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WTP-RPT-092 Rev. 0

Vitrification and Product Testing of AP-101 Pretreated LAW Envelope A Glass

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June 2004

Prepared for Bechtel National Inc.
by Battelle—Pacific Northwest Division (PNWD)
under Contract 24590-101-TSA-W000-00004

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6/17/04
for W. L. Tamosaitis

ACCEPTED FOR
PROJECT USE

Test Specification: 24590-LAW-TSP-RT-01-011, Rev. 1
Test Plan: TP-RPP-WTP-121 Rev 0
R&T Focus Area: Waste Form Qualification
Test Scoping Statement(s): B-11
Test Exceptions: 24590-WTP-TEF-RT-03-025

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COMPLETENESS OF TESTING

This report describes the results of work and testing specified by Test Specification 24590-LAW-TSP-RT-01-011, Rev. 1, Test Plan TP-RPP-WTP-121, Rev 0, and Test Exception 24590-WTP-TEF-RT-03-025. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

Gordon H. Beeman, Manager
WTP R&T Support Project

6-11-04
Date

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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
CMC	Chemical Management Center
CoPC	Constituents of Potential Concern
CUA	Catholic University of America
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
IDF	Hanford Integrated Disposal Facility
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
ORP	Office of River Protection
PCT	Product Consistency Test
PNWD	Battelle—Pacific Northwest Division
PS	particle size
PSD	particle-size distribution
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
RT	room temperature
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

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Summary of Testing

This document describes work performed under Battelle—Pacific Northwest Division (PNWD) Test Plan TP-RPP-WTP-121 Rev 0, "Vitrification of AP-101 LAW Pretreated Waste (Envelope A) Sample and Product Testing," by G. L. Smith (2002), which is based on Test Specification, 24590-LAW-TSP-RT-01-011, Rev 1, *AP-101 (Envelope A) LAW Vitrification, Product Testing, and Regulatory Analyses*. 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 Hanford Waste Treatment and Immobilization Plant (WTP) (U.S. Department of Energy, Office of River Protection [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) chemical-composition 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) (see Table S.1). These work elements will help demonstrate the River Protection Project-Waste Treatment and Immobilization 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. Summary of Test Objectives and Results

Test Objective	Objective Met	Discussion
1. Glass Fabrication	Yes	~295 grams of glass fabricated
2. Chemical Composition Analyses	Yes	ICP-AES[(a)] – statistically refined
3. Radiochemical Composition Analyses	Yes	A combination of Radiochemistry and ICP-MS[(b)]
4. Waste loading	Yes	>14 Wt % of glass consists of waste Na_2O
5. Determination of Crystalline and Noncrystalline Phases	Yes	A combination of XRD[(c)], optical microscopy, and SEM[(d)] indicated no crystalline phase present.
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) 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.

Test Exceptions

Test Exception 24590-WTP-TEF-RT-03-025 is summarized in Table S.2.

Table S.2. Test Exceptions

Test Exceptions	Description
1. 24590-WTP-TEF-RT-03-025	1) Reporting of boron shall be included in the analysis of the TCLP extract. The EQL for boron shall be 0.05 mg/L 2) 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. 3) Delete the requirement to perform cyanide analyses from the test specification and test plan. 4) Replace method RPG-CMC-134 in section 3.0 with method RPG-CMC-138 or equivalent method. The exception was implemented through ICN-TP-RPP-WTP-121.1.

Results and Performance against Success Criteria

The primary objective for vitrifying the LAW sample was to generate a glass product and conduct product testing. Testing sought to demonstrate the RPP-WTP project's ability to satisfy the product requirements concerning (See Table S.3.):

Table S.3. Success Criteria

<table>
<tr><th>Success Criteria</th><th>How the Criteria were Met</th></tr>
<tr><td>1. Chemical constituents present in the glass at concentrations greater than 0.5 wt% are identified and quantified.</td><td>Met. The AP-101 LAW glass contains 11 constituent oxides with concentration >0.5 mass%. These oxides are (with best analytical estimates in mass%): SiO_2 (44.72), Na_2O (18.62), B_2O_3 (9.93), Fe_2O_3 (5.73), Al_2O_3 (5.56), ZnO (2.92), K_2O (2.83), ZrO_2 (2.73), TiO_2 (2.18), CaO (2.00), and MgO (1.59).</td></tr>
<tr><td>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.</td><td>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 6.3 and allows the values reported to be indexed to any date desired.</td></tr>
<tr><td>3. The concentrations of ^{137}Cs, ^{90}Sr, ^{99}Tc, and transuranic (TRU) radionuclides in the ILAW product are less than 0.3 Ci/m^3, 20 Ci/m^3, 0.1 Ci/m^3, and 100 nCi/g, respectively.</td><td>Met. The AP-101 LAW glass contains ^{90}Sr, ^{99}Tc, ^{137}Cs, and TRU at levels considerably below the contract limits as shown in the table.
<table>
<tr><td>^{90}Sr (Ci/m^3)</td><td>1.93E-1</td></tr>
<tr><td>^{99}Tc (Ci/m^3)</td><td>1.06E-3</td></tr>
<tr><td>^{137}Cs (Ci/m^3)</td><td>6.7E-4</td></tr>
<tr><td>TRU (nCi/g)</td><td>6.48E-1</td></tr>
</table></td></tr>
<tr><td>4. The mass fraction of Na_2O from LAW for Envelope A in the LAW glass is >14 wt%.</td><td>Met. The measured Na_2O mass fraction in the AP-101 LAW glass is 18.62 mass%. Essentially all the sodium comes from the LAW.</td></tr>
<tr><td>5. Crystalline and non-crystalline phases are identified and quantified.</td><td>Met. The AP-101 LAW glass subjected to CCC contained no crystalline phases.</td></tr>
<tr><td>6. The normalized mass loss of sodium, silicon, and boron is <2.0 g/m^2 measured with a 7-day Product Consistency Test (PCT) at 90°C as defined in C1285-97 (ASTM 1997).</td><td>Met. The measured normalized PCT releases from the AP-101 LAW glass are 0.65 g/m^2 for B, 0.21 g/m^2 for Si, and 0.65 g/m^2 for Na. These values are well below the limit of 2.0 g/m^2.</td></tr>
<tr><td>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 test was used to demonstrate that the release of hazardous inorganics met the UTS for the Land Disposal Restrictions), or the TCLP response of the LDR components meet the UTS limits.</td><td>Met. The TCLP leachate from the AP-101 LAW glass had inorganic hazardous constituent concentrations below the UTS limits of the LDR regulations for Washington state and RCRA.</td></tr>
</table>

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 tests reported in Sections 5.2.1, 5.2.2, and 6.3 and all analytical data collection were conducted in the summer of 2002 in accordance with PNWD's *Conducting Analytical Work in Support of Regulatory Programs*. The tests reported in Sections 5.2.4 and 6.7 and all analytical data collections were performed in the fall of 2003 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 PNWD's procedures for this work is given in Test Plan TP-RPP-WTP-121, Rev 0, Table 2. It includes justification for those requirements not implemented.

Conduct of Experimental and Analytical Work

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

As specified in Test Specification, 24590-LAW-TSP-RT-01-011, Rev 1, *AP-101 (Envelope A) 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.

Internal Data Verification and Validation

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

R&T Test Conditions

Table S.4 lists the required R&T test requirements and briefly summarizes the successful outcome of these tests.

Table S.4. R&T Test Conditions

R&T 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 380°C, calcined at 628°C to 721°C and melted at 1150°C.
2. Chemical 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. After a thorough search for noncrystalline phases via optical microscopy and SEM it was concluded that the AP-101 glass contained no noncrystalline phases.
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 AP-101 LAW glass are 0.65 g/m^2 for B, 0.21 g/m^2 for Si, and 0.65 g/m^2 for Na. These values are well below the limit of 2.0 g/m^2. 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^2.
6. Performed the Toxic Characteristic Leaching Procedure on glass samples.	Yes. The TCLP leachate from the AP-101 LAW glass had inorganic hazardous constituent concentrations below the UTS limits of the LDR regulations for Washington state and RCRA.

Test Methodology

A pretreated tank supernatant, low-activity waste originating from Hanford Tank 241-AP-101 (AP-101) along with a process simulant (indicated as the Process Blank, Russell 2002) were prepared as melter feeds for vitrification. The analyzed composition of the pretreated AP-101 waste was used by Catholic University of America's (CUA's) Vitreous State Laboratory (VSL) to formulate the target glass composition (LAWA126). Product testing of the immobilized LAW (ILAW) form, as prescribed by the RPP-WTP project, was performed by PNWD.

The supernatant tank samples from AP-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, and the resulting decontaminated supernatant was converted to LAW glass. The AP-101 supernatant sample was processed through the following unit operations to simulate the RPP-WTP project flowsheet: 1) dilution of the batch, 2) removal of ^{137}Cs by ion exchange, and 3) removal of ^{99}Tc by ion exchange.

Project-approved glass-former additives (kyanite (Al_2SiO_5), orthoboric acid, (H_3BO_3), wollastonite ($CaSiO_3$), red iron oxide pigment (Fe_2O_3), olivine (Mg_2SiO_4), silica sand (SiO_2), rutile ore (TiO_2), zinc oxide (ZnO), and zircon sand ($ZrSiO_4$) were added to the pretreated LAW to produce a melter feed. The AP-101 melter feed was dried (100°C), calcined (to 721°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, mixed, added back into the crucible, and melted for an additional hour at 1150°C. The melt had an estimated viscosity of about 5 Pa·s based on visual observation coupled with past experience (e.g., bubbles present in the meniscus burst while being poured).

