="5">Kecovery</td></eql<>	Kecovery					
ļ	Success		1					
	Criteria	Prep Blank	Expected	LCS/BS				
	(EQL)	Results	Spike Cone	Results	Recovery <sup>(a)</sup>			
Analyte	mg/L	mg/L	mg/L	mg/L	(%)			
Antimony	1.15	0.028 U	2.21	2.26	102			
Arsenic	5.0	0.045 U	3.10	3.09 J	100			
Barium	21	0.20 J	2.21	2.38 J	98			
Beryllium	1.22	0.0002 U	1.11	1.08 J	97			
Boron	0.05	0.049 J	8.86	8.90	100			
Cadmium	0.11	0.020 J	1.11	1.08	96			
Chromium	0.6	0.005 J	2.21	2.27	102			
Lead	0.75	0.035 U	1.33	1.38	104			
Mercury	0.025	0.000045 U	0.00260	0.00208	80 <sup>(b)</sup>			
Nickel	11	0.019 J	4.43	4.57 J	103			
Selenium	1.0	0.042 U	1.77	1.78	100			
Silver	0.14	0.005 U	0.664	0.649	98			
Thallium	0.20	0.00027J	3.10	3.38	109			
Vanadium	1.6	0.003 U	2.21	2.07	93			
Zinc	4.3	0.27 J	4.43	4.80	102			
(a) LCS/BS rein the prep	ecoveries have bee paration blank.	en corrected for co	ntribution of analy	yte concentration				
(b) No acceptance criteria provided for mercury analysis.								

Table E.2.	Preparation	Blank (PB	b) and Laboratory	y Control Sam	ple (LCS	) Results
------------	-------------	-----------	-------------------	---------------	----------	-----------

### E.3.2 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 both process blanks was within the acceptance criteria of  $\leq$ EQL or  $\leq$  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 both process blanks was within the acceptance criteria of  $\langle EQL \text{ or } \leq 5\%$  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  $\leq$ EQL or  $\leq$  5% of the concentration in the samples.

### E.3.3 Laboratory Control Sample (i.e., Blank Spike):

Two blank spikes were prepared (one for each digestion option) by addition of 0.2 mL of multielement spike solution INT-QC-TCLP-A (containing all analytes of interest except B, Cu, Sb, Tl, 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.

#### ICPAES (Metals, except Hg and Tl)

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

#### Mercury Analysis

Although the blank spike mercury recovery was on the low side, the recovery value 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.

### E.4 Matrix Spike (MS) Results

	Expected Spike Conc.	Sample Results	Matrix Spike	Recovery
Analyte	(mg/L)	(mg/L)	(mg/L)	(%) <sup>(a)</sup>
Antimony	1.11	0.028 U	1.13 J	102
Arsenic	1.55	0.045 U	1.56 J	101
Barium	1.11	0.24 J	1.32 J	97
Beryllium	0.553	0.0002 U	0.53 J	96
Boron	4.43	0.428	4.82	99
Cadmium	0.549	0.006 U	0.531	96
Chromium	1.10	0.01 J	1.14	102
Lead	0.664	0.035 U	0.68 J	103
Mercury	0.00131	0.000049 J	0.000819	62 <sup>(b)</sup>
Nickel	2.21	0.014 U	2.28 J	103
Selenium	0.885	0.042 U	0.91 J	103
Silver	0.332	0.005 U	0.320	96
Thallium	1.549	0.00011J	1.41	91
Vanadium	1.11	0.003 U	1.03 J	93
Zinc	2.21	0.79 J	3.03 J	101

Table E.3. Matrix Spike (MS) Results

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.

#### ICPAES (Metals, except Hg and Tl)

Recovery values were within the success criterion for all analytes measured by ICPAES.

#### Mercury Analysis

The test plan defined no success criterion for mercury. However, the matrix spike recovery was outside the success criterion defined by the QA Plan, and post spike were prepared and analyzed. Results of the matrix spike, as well as the lower than normal recovery of the LCS (spike prior to acidification), appear to indicate a matrix related problem or loss of mercury prior to or during acidification.

#### ICP-MS (Tl only)

The recovery value for thallium was within the success criteria.