Vitrification of slurry melter feed in an actual melter progresses continuously through three distinct stages: drying, calcining, and melting. All of these stages of liquid-fed ceramic melter (LFCM) batch processing have been individually reproduced in the crucible studies. What was not truly represented, however, was the complex stages and nature of the cold-cap chemistry that occurs in the LFCM. For nonvolatile, inorganic batch constituent, the differences between crucible and melter vitrification conditions are inconsequential. For all other batch components, cold-cap chemistry can influence both partitioning behavior and chemical byproduct yields.

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 melt/glass. Because the composition of the glass is not significantly affected by the differences in processes, no impact is expected on the properties due to composition. 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 selected testing, and these results are presented in this report.

Test Results

The measured chemical composition of AP-101 glass is close to its target composition (that of LAW-A126). Per the RPP-WTP project LAW glass Test Plan TP-RPP-WTP-121, Rev 0, "Vitrification of AP-101 LAW Pretreated Waste (Envelope A) Sample and Product Testing," the concentration of the waste sodium oxide shall be greater than 14 mass%. The target concentration of sodium oxide for the AP-101 glass is 18.46 mass%. The measured sodium oxide content for the AP-101 glass is 18.62 mass%. As all of the sodium oxide content for the AP-101 glass originated from the initial tank waste, the AP-101 glass easily exceeds the task and ORP contract specification sodium oxide concentration level of 14 mass%.

The waste loading was calculated from the dilution factor (decrease in concentration) of elements contained in either the waste or the glass-forming additives. The results indicate that the waste mass fraction glass is near its target, i.e., 24.7% for AP-101 (23.8% based on waste dilution and 24.8% based on additive dilution).

In Table S.5, the percent difference in the analyzed values for AP-101 is compared with the targeted values. The observed differences for some of the major oxides are -1.8% for alumina, +0.8% for boron oxide, 0.0% for calcium oxide, +3.1% for iron oxide, -25.9% for potassium oxide, +6.7% for magnesium oxide, +0.9% for soda, +1.0% for silica, +8.5% for titania, -1.7% for zinc oxide, and -9.3% for zirconia.

Table S.5. Comparison of the Target Glass Composition with the Best Analytical Estimate for the Glass

	AP-101 Target mass%	Final Estimate mass%
Ag_2O	0.00	0.02
Al_2O_3	5.66	5.56
B_2O_3	9.85	9.93
BaO	0.00	0.01
CaO	2.00	2.00
CdO	0.00	0.00
Cr_2O_3	0.03	0.05
Fe_2O_3	5.56	5.73
K_2O	3.82	2.83
Li_2O	0.00	0.02
MgO	1.49	1.59
MnO	0.01	0.01
MoO_3	0.00	0.02
Na_2O	18.46	18.62
NiO	0.01	0.00
P_2O_5	0.09	0.12
PbO	0.00	0.03
SiO_2	44.27	44.72
SnO_2	0.01	0.16
SrO	0.00	0.00
TiO_2	2.01	2.18
V_2O_5	0.01	0.02
ZnO	2.97	2.92
ZrO_2	3.01	2.73
SO_3	0.31	0.31
F	0.27	0.27
Cl	0.17	0.17
Sum	100	100

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 Test Plan TP-RPP-WTP-121, Rev 0, "Vitrification of AP-101 LAW Pretreated Waste (Envelope A) Sample and Product Testing," and 49 CFR 172.101, the radionuclides of interest in the AP-101 glass were determined and analytically measured specific to the task specification. The activity of ^{90}Sr, ^{99}Tc, ^{137}Cs, and transuranic (TRU) radionuclides is less than 20 Ci/m^3, 0.1 Ci/m^3, 0.3 Ci/m^3, 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 was performed on glass subjected to a slow cool-down that simulates the cooling profile for glass at the centerline of a LAW container. Using XRD, optical microscopy, and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), the AP-101 glass was found to be completely amorphous. The SEM EDS composition analysis agreed with both the inductively coupled plasma (ICP) analysis and the target composition of the AP-101 glass.

The release of sodium, silicon, and boron from crushed AP-101 glass into water was measured with a 7-day PCT at 90°C as defined in ASTM C1285-97 (ASTM 1997). The normalized mass loss is required to be less than 2.0 g/m^2. The measured normalized PCT releases of the AP-101 LAW glass (measured in triplicate) were 0.65 g/m^2 for B, 0.65 g/m^2 for Na, and 0.21 g/m^2 for Si, meeting the contract specification with a wide margin.

Dangerous waste limitations testing (the Toxicity Characteristic Leaching Procedure or TCLP test) was completed on 10 g of quenched ILAW glass. As shown in Table S.6, AP-101 passes this test and qualifies for land disposal. Note that ICP-AES analysis was not sufficient for quantification of thallium below the Universal Treatment Standards (UTS) limit; therefore, the TCLP leachate was analyzed by ICP-MS, and thallium was quantified below the UTS limit.

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

CAS#	Constituent	Symbol	Required for LDR	UTS[a] mg/L-TCLP	ICP-AES mg/L-TCLP (ave. of two)	MDL[c] mg/L
7440-36-0	Antimony	Sb	X	1.15	0.028 U	0.028
7440-38-2	Arsenic	As	VIT	5.0	0.045 U	0.045
7440-39-3	Barium	Ba	VIT	21	0.32 J	0.0019
7440-41-7	Beryllium	Be	X	1.22	0.0002 U	0.0002
7440-42-8	Boron	B	n/a	n/a	1.3	0.012
7440-43-9	Cadmium	Cd	VIT	0.11	0.009 J	0.0056
18540-29-9	Chromium	Cr	VIT	0.6 total	0.015 J	0.0035
7439-92-1	Lead	Pb	VIT	0.75	0.035 U	0.034
7439-97-6	Mercury[b]	Hg	VIT	0.025	0.000092 J	0.000045
7440-02-0	Nickel	Ni	X	11	0.015 J	0.014
7782-49-2	Selenium	Se	VIT	5.7	0.042 U	0.042
7440-22-4	Silver	Ag	VIT	0.14	0.005 U	0.004
7440-28-0	Thallium[b]	Tl	X	0.20	0.00016J	0.000013
7440-62-2	Vanadium	V	n/a	1.6	0.003 U	0.003
7440-66-6	Zinc	Zn	n/a	4.3	1.3 J	0.005

(a) UTS = Universal Treatment Standard, 40 CFR 268.48.
(b) Average of sample and duplicate; Hg was measured with CVAA; Tl was measured with ICP-MS.
(c) MDLs were determined with dilute acidified water (2% HNO_3) per ASO-QAP-001 and adjusted by the average sample processing factor (~1.01).
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.
U = Undetected. Analyte was analyzed but not detected (e.g., no measurable instrument response), or response was less than the MDL.
J = Estimated value. Value is below EQL and above MDL.

Simulant Use

The physical, chemical, and rheological properties for actual and simulated AP-101 waste, melter feed, and glass are compared. See Section 6.8. The actual and simulated wastes have similar pH values, and the actual and simulated melter feed have similar bulk densities. Regarding the rheological properties, two values, one for the yield stress and one for the consistency, are in good agreement.

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 Hanford Waste Treatment and Immobilization 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 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) waste form from the AP-101 Envelope A 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 241-AP-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 AP-101 supernatant sample was processed through the following unit operations to simulate the RPP-WTP project flowsheet: 1) dilution of the batch, 2) removal of ^{137}Cs by ion exchange (Fiskum 2002), and 3) removal of ^{99}Tc by ion exchange.

The primary objective for vitrifying the Tank AP-101 (Envelope A) pretreated waste sample was to characterize the glass produced from the crucible melt (Sidibe 2001). 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 seven work elements: 1) glass fabrication, 2) chemical composition analyses, 3) radiochemical composition analyses, 4)waste sodium loading, 5) identification of crystalline and noncrystalline phases, 6) waste-form leachability (PCT), and 7) Toxicity Characteristic Leaching Procedure (TCLP [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 Vitreous State Laboratory (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 and noncrystalline 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 tests reported in Sections 5.2.1, 5.2.2 and 6.3 and all analytical data collection were conducted in the summer of 2002 accordance with PNWD's *Conducting Analytical Work in Support of Regulatory Programs*. The tests reported in Sections 5.2.4 and 6.7 and all analytical data collections were performed in the fall of 2003 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 PNWD's procedures for this work is given in test plan TP-RPP-WTP-121, Rev 0, Table 2 (Smith 2002). 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-01-011, Rev 1, *AP-101 (Envelope A) 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 TP-RPP-WTP-121 Rev 0 (Quality Control Parameters for ILAW Analysis).

The ICP-AES analysis of the AP-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 QC issues with the analysis using the KOH, KNO_3 – Ni crucible Na_2O_2-NaOH fusion were low recoveries for lithium with two of the laboratory control standards and titanium with one of the laboratory control standards. The low result for titanium is believed to be a manifestation of the difficulty in getting titanium into a solution. Lithium was not expected in the ILAW samples at measurable levels. For the Na_2O_2-NaOH - Zr crucible fusion a QC issue arose for Ca, which consisted of a low recovery for a LCS and a high RPD (%) for a sample. A high variability for Ca is expected because it is a common contaminant in the highest quality available sample preparation chemicals.

TCLP Results and QA data for AP-101 Envelope A 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)* with samples of LAW. See 24590-WTP-TEF-03-025, Rev. 0, *AP-101 (Envelope A) LAW Vitrification, Product Testing, and Regulatory Analyses* and TP-RPP-WTP-121, Rev 0, *AP-101 (Envelope A) 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 LAW sample (see Brackenbury 2001) was to generate a glass product for subsequent testing to demonstrate the WTP project's ability to satisfy the product requirements concerning (Sidibe 2001) (Smith 2002):

- chemical and radionuclide reporting
- waste loading
- identification and quantification of crystalline and non-crystalline phases
- waste-form leachability
- dangerous waste limitations.

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 (*WTP Contract- DE-AC27-01RV1413 Modification No. M033*). All work was performed to the test plan (Smith 2002), which was based on the test specification (Sidibe 2001) and approved by BNI. These criteria are:

- Chemical constituents present at concentrations greater than 0.5 mass% will be identified and quantified. [2.2.2.6.1 Chemical Composition Qualification clause *Section C* from *WTP Contract- DE-AC27-01RV1413 Modification No. M033]*
- The identification and quantification of radionuclides identified as significant per NUREG/BR-0204 (NRC 1998) and 40CFR 172.101 Table 2 in Appendix A (current and indexed to December 31, 2002). [2.2.2.7 Radiological Composition Documentation clause *Section C* from *WTP Contract- DE-AC27-01RV1413 Modification No. M033]*
- The concentrations of ^{137}Cs, ^{90}Sr, ^{99}Tc and transuranic (TRU) radionuclides in the ILAW product shall be less than 0.3 Ci/m^3, 20 Ci/m^3, 0.1 Ci/m^3, and 100 nCi/g, respectively. [2.2.2.8 Radionuclide Concentration Limitations clause *Section C* from *WTP Contract- DE-AC27-01RV1413 Modification No. M033]* Note Waste Treatment and Immobilization Plant Unit Operation – iii - Cs Removal: This operation removes ^{137}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, ^{137}Cs will be further removed, to achieve a 0.3 Ci/m^3 in the ILAW product, to facilitate the maintenance concept established for the ILAW melter system. Hence our target is actually 0.3 Ci/m^3 in the ILAW product.
- The concentration of waste sodium oxide for Envelope A in the ILAW glass shall be greater than 14 wt%. [2.2.2.2 Waste Loading: The loading of waste sodium from Envelope A in the ILAW glass shall be greater than 14 weight percent based on Na_2O. The loading of waste sodium from Envelope B in the ILAW glass shall be greater than 3.0 weight percent based on Na_2O. The loading of waste sodium from Envelope C in the ILAW glass shall be greater than 10 weight percent based on Na_2O. 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_2O.]
- The identification and quantification of crystalline and non-crystalline phases. [2.2.2.6.3 Crystalline Phase Identification: 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.]
- The normalized mass loss of sodium, silicon and boron, shall be less than 2.0 $grams/m^2$ measured using a seven-day PCT run at 90°C as defined in ASTM C1285-97 (ASTM 1997). [2.2.2.17.2 Product Consistency Test: 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.]
- Generation of data for the evaluation of the glass form against Land Disposal Restrictions (LDR) of Washington Dangerous Waste Regulations, WAC 173-303 (WAC 2000), and RCRA LDR in 40 CFR268 (TCLP test was used to demonstrate that the release of hazardous inorganics met the UTS for the Land Disposal Restrictions).[2.2.2.20 Dangerous Waste Limitations: The ILAW

product shall be acceptable for land disposal under the State of Washington Dangerous Waste Regulations, WAC 173-303, and RCRA LDR in 40 CFR 268.]

5.0 Experimental Method

5.1 Glass Fabrication

A pretreated tank supernatant LAW (AP-101) (Fiskum et al. 2000) was prepared as a melter feed for vitrification. The analyzed composition of the pretreated AP-101 wastes was used by Catholic University of America (CUA) VSL to formulate the target glass composition (LAWA126). The recipe was forwarded to PNWD for preparation of the waste glass (See Appendix D).

5.1.1 Pretreated AP-101 Waste

The pretreated AP-101 waste (Figure 5.1) was blended with glass-forming additives. Before preparing 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, and if weight changes were noted, i.e., due to evaporation, appropriate adjustments to the melter feed recipe were made. The composition and properties of the pretreated AP-101 waste are given in Table 5.1 through Table 5.3.

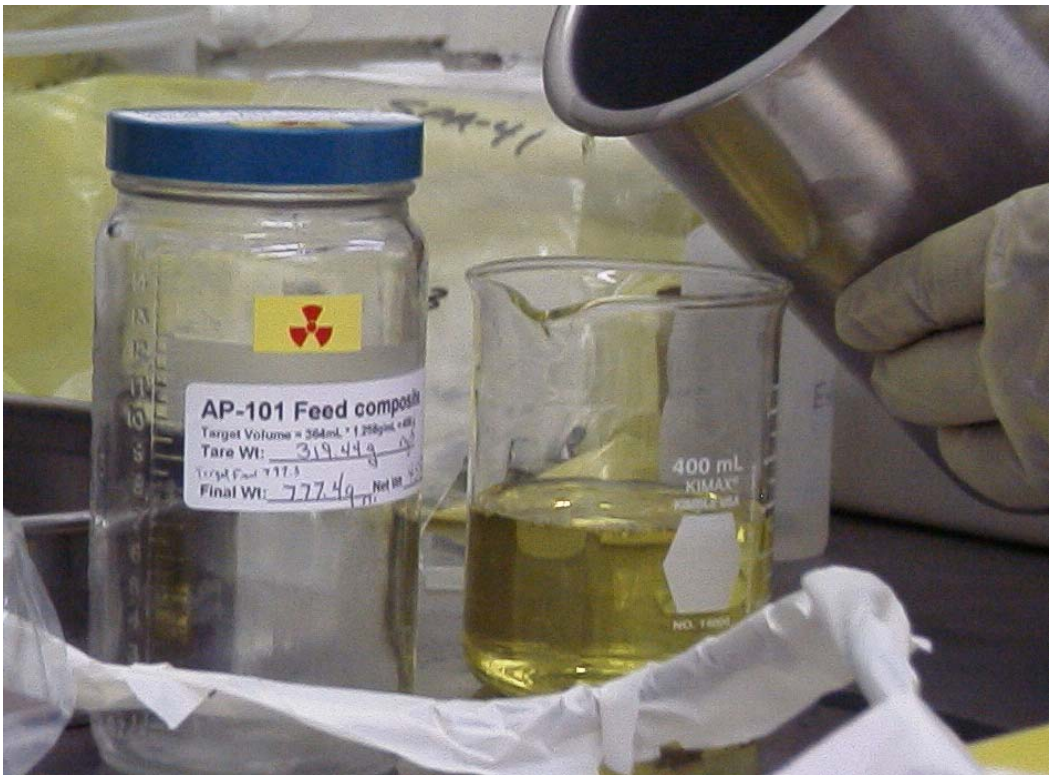

Figure 5.1. AP-101 Pretreated Waste before Adding Glass Former Chemicals (shown in a 400-mL glass beaker; waste solution was originally stored in the 0.5-L container on the left)

Table 5.1. Chemical Composition of AP-101 Pretreated Waste

Analyte	mole/L
$Na^{+(a)}$	4.85
K^{+}	0.661
Cs^{+}	~0
$AlO_2^{-(b)}$	0.234
$BO_2^{-(b)}$	0.0078
Cl^{-}	0.039
F^{-}	0.118
$CO_3^{-2(c)}$	0.438
$CrO_4^{-2(b)}$	0.0025
NO_2^{-}	0.739
NO_3^{-}	1.551
OH^{-}	1.94
$PO_4^{-3(b)}$	0.0093
SO_4^{-2}	0.031
$C_2O_4^{-2}$	0.011

(a) Based on the average of duplicate samples diluted 127.5 and 127 times.
(b) Al, B, Cr, and P determined by ICP-AES. Anionic form is assumed on the basis of waste chemistry.
(c) CO_3^{-2} determined from TIC.