### E.5 Post Spike Results

Post Spike Success Criteria: 75%-125%									
Expected Spike Conc	Sample	Post Spike	Recovery						
(mg/L)	(mg/L)	(mg/L)	(%) <sup>(a)</sup>						
1.25	0.028 U	1.31	105						
1.25	0.045 U	1.27 J	101						
0.25	0.25 J	0.38 J	103						
0.05	0.0002 U	0.05 J	98						
1.00	0.431	1.27	105						
0.25	0.006 U	0.246	99						
0.50	0.01 J	0.53 J	105						
0.00200	0.0000029 J	0.00209	105 <sup>(b)</sup>						
1.25	0.035 U	1.31	105						
0.50	0.014 U	0.53 J	106						
1.25	0.042 U	1.29	103						
0.25	0.005 U	0.241	96						
(c)	(c)	(c)	(c)						
0.50	0.003 U	0.48 J	95						
0.75	0.80 J	1.22 J	109						
<ul> <li>(a) PS recoveries have been corrected for contribution of analyte concentration in the preparation blank.</li> <li>(b) No acceptance criteria provided for mercury analysis.</li> </ul>									
	Expected Spike Conc (mg/L) 1.25 1.25 0.25 0.05 1.00 0.25 0.50 0.00200 1.25 0.50 0.50 0.50 0.50 0.50 0.50 0.50 0	Expected Spike Conc         Sample (mg/L)           1.25         0.028 U           1.25         0.045 U           0.25         0.25 J           0.05         0.0002 U           1.00         0.431           0.25         0.01 J           0.25         0.006 U           0.50         0.0000029 J           1.25         0.035 U           0.50         0.014 U           1.25         0.042 U           0.50         0.014 U           1.25         0.005 U           0.50         0.014 U           1.25         0.005 U           0.50         0.014 U           1.25         0.005 U           0.50         0.003 U           0.75         0.80 J           thave been corrected for contribution of in the preparation blank.           e criteria provided for mercury analysis           e analyses were performed on the AP-10	Expected Spike ConcSample (mg/L)Post Spike (mg/L) $1.25$ $0.028 U$ $1.31$ $1.25$ $0.028 U$ $1.31$ $1.25$ $0.045 U$ $1.27 J$ $0.25$ $0.25 J$ $0.38 J$ $0.05$ $0.0002 U$ $0.05 J$ $1.00$ $0.431$ $1.27$ $0.25$ $0.006 U$ $0.246$ $0.50$ $0.01 J$ $0.53 J$ $0.00200$ $0.0000029 J$ $0.00209$ $1.25$ $0.035 U$ $1.31$ $0.50$ $0.014 U$ $0.53 J$ $1.25$ $0.005 U$ $0.241$ (c)(c)(c) $0.50$ $0.003 U$ $0.48 J$ $0.75$ $0.80 J$ $1.22 J$ shave been corrected for contribution of analyte in the preparation blank.e criteria provided for mercury analysis.e analyses were performed on the AP-101 TCLP						

#### **Table E.4. Post Spike Results**

c) The post spike analyses were performed on the AP-101 TCLP extract sample run with the AZ-101 glass in this batch. The post

spike recovery was within acceptance limit at 76%.

## E.6 Post Spike Results Narrative:

#### ICPAES (Metals, except Hg and Tl)

A post spike (containing all ICPAES 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  $\geq 25\%$  of that in the sample. The recovery values were within the success criterion for all analytes of interest.

#### Mercury Analysis

A post spike was prepared and analyzed for the AZ-101 LAW glass sample. The post spike recoveries were well within the success criterion.

#### ICP-MS (Tl only)

A post spike was prepared and analyzed for the AP-101 TCLP extract sample run with the AZ-101 glass in this batch. The post spike recovery was within the success criteria.

## E.7 Serial Dilution Results (ICPAES Only):

For both sample digestions (nitric/HCl 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.

## **E.8 Modifications to Procedures**

No modifications were made to the test plan.

H4-02

H4-02

# Distribution

No. of Copies

### OFFSITE

No. of Copies

### ONSITE

C. A. Musick

D. B. Blumenkranz

1 <u>Savannah River National Laboratory</u> Richard Edwards Westinghouse SA Aiken SC 29808-0001

11	Battelle - Pacific Northwest Divisi	on
	R. J. Bates	K5-12
	P. R. Bredt	P7-25
	J. V. Crum	K6-24
	P. R. Hrma	K6-24
	D. E. Kurath	P7-28
	M. J. Schweiger	K6-24
	H. D. Smith	K6-24
	Project File (2)	P7-28
	Information Release (2)	K1-09
5	Dechtel National Inc	
3	Bechter National, Inc.	
	J. F. Doyle (2)	H4-02
	D. E. Larson	H4-02