Table 5.2. Radionuclide Activity of AP-101 Pretreated Waste in µCi/mL (unless noted otherwise)

Isotope	µCi/mL	Reference Date	Isotope	µCi/mL	Reference Date
^{3}H	3.19E-3	9/21/01	^{137}Cs	8.0E-5	9/18/01
^{14}C	4.71E-4	3/08/02	^{144}Ce	<6.0E-5	9/18/01
^{51}Cr	<7.0E-5	9/18/01	^{151}Sm	7.79E-4	11/02/01
$^{54}Mn^{(a)}$	---		^{152}Eu	<2.0E-5	9/18/01
^{59}Fe	<2.0E-5	9/18/01	^{154}Eu	5.22E-5	9/18/01
^{60}Co	2.05E-3	9/18/01	^{155}Eu	2.57E-5	9/18/01
^{63}Ni	2.07E-3	2/12/02	^{232}Th	<2.0E-5	9/18/01
^{79}Se	9.0E-6	9/12/01	^{236}Pu	<4.0E-8	9/27/01
^{88}Y	<1.0E-5	9/18/01	$^{237}Np^{(a)}$	---	
^{90}Sr	5.38E-2	10/01/01	^{238}Pu	2.4E-6	9/27/01
^{95}Nb	<8.0E-6	9/18/01	^{239}Pu	1.74E-5	9/27/01
^{99}Tc	3.42E-4	9/26/01	$^{239}Pu + ^{240}Pu^{(a)}$	---	
^{103}Ru	<8.0E-6	9/18/01	^{241}Pu	1.14E-4	10/05/01
$^{106}RuRh$	6.0E-4	9/18/01	^{241}Am	1.01E-4	9/26/01
^{113}Sn	<1.0E-5	9/18/01	^{242}Cm	7.8E-8	9/27/01
^{125}Sb	1.26E-3	9/18/01	$^{243}Cm + ^{244}Cm$	8.3E-7	9/27/01
$^{126}SnSb$	2.2E-4	9/18/01	Total Alpha	7.51E-5	9/18/01
^{134}Cs	<9.0E-6	9/18/01	Total $U^{(b)}$	1.09	---

(a) Nondetect – interference
(b) in µg/mL

Table 5.3. Solution Properties of AP-101 Pretreated Waste (Bredt et al. 2003)

Solution Density,	g/mL	1.258
Fraction of Solids[(a)]	Mass %	30.9
Fraction of Oxides[(b)]	Mass %	17.0
(a) Dried to constant weight at 105°C. (b) Fired to constant weight at 1050°C.		

5.1.2 RPP-WTP Mineral Additives

Table 5.4 lists the project-approved glass-former minerals (Hansen and Schumacher 2003) for the target glass composition. The project-approved glass-former minerals that were received from each vendor (see Table 5.4) are believed to be typical of those that would be received and used by the vitrification plant at Hanford.

5.1.3 Batch Recipe

The batch composition used to batch the AP-101 glass LAWA126 was formulated by VSL (see the table in Appendix D) (Muller and Pegg 2003). The VSL batch is based on the analysis of Fiskum et al. (2000) and incorporates 10 moles of waste sodium. It is projected to make 1678.1 g of glass. For this work the waste was reanalyzed and found to be essentially the same as the previous analysis, but it had been diluted with some rinse water which reduced the sodium concentration from 5.62 molar to 4.85 molar (see Table 5.1). The batching amounts were adjusted on the basis of the new waste analysis to give the original VSL LAWA126 composition as close as possible.

One exception was made to the batch given in Appendix D, no sugar was added. Sugar is added to cause the nitrate fraction of the pretreated waste to break down into more N_2 and N_2O and less NO_x, which is the principle product when it undergoes just thermal decomposition. The sugar–nitrate reaction goes at about 260°C, is exothermic, and produces considerable airborne particulate depending on the amount of nitrate and sugar present when it occurs in a dried melter feed batch. Hence, the decision was made to add no sugar to the melter feed for the crucible melt.

The batch amounts given in Table 5.5 were calculated by PNWD batching to the VSL formulation using a linear algebra approach as follows. The component mass balance requires that

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

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_j = 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 5.6. The m_j values determined for M_G = 296.91 g are in Table 5.5 and the bottom row of Table 5.6.

Table 5.4. Mineral and Chemical Additives

Oxide	Mineral	Grade	Company	Telephone No.
Al_2O_3	Kyanite Al_2O_3-SiO_2	Raw -325	Kyanite Mining Corp Dillwyn, VA, 23936 www.kyanite.com	804-983-2043 Carrol Kay VP
	Alumina Al_2O_3	A-2 <325M	Alcoa Alumina Bauxite, AK 72011 www.alunina.alcoa.com	800-874-0481
B_2O_3	Boric Acid H_3BO_3	Technical Grade-Granular	U.S. Borax Valencia, CA, 91355-1847 www.borax.com	805-287-5400
	10M Borax $Na_2B_4O_7$-$10H_2O$	Technical 10Mole Borax	U.S. Borax Valencia, CA, 91355-1847 www.borax.com	805-287-5400
Na_2O	Na_2CO_3 Anhydrous	Dense Soda Ash	Solvay Minerals Houston, TX www.solvayminerals.com	713-525-6800 Fax-713-525-7805
CaO	Wollastonite $CaSiO_3$	NYADM325 NWest Mexico	NYCO Wilsboro, NY www.nycominerals.com	518-963-4262
Fe_2O_3	Hematite Fe_2O_3	Fe_2O_3 5001	Prince Mfg. Co. Quincey, IL 62306 www.princemfg.com	217-222-8854
Li_2O	Li_2CO_3	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_2	SiO_2	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_2	Rutile (Air floated) TiO_2/Fe_2O_3	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_2	$ZrSiO_4$	Zircon Flour	Amer. Miner. Inc. Monaca, PA 19406 www.americanminerals.net	610-652-3301
C	Sugar	Granular Portland OR	Amalgamated Sugar Co. Ogden, UT www.gfhandle/industry	503-282-5573

Table 5.5. Mineral Additives Added to 457.9 g of Pretreated LAW AP-101 Waste[(a)]

	Additives	Mass (g) - m_j
Al_2O_3	Kyanite (Al_2SiO_5) 325 Mesh	20.99
B_2O_3	H_3BO_3 (Technical - Granular)	51.58
CaO	Wollastonite NYAD 325 Mesh	12.45
Fe_2O_3	Fe_2O_3 (-325 Mesh)	16.01
MgO	Olivine (Mg_2SiO_4) 325 Mesh	9.12
SiO_2	SiO_2 (Sil-co-Sil 75)	108.06
TiO_2	TiO_2 (Rutile - Airfloated)	6.19
ZnO	ZnO (K-920)	8.82
ZrO_2	Zircon $ZrSiO_4$ (Flour) 325 Mesh	13.34
	Total	246.55

(a) See 5.7; 457.9 g of pretreated AP-101 waste and 246.55 g of mineral additives make 296.9 g of glass.

The batch composition was determined using the analyzed composition of AP-101 LAW (Table 5.1 and Table 5.2) with the waste loading of 0.247 g (oxides + halogens) from the waste per g of glass.

Table 5.7 lists the compositions of the AP-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_2 in the glass is 131.45 g ($= g_{SiO2} \times M_G$) = 73.33 g × 0.004 + 20.99 g × 0.4067 + 12.45 g × 0.51 + ----- + 108.06 g × 0.997 + ---- + 13.34 g × 0.3225 and so forth for each oxide in the glass.

Table 5.6. Composition of Glass Forming Minerals and Pretreated AP-101 (A) 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} relates 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 values in the table are for 364 mL or 457.9 g of waste, which will make up 296.91 g (M_G) of ILAW glass.

Oxide	Waste Oxide	Kyanite	Boric Acid	Wollanstonite	Hemetite	Olivine	Silica	Rutile	Zincite	Zircon	LAWA126
	x_{ij}										$g_i \times M_G$
Al_2O_3	0.0591	0.5703	0.0000	0.0020	0.0150	0.0019	0.0014	0.0050	0.0000	0.0025	16.80
B_2O_3	0.0013	0.0000	0.5652	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	29.25
CaO	0.0001	0.0003	0.0000	0.4750	0.0004	0.0002	0.0001	0.0000	0.0000	0.0000	5.94
Cl	0.0069	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.51
Cr_2O_3	0.0010	0.0000	0.0000	0.0000	0.0000	0.0013	0.0000	0.0016	0.0000	0.0000	0.09
F	0.0111	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.81
Fe_2O_3	0.0000	0.0078	0.0000	0.0040	0.9700	0.0768	0.0002	0.0070	0.0000	0.0008	16.51
K_2O	0.1546	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	11.33
MgO	0.0000	0.0001	0.0000	0.0010	0.0010	0.4801	0.0001	0.0000	0.0000	0.0000	4.42
MnO	0.0000	0.0000	0.0000	0.0010	0.0012	0.0000	0.0000	0.0000	0.0000	0.0000	0.03
MoO_3	0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.01
Na_2O	0.7461	0.0042	0.0000	0.0000	0.0000	0.0003	0.0002	0.0000	0.0000	0.0000	54.82
NiO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0037	0.0000	0.0000	0.0000	0.0000	0.04
P_2O_5	0.0029	0.0000	0.0000	0.0000	0.0027	0.0000	0.0000	0.0000	0.0000	0.0000	0.25
PbO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.00
SiO_2	0.0040	0.4067	0.0000	0.5100	0.0135	0.4252	0.9970	0.0220	0.0000	0.3225	131.45
SnO_2	0.0004	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.03
SO_3	0.0123	0.0000	0.0000	0.0000	0.0007	0.0000	0.0000	0.0000	0.0000	0.0000	0.91
TiO_2	0.0000	0.0079	0.0000	0.0002	0.0000	0.0000	0.0001	0.9320	0.0000	0.0010	5.96
ZnO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.9990	0.0000	8.82
ZrO_2	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0190	0.0000	0.6600	8.93
m_j (g)	73.33	20.99	51.58	12.45	16.01	9.12	108.06	6.19	8.82	13.34	SUM($g_i \times M_G$)= 296.91g

Table 5.7. Mass Fractions of Glass Components in AP-101 Pretreated LAW Waste, Glass Former Chemicals, and AP-101 Glass

	w_i – AP-101 LAW	a_i - GFC	g_i – AP-101 Glass
Al_2O_3	0.0591	0.0557	0.0566
B_2O_3	0.0013	0.1304	0.0985
CaO	0.0001	0.0266	0.0200
Cl	0.0069	0.0000	0.0017
Cr_2O_3	0.0010	0.0001	0.0003
F	0.0111	0.0000	0.0027
Fe_2O_3	0.0000	0.0738	0.0556
K_2O	0.1546	0.0000	0.0382
MgO	0.0000	0.0198	0.0149
MnO	0.0000	0.0001	0.0001
MoO_3	0.0001	0.0000	0.0000
Na_2O	0.7461	0.0005	0.1846
NiO	0.0000	0.0002	0.0001
P_2O_5	0.0029	0.0002	0.0009
PbO	0.0000	0.0000	0.0000
SeO_2	0.0000	0.0000	0.0000
SiO_2	0.0040	0.5865	0.4427
SnO_2	0.0004	0.0000	0.0001
SO_3	0.0123	0.0001	0.0031
TiO_2	0.0000	0.0266	0.0201
UO_2	0.0000	0.0000	0.0000
V_2O_5	0.0000	0.0001	0.0001
ZnO	0.0000	0.0394	0.0297
ZrO_2	0.0000	0.0399	0.0301
Total	1.0000	1.0000	1.0000

5.1.4 Melter Feed Preparation

The mineral additives were weighed (to the nearest 0.01 g), combined as dry powders, and mixed in an agate milling chamber for several minutes. The exact amount of the mineral batch needed to combine with the waste (Table 5.5) was then weighed out from the blended minerals.

The additives were combined and processed for each melter feed as follows. Each mineral component was weighed on a balance capable of accurately measuring to 0.01 g; the combined mineral additives for each melter feed were mixed for several minutes in an agate-milling chamber; the exact amount of the mineral batch needed to combine with the waste was then weighed from the blended minerals and mixed with the pretreated LAW to prepare the melter feed.

The waste and mineral additives were combined by pouring the liquid LAW pretreated waste into a 2-L glass beaker containing a magnetic stir bar. The pretreated waste was heated and stirred on a hot plate to evaporate water. While heating and stirring, the mineral additives were slowly added into the vortex of the slurry. Mixing was vigorous so that solids from the mineral additives could not settle. The

heating/stirring process took 3 to 5 hours to thicken the batch to the point at which the stir bar would no longer rotate. Hand blending was used until the batch was dry; this took an additional 2 to 3 hours to complete. The batch was dried further in an oven by slowly increasing the temperature from approximately 100° to 400°C over a 48- to 72-hour period.

5.1.5 Glass Melting

The dry cake that was produced was observed to be hard and brittle. The blended and dried batch was then added to a 500-cc Pt-10% Rh crucible with a Pt/Rh lid, placed into a furnace, and calcined. The calcination process began at a furnace setting of 600°C, increased by 25°C intervals to 675°C, where it was held for more than 2 hours. The temperature was monitored with a calibrated Type K thermocouple and thermocouple readout. A thermocouple reading (not the controlling thermocouple) over this range of furnace controller settings was 628°C to 721°C. Then the batch was removed and the furnace temperature increased to 1150°C. When the furnace temperature reached 1150°C, the 500-cc crucible was placed in the furnace, and the batch was melted for approximately 1 hour with a tight-fitting lid.

The glass melt was then poured onto a stainless steel plate. The subsequent glass was crushed to a fine powder (<100 μm) and mixed to ensure homogeneity using a 100-mL tungsten carbide disc mill. The crushed glass was placed back into the Pt-Rh crucible, covered with a lid to minimize the loss of volatile and semi-volatile components, and remelted at 1150ºC for approximately 1 hour. During the final molten glass pour, the glass was quenched on the stainless steel plate, cooled to room temperature, and handled in such a way as to avoid organic contamination.

5.1.6 Container-Centerline Cooling

The container centerline cooling (CCC) schedule given in Table 5.8 was provided by BNI in the form of a letter.[(a)] The CCC data in the referenced letter is based on actual LAW Container cooling test data. The measured CCC time-temperature history is approximated by a series of seven linear time-temperature segments duplicated with a programmable furnace.

The amount of 27.68 g quenched glass was placed into a 25 mm-on-a-side cubic Pt-10%Rh crucible with a tight fitting lid. The crucible was then placed into a furnace and isothermally heat treated for 1 hour at 1150°C. Then the CCC heat treatment schedule (Table 5.8) was started and temperature was logged once a minute. Figure 5.2 shows good agreement between the targeted temperature and measured temperature during the CCC heat treatment. Following the heat treatment, the sample was removed from the crucible and used for the PCT and evaluation of crystallinity by optical microscopy, scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS), and X-ray diffraction (XRD).

(a) L. Petkus to C. Musick. October 16, 2003. "LAW Container Centerline Cooling Data." CCN 074181, Contract No. DE-AC27-01RV14136.

Table 5.8. CCC Schedule for Crucible Testing

Segment	Start Time min	Interval min	Start 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
End	3710		400	

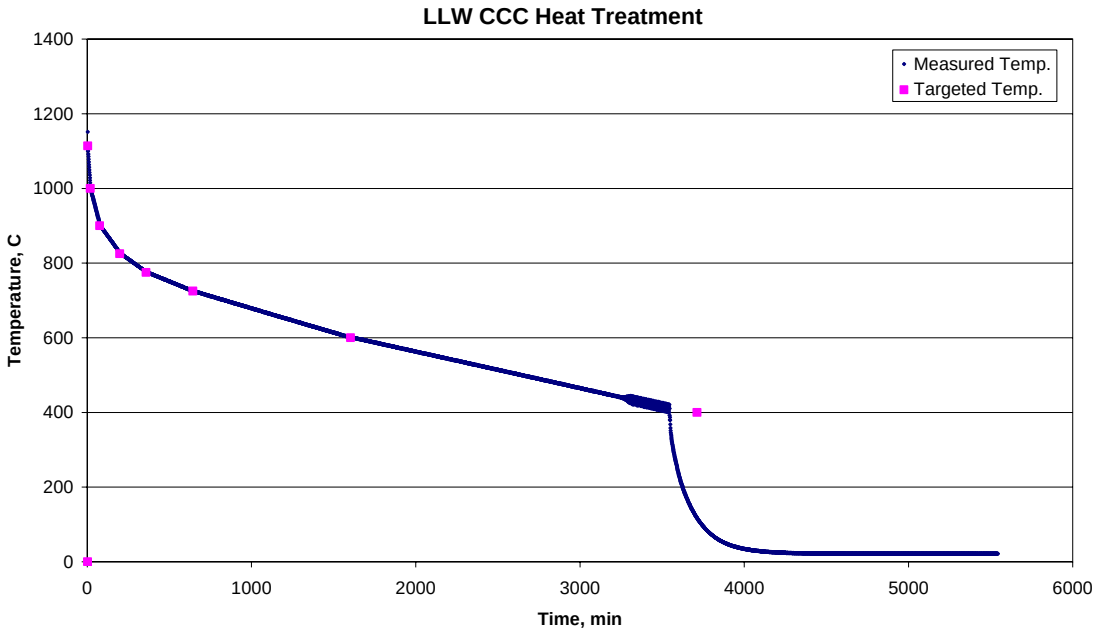

Figure 5.2. CCC Heat Treatment for AP-101 Envelope A Glass

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 AP-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

The chemical composition of the ILAW glass (i.e., elements excluding oxygen and present in concentrations greater than 0.5% by weight) was measured in duplicate along with low-activity test reference material (LRM) and analytical reference glass-1 (ARG-1) powdered glass reference standards (Ebert and Wolf 1999; Smith 1993) using a Na_2O_2-NaOH fusion, according to procedure PNL-ALO-114, and a potassium hydroxide (KOH) fusion, according to procedure PNL-ALO-115. The KOH fusion uses a nickel crucible, and the Na_2O_2 -NaOH fusion uses a zirconium crucible. ARG-1 and LRM are compositionally well-characterized glasses and provide an excellent independent check of the analytical processes and results. Table 5.9 provides a summary of the preparation and analysis methods performed.

Cation analysis was performed using inductively coupled plasma-atomic emission spectrometry (ICP-AES). All sample material after processing appeared to go into solution (no apparent residue remained in fusion crucibles or as precipitate in final solution). Analytical dilutions of 5-, 10-, and 50-fold were prepared for each fusion preparation and analyzed by ICP-AES. Both fusion procedures were modified slightly by including additional hydrochloric acid to assist solubilization of silver by complex formation, if silver is present. Before ICP-AES analysis, a small amount (0.1 mL) of hydrofluoric acid was added to the prepared samples. Portions of the samples prepared with Na_2O_2-NaOH fusion were submitted for radiochemical analysis and inductively coupled plasma-mass spectrometry (ICP-MS) analysis (see Section Radiochemical Composition). No hydrofluoric acid was added to the aliquots submitted for radiochemistry or ICP-MS analysis.

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 by inductively coupled argon plasma mass spectrometry per 329-OP-SC01.

Corrections to the waste glass analysis were applied using a procedure developed by Weier and Piepel (2002). See Section 6.2.1. Note that elements such as sulfur and chlorine were estimated for the glass based on their presence in the waste.

5.2.2 Radiochemical Composition

Radiochemical analyses were performed on the AP-101 ILAW glass product. Analyses included ^{99}Tc, ^{129}I, ^{237}Np, ^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{241}Pu / ^{241}Am, and ^{242}Pu by ICP-MS; ^{63}Ni, ^{79}Se, ^{90}Sr, ^{151}Sm, and ^{241}Pu by separation and beta counting; ^{236}Pu, ^{238}Pu, $^{239/240}Pu$, ^{241}Am, ^{243}Am, ^{242}Cm, ^{242}Pu, and $^{243/244}Cm$ by separation and alpha energy analysis (AEA); and ^{60}Co, ^{95}Nb, ^{113}Sn, ^{125}Sb, $^{126}Sn/Sb$, ^{134}Cs, ^{137}Cs, ^{144}Ce, ^{152}Eu, ^{154}Eu, ^{155}Eu, and ^{232}Th by extended counting time gamma energy analysis (GEA). Concentration values or less-than values of other gamma emitters, e.g., ^{51}Cr, ^{59}Fe, ^{88}Y, ^{95}Zr, ^{103}Ru, and ^{106}Ru, were obtained by GEA depending on concentrations and detection limits.

Samples of the powdered waste glass were solubilized in the laboratory using a Na_2O_2-NaOH fusion in a Zr crucible according to procedure PNL-ALO-114. About 0.1 g of material was fused and then dissolved in nitric acid and brought to a volume of 100 mL. This fused material preparation was sampled directly for gamma energy analysis (GEA). Ten-mL aliquots of fused material preparation were directly gamma counted for 14 hours on high-efficiency Ge detectors according to procedure PNL-ALO-450.

Table 5.9. Summary of Analytical Preparative and Analysis Methods

Analysis	Preparative Method	Analysis Method
Density	Direct	PNL-ALO-501
Mass% Total Solids/ (TDS)[a]	Direct	PNL-ALO-501
ICP-AES[b] (metals)	PNL-ALO-128	RPG-CMC-211 Rev. 0
ICP-MS[c] (except iodine)	PNL-ALO-128	329-OP-SC01 Rev. 0
ICP-MS (iodine)	Direct	329-OP-SC01 Rev. 0
KPA[d] (uranium)	PNL-ALO-128	RPG-CMC-4014
IC[e]-Inorg (inorganic anions)	Direct	PNL-ALO-212
IC-F[f] (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[i]	PNL-ALO-287	PNL-ALO-289
Hg	RPG-CMC-131	RPG-CMC-201 Rev. 0
OH[j]	Direct	PNL-ALO-228
ISE[k] (ammonia)	Direct	RPG-CMC-226
GEA[l]	PNL-ALO-128	PNL-ALO-450
Total α	PNL-ALO-128	RPG-CMC-4001, RPG-CMC-408
Total β	PNL-ALO-128	RPG-CMC-4001, RPG-CMC-408
^{90}Sr	PNL-ALO-128, PNL-ALO-476	RPG-CMC-408, PNL-ALO-450
$^{99}Tc^{+7}$	PNL-ALO-432[m]	RPG-CMC-474
^{3}H	PNL-ALO-418	RPG-CMC-474
^{14}C	PNL-ALO-482	RPG-CMC-474
^{79}Se	PNL-ALO-128, PNL-ALO-440	RPG-CMC-474
Pu, Am, Cm	PNL-ALO-128, PNL-ALO-417, PNL-ALO-496	RPG-CMC-422
Toxic Characteristic Leaching Procedure (TCLP)	RPG-CMC-110 Rev. 1 RPG-CMC-139 Rev. 0 RPG-CMC-101 Rev. 0	RPG-CMC-211 Rev. 0 RPG-CMC-201 Rev. 0

(a) TDS = total dissolved solids
(b) ICP-AES = inductively coupled plasma-atomic emission spectroscopy
(c) ICP-MS = inductively coupled plasma-mass spectroscopy
(d) KPA = kinetic phosphorescence analysis
(e) IC = ion chromatography
(f) F = fluorine
(g) TOC = total organic carbon
(h) TIC = total inorganic carbon
(i) CN = cyanide
(j) OH = hydroxide
(k) ISE = ion specific electrode
(l) GEA = gamma energy analysis
(m) Without sodium dichromate added.

A 10-mL aliquot was evaporated to dryness to remove Cl^-, then brought back to volume with 2 molar HNO_3 and filtered through a 0.45-micron filter. This matrix-adjusted material was used for Pu, Am, Cm,

and Sr analyses. Where appropriate, relatively large sample sizes were taken for analysis to obtain lower detection limits.

The Pu and Am/Cm separations were performed on a 4-mL Na_2O_2-NaOH 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 ^{242}Pu. The curium is known to follow the americium, and both these isotopes were traced with ^{243}Am.

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

Samples of the AP-101 glass were analyzed for ^{99}Tc, ^{237}Np, ^{239}Pu, and ^{240}Pu according to 329-OP-SC01 Rev. 0 using an ICP-MS set up to handle radioactive materials. Dilutions of isotope product standards for ^{237}Np and ^{239}Pu and an Amersham ^{99}Tc standard were used to generate calibration curves. The 1% high-purity nitric acid solution used to dilute the standards and samples was used as a reagent blank.

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× to 70×) and a transmitting light Olympus PMG-3 microscope (magnification at 100× to 250×).

XRD was performed with a model SCINTAG PAD V X-ray diffractometer using Cu K∀ radiation (1.54056) having a scan 2θ increment of 0.05°, a dwell time of 40 to 52 s, and a 2θ range of 5 to 75°. The glass was powdered 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 X-ray beam height, encapsulated in Mylar film, transported to XRD facility, and analyzed.

A SEM (model VG elemental shielded PQ2) with EDS capabilities was used to look for phase and chemical inhomogeneities. A thin section of the LAW glass sample, approximately 1-cm^2 in area and 4-mm-thick, was polished and mounted on aluminum SEM specimen holders for microscopy. 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, such as 500×, 1000×, 3000×, 10,000×, and 20,000×.

5.2.4 TCLP

A TCLP test was performed, and leachates were analyzed for antimony, arsenic, barium, beryllium, boron, cadmium, chromium, lead, mercury, nickel, selenium, silver, thallium, vanadium, and zinc. The testing was conducted per EPA's SW-846, Method 1311 using PNL-ALO-110 (EPA 1992). TCLP testing was conducted using the quenched AP-101 ILAW glass product. Particle-size reduction was

required so that the glass particles were capable of passing through a 9.5-mm (0.375-in.) standard sieve. The reduced glass sample was placed into an extractor vessel with an extraction fluid equal to 20 times the weight of the glass sample. The sample was rotated head over heel at 30 rpm for 18 hours at room temperature. The liquid was separated from the solid phase by filtration and the leachate analyzed for the analytes (with corresponding concentration limits) listed in Table 5.10.

Table 5.10. TCLP Inorganic Constituents of Potential Concern (CoPC)

CAS#	Constituent	Symbol	UTS[(a)] 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	B	n/a
7440-43-9	Cadmium	Cd	0.11
18540-29-9	Chromium (VI)	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	5.7
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 = Universal Treatment Standard, 40 CFR 268.			

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). It was used for AP-101 and LRM glasses. The glass was ground in an automated alumina mortar and pestle (grinding chamber) 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 was weighed and placed into a 22-mL desensitized Type 304L stainless steel container (see Figure 5.3). The volume of water for each sample was measured by mass and added to the requisite stainless steel container. 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 90ºC 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^{-1}. This estimate is based on the assumption that spherical particles with Gaussian size distribution range from 74 μm to 149 μm 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 low-activity test reference material (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 AP-101 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 90ºC for 7 days for each PCT conducted with each glass sample.

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

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 MΩ·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_3, 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.

6.0 Results

The AP-101 glass melter feed was successfully processed and melted into an ILAW glass form. The glass was prepared for chemical and radiochemical composition determination. Approximately 217.7 g of usable, i.e., poured from crucible, quenched AP-101 glass was produced, and 77.5 g remained in the crucible, summing up to 295.2 g; this amount is close to that of 296.9 g based on batch calculation.

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 Batch Preparation and Vitrification

Before batch preparation, the density of AP-101 pretreated waste (4.85 M Na) was determinate to confirm that no significant change had occurred in the waste since the previous density determination. The measured waste density was 1.252 g/cm^3; this was only 0.006 g/cm^3 lower than the measurement made immediately after the pretreatment of the waste. Hence, the requirement that the difference be < 0.01 g/cm^3 was met. It was noted that a trace of precipitate was present.

The required amount of the waste, 457.9 g, was measured into a 2-L stainless steel beaker, stirred, and heated for 2.5 hours on a stirrer/hot plate to evaporate water. The waste solution bubbled after about 2 hours. The mineral additives [kyanite (Al_2SiO_5), orthoboric acid (H_3BO_3), wollastonite ($CaSiO_3$), red iron oxide pigment (Fe_2O_3), olivine (Mg_2SiO_4), silica sand (SiO_2), rutile (TiO_2), zinc oxide (ZnO), and zircon sand ($ZrSiO_4$)] were added after a little over 1 hour of additional heating and stirring. When the slurry became too thick for the magnetic stirrer to work, it was stirred by hand. The final well dried melter feed consisted of hard chunks.

The dried batch was transferred to the 500-cc Pt/10% Rh melting crucible and heated at 130°C overnight. The batch was removed from the drying oven when the temperature reached about 140°C and was placed in the melting furnace at 200°C. The temperature was raised to 280°C and then further raised to about 380°C over a period of about 1 hour. The well dried melter feed weighed 345.1 g at this stage. The dried batch was then calcined for about 2.5 hours, starting at 628°C. The temperature was gradually increased to a maximum of 721°C. At 685°C, the batch did not show any visible signs of offgassing. At 721°C, the batch was sintering and foaming. The sintered batch had a foamy texture that could easily be crushed with a half-inch alumina rod. The weight of the calcined melter feed was 321.3 g.

The AP-101 glass was melted at 1150°C. Initially, the batch fused into a melt with vigorous foaming and NO_x evolution. Once the batch had melted, a Pt/10% Rh lid was placed on the crucible. After 1 hour at 1150°C, the melt was poured onto a stainless steel plate. The melt viscosity was estimated as ~ 2-3 Pa·s (2000 to 3000 cP); the technician made the estimate of viscosity based on his previous experience. Cooled glass was crushed to a fine powder in a 100-cm^3 tungsten carbide grinding chamber, returned to the crucible with a Pt/10% Rh lid, and melted for 1 hour. A good glass was produced with the viscosity of the melt at about 8 Pa·s. This viscosity estimate is somewhat higher than that of the first melt because the pouring was delayed about 15 seconds while the platinum lid was removed. No fumes were observed

during the pour (Figure 6.1). The slab of glass on the stainless steel pour plate did not break from thermal shock. The total glass weight was 295.3 g.

Laboratory crucible melting and continuous slurry-fed cold-crown melting of the glass batch compare as follows: The vitrification of melter feed in a slurry-fed cold-crown melter progresses through three stages, 1) drying, 2) calcining, and 3) melting in one continuous operation. The aqueous slurry that is introduced into the high-temperature melter environment spreads out over an existing cold cap where it dries and becomes part of the melter cold-cap structure. This dried material moves down through the cold cap as it becomes submerged by incoming feed while the material at the molten-glass cold-cap interface is becoming melt. During this continuous progression through the cold cap, the feed temperature increases from the boiling point of water (~100°C) to the molten glass temperatures (~1150°C). During this continuous transition, inorganic salts form eutectics melt and react with or dissolve other, more refractory components; thus, ultimately, all nonvolatile components are incorporated into the molten-glass pool. These stages were achieved in the laboratory hood as three separate operations.

Figure 6.1. Freshly Poured AP-101Glass Quenched on the Stainless Steel Plate

6.2 LAW Glass AP-101 Chemical Composition

Table 6.1 provides analyzed chemical compositions in mass fractions. The reported concentrations were corrected according to the analytical process blank. Appendices A, B, and C summarize the analytical chemistry and the radiochemistry data for the AP-101 glass and pretreated waste. The results of the ARG-1 and the LRM glass analyses are found in Table A.1.

Table 6.1. Comparison of the Target AP-101 Glass Composition with the Best Analytical Estimate for the Glass in Mass Fractions

	Target	Final Estimate	Squared Error (Δ^2) $\times 10^5$	Estimate Uncertainty
Ag_2O		0.0002	0.0	0.0002
Al_2O_3	0.0566	0.0556	0.1	0.0009
B_2O_3	0.0985	0.0993	0.1	0.0014
BaO		0.0001	0.0	0.0000
CaO	0.0200	0.0200	0.0	0.0033
Cr_2O_3	0.0003	0.0005	0.0	0.0000
Fe_2O_3	0.0556	0.0573	0.3	0.0016
K_2O	0.0382	0.0283	9.8	0.0013
Li_2O		0.0002	0.0	0.0000
MgO	0.0149	0.0159	0.1	0.0024
MnO	0.0001	0.0001	0.0	0.0000
MoO_3		0.0002	0.0	0.0000
Na_2O	0.1846	0.1862	0.3	0.0006
NiO	0.0001	0.0000	0.0	0.0000
P_2O_5	0.0009	0.0012	0.0	0.0002
PbO		0.0003	0.0	0.0002
SiO_2	0.4427	0.4472	2.0	0.0038
SnO_2	0.0001	0.0016	0.2	0.0015
TiO_2	0.0201	0.0218	0.3	0.0013
V_2O_5	0.0001	0.0002	0.0	0.0002
ZnO	0.0297	0.0292	0.0	0.0016
ZrO_2	0.0301	0.0273	0.8	0.0015
SO_3	0.0031	0.0031	0.0	0.0000
F	0.0027	0.0027	0.0	0.0000
Cl	0.0017	0.0017	0.0	0.0000
Sum	1.0001	1.0000	14.1	0.0220
Δ = Target – Estimate = Error				

Standard glasses are used to screen out matrix effects when doing analyses with the ICP-AES technique where a large number of elements are analyzed simultaneously. Under these conditions, the instrument cannot be optimized for each element. 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. The following 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.

6.2.1 Data Adjustment and Normalization for AP-101 Glass Analyses

Quality control objectives were met for all analytes whose concentration was equal to or greater than 0.5 mass% as required. Concentrations of analytes in the ARG-1 laboratory control standard (LCS) that were present at levels greater than the estimated quantification limits (EQL) were within ± 10% of the values listed for the "Consensus Composition Determined by Round Robin 6" (Smith 1993, Table 3.1). Except for zinc, all other analytes detected in the LCS were recovered within the acceptance limits of 75 to 125%. The summation of measured mass% oxides in the LCS was about 98%. The total accountability of mass in the glass by ICP-AES is 92 to 96 mass% for Envelope A (AP-101), including SO_3 and the halides Br, Cl, and F, which are included as their target values.

One reason for the approximately 4 to 8 mass% discrepancy in total mass% oxides is because certain elements (such as trace metal oxides) were not included in the analyses. Another reason can be the lack of complete recovery of SiO_2, Na_2O, and ZrO_2 during the preparation of the sample for analysis. However, when omitted or discrepant components are appropriately adjusted based on analytical QC results, the sum of mass fractions of glass components is generally close to 1. The final normalization step then adjusts the component fractions, relative to their estimated uncertainties, to attain the total of 1.

The following steps were performed to obtain a "best" estimate from AP-101 glass sample results.

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

This sequence of steps was developed by Weier and Piepel (2002) and applied to AP-101 glass with minor modifications. Initial data were obtained from laboratory report ASR-6551. The resulting "Final Estimate" is shown in Table 6.1. It outperforms previous estimates (the squared error of only 1.41×10^{-4}) and is proposed as the final and best estimate of the glass composition. Note that 0.98×10^{-4} of the 1.41×10^{-4} squared error is due to K_2O missing its target. This demonstrates that when there is a low analytical precision for an element, such as for K_2O, a good estimate is difficult to achieve for that component.

The uncertainties associated with this final estimate are given in Table 6.1. These are absolute uncertainties corresponding to one standard deviation. They take into consideration the originally estimated relative standard deviations (RSDs) (reduced for K_2O and ZrO_2), the appropriate modifications for bias-corrected values, and the impact of normalization. Uncertainty values listed as zero only appear so because of the limited number of digits displayed. These uncertainty values indicate how precise the estimates are. Ideally, the final estimates would fall within two to three standard deviations of their

targets. Note that among the constituents with >0.02 mass%, K_2O is the only one with the estimate farther than this from its target. This again shows the difficulty encountered in measuring K_2O.

6.2.2 Comparison with Target Objectives for the LAW Glass AP-101 Composition

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, Specification 2, Immobilized Low-Activity Waste, Section 2.2.2.2, Waste Loading) states, "The loading of waste sodium from Envelope A in the ILAW glass shall be greater than 14 weight percent based on Na_2O." The target and measured mass fractions of sodium oxide for AP-101glass is 0.1846 and 0.1862, respectively. Because all of the sodium oxide content of the AP-101 glass originated from the tank waste, the AP-101 glass easily exceeds the Task Specification requirement that the waste glass contain >14 mass% sodium oxide originating from the waste.

The theoretical mass fractions of the waste components in AP-101 is $W = 0.247$. This waste-loading fraction in the glass can be obtained from 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 was calculated by expressing W from Equation 3 as follows

$$W = \frac{g_i - a_i}{w_i - a_i} \tag{5}$$

Table 6.2 summarizes the value of the dilution factor for nine major components of the AP-101 glass; K_2O was not included because of its inaccurate analytical value as discussed above. The average of the dilution factors is 0.239, which is in good agreement with the theoretical values.

Table 6.2. Waste Loading/Dilution Factors for LAW Waste Glass AP-101

	w_i - *AP-101 LAW*	a_i - *GFC*	g_i - *AP-101 Glass*	W[(a)(b)]
B_2O_3	0.0013	0.1304	0.0993	0.241
CaO	0.0001	0.0266	0.0200	0.247
Fe_2O_3	0.0000	0.0738	0.0573	0.224
MgO	0.0000	0.0198	0.0159	0.195
Na_2O	0.7461	0.0005	0.1862	0.249
SiO_2	0.0040	0.5865	0.4472	0.239
TiO_2	0.0000	0.0266	0.0218	0.180
ZnO	0.0000	0.0394	0.0292	0.259
ZrO_2	0.0000	0.0399	0.0273	0.316
			Average	0.239

(a) Potassium fraction in glass was not included because is known to be in error.
(b) The waste dilution factor (W) was calculated from Equation 5; g_i, w_i, and a_i are the i-th component mass fractions in waste, additive mix, and glass.

Summarizing, the waste loading was calculated from the dilution factor (decrease in concentration) of elements contained in either the waste or the glass-forming additives. The results indicate that the waste fraction of the glass AP-101 is near its target of 0.247. The measured glass-to-target composition comparison of the oxides shows a small difference, and the calculated waste loading values are close to

the target. Both support the conclusion that the actual waste loading in the glass met or exceeded the target waste loading.

6.3 LAW Glass AP-101 Radiochemical Composition

Table 6.3 summarizes the radioisotope-analysis results for the quenched AP-101 glass (See Table A.2 for a more detailed summary). 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 ^{99}Tc and Uranium, which are based on ICP-MS data. The dates of analysis are also given there so the analytical values can be indexed to any date. Of the radioisotopes looked for, only ^{60}Co, ^{63}Ni, ^{90}Sr, ^{106}RuRh, ^{125}Sb, ^{126}SnSb, ^{137}Cs, ^{151}Sm, ^{154}Eu, ^{238}Pu, ^{239}Pu + ^{240}Pu, ^{241}Am (AEA), and ^{243}Cm + ^{244}Cm were quantifiable. The ^{237}Np concentration in the glass, $<4.5\times10^{-5}$ μCi/g, was generated from the ICP-MS number using the specific activity of ^{237}Np, which is 7.05×10^{-4} Ci/g.

Glass-powder samples were directly gamma counted via procedure PNL-ALO-450. The samples showed measurable activities of ^{60}Co, ^{106}RuRh, ^{125}Sb, ^{126}SnSb, and ^{137}Cs with one-sigma errors of 2, 9, 3, 3, and 4%, respectively. Other requested analytes, including ^{51}Cr, ^{59}Fe, ^{95}Nb, ^{103}Ru, ^{113}Sn, and ^{152}Eu, were not detected in any of the samples. The detection limits for the AP-101 samples in units of μCi/g glass are ^{51}Cr $<9\times10^{-5}$, ^{59}Fe $<3\times10^{-5}$, ^{88}Y $<2\times10^{-5}$, ^{95}Nb $<2\times10^{-5}$, ^{95}Zr $<2\times10^{-5}$, ^{103}Ru $<2\times10^{-5}$, ^{113}Sn $<2\times10^{-5}$, ^{134}Cs $<2\times10^{-5}$, ^{144}Ce $<7\times10^{-5}$, and ^{152}Eu $<3\times10^{-5}$.

Table 6.3. Radioisotope Activity in AP-101 Glass in µCi/g (including dates of analysis)

Isotope	Activity µCi/g	RPD[e] %	Date	Isotope	Activity µCi/g	RPD %	Date
^{51}Cr	<9.0E-5	---	07/08/02	^{151}Sm	9.0E-4	36	09/06/02
^{59}Fe	<3.0E-5	---	07/08/02	^{152}Eu	<3.0E-5	---	07/08/02
^{60}Co[c]	2.29E-3	---	07/08/02	^{154}Eu	6.42E-5	---	07/08/02
^{63}Ni	3.96E-3	39	09/23/02	^{155}Eu	<4.0E-5	---	07/08/02
^{79}Se	<4.8E-4	---	07/30/02	^{232}Th	<2.0E-5	---	07/08/02
^{88}Y	<2.0E-5	---	07/08/02	^{236}Pu	<3.0E-6	---	08/08/02
^{90}Sr	7.14E-2	26	08/12/02	^{237}Np[b]	<4.5E-5	---	11/06/02
^{95}Nb	<2.0E-5	---	07/08/02	^{238}Pu	3.7E-6	30	08/08/02
^{95}Zr	<2.0E-5	---	07/08/02	$^{239}Pu + ^{240}Pu$[a]	3.15E-5	61	08/08/02
^{99}Tc[b]	<1.85 µg/g	---	11/26/02	^{241}Pu	<4.0E-4	---	09/06/02
^{103}Ru	<2.0E-5	---	07/08/02	^{242}Pu	<4.0E-6	---	08/08/02
^{106}Ru[c]	3.46E-4	---	07/08/02	$^{241}Am^{C}$	1.54E-4	---	07/08/02
^{113}Sn	<2.0E-5	---	07/08/02	^{241}Am[d]	1.23E-4	2	08/08/02
^{125}Sb[c]	1.3E-3	---	07/08/02	^{242}Cm	<2.0E-6	---	08/08/02
$^{126}SnSb$[c]	2.82E-4	---	07/08/02	^{243}Am	<3.0E-6	---	08/08/02
^{134}Cs	<2.0E-5	---	07/08/02	$^{243}Cm + ^{244}Cm$	3.0E-6	---	08/08/02
^{137}Cs[c]	2.48E-4	---	07/08/02	Total Alpha	1.59E-4	---	08/08/02
^{144}Ce	<7.0E-5	---	07/08/02	Total U[b] (µg/g)	55.5	---	12/03/02

(a) ^{239}Pu, ^{240}Pu isotopes were not detected by ICP-MS because of extremely high dilution factors.
(b) ICP-MS
(c) GEA – duplicate values not reported
(d) AEA
(e) Relative percent deviation (RPD) is a measure of repeatability of a measured value that is equal to the difference of the two values divided by the average of the two values times 100.

For AP-101, only ^{238}Pu, $^{239+240}Pu$, and ^{241}Am were detected with procedures PNL-ALO-417, -496, and -422. Radiochemical yields for Am/Cm were in a good range. Yields for Pu were within the expected range of >80%. No Cm was detected. The detection limits are listed. The duplicate results are in agreement with the RPD value of 36% for ^{238}Pu for the sample, where the 1-sigma measurement uncertainties were 27 to 35%. Plutonium and americium were detected in the process blank.

The total uranium was initially determined on the pretreated waste by ICP-AES, but the detection limit was quite high at about 50 µg/mL, so this did not answer any questions about elevated uranium in the product glass. The total uranium was then determined on acidified pretreated waste via procedure PNL-ALO-4014, Rev.1, "Kinetic Phosphorescence Analysis (KPA)." By this method, uranium was detected at 1.09 µg/mL or 1.25 µg/g of glass. When an acid-dissolved Na_2O_2-NaOH fusion of the AP-101 glass was analyzed for uranium via procedure 329-OP-SCO1, Rev.1 (ICP-MS), an average value for uranium was reported to be about 55 µg/g while the expected value was only 1.25 µg/g. Analysis of the glass by KPA gave a value of 36 µg/g, which is viewed as supporting the ICP-MS number. The reason for this sizable discrepancy has not yet been completely determined. It is known that the zircon sand added as a glass forming chemical contains some natural uranium (~400 ppm), enough to account for about 18 µg/g, but the ^{238}U to ^{235}U ratio for that material should be 0.993/0.007 = 142. The observed ratio for the glass was observed to be about 250. These numbers are consistent with the glass being loaded with about a 50 µg/g mixture of natural (zircon) and depleted uranium. Previous melts containing depleted uranium have been made in this crucible, and the crucible had been cleaned physically only;

hence, uranium from a previous melt could have contaminated the AP-101 LAW glass. Mass spectrometry measurements on the waste and on the glass show that they do not have the same ^{235}U to ^{238}U ratio and neither do the measurements show the natural ratio of 142. The glass must contain depleted uranium in addition to that contributed by the zircon. This is consistent with the melting crucible being contaminated with a small amount of depleted uranium that ends up in the glass. Note that this level of contamination should not have any detectable influence on the glass physical or chemical properties.

The glass as fabricated appears to have also been contaminated with ^{137}Cs. The AP-101 LAW glass was measured in duplicate for ^{137}Cs, and then another sample was measured in duplicate. Both samples indicated a ^{137}Cs level about 2.7 times the expected level based on the measured amount in the pretreated waste. Note that an unexpectedly high value of ^{137}Cs was measured for AW-101 but not AN-107 Glass (Smith et al. 2000). The amount of additional C-137 indicated here is about 5.3E-10 grams (a particle about 5 microns in diameter) dissolved in ~300 g of glass. This level of contamination will occur occasionally in a facility that routinely handles cesium containing samples. It is only the high sensitivity of the measurement technique that allows such a contamination to be detected. Observe that the "contaminated" glass still meets the most stringent Cs-137 concentration requirement of < 0.3 Ci/m^3 (see Section 6.4). Hence this level of occasional contamination can be tolerated and does not appear to be a QA issue

6.4 Radiochemical Data Comparison with Requirements

Table 6.4 gives the analysis for AP-101 glass determined by radiochemistry or ICP-MS for radioisotopes that could be measured in the AP-101 waste solution given in Table 5.2. The expected loading (µCi/g glass) was calculated from the radiochemical analysis of the waste by taking those analytical values (Table 5.2) that are in µCi/mL, converting to µCi/g dried solids by dividing by the density (1.26 g/mL) and then by the weight fraction of dried solids (0.309), and converting that value to µCi/g waste oxides by dividing by the calcination factor (17.0/30.9 = 0.550 weight fraction of oxide in dried solids). The µCi/g waste oxides were then multiplied by the waste loading factor (0.247) to give µCi/g glass. All of these operations can be combined into one factor (1.153), which multiplies the original waste analytical value (Table 5.2) to give the expected radionuclide content of the glass.

The activity of ^{90}Sr is present in the glass at 7.14E-2 µCi/g of glass. Assuming conservatively that the density of the glass is 2.7 g/cc, there are 1.93E-1 Ci of ^{90}Sr in a cubic meter of glass. The requirement is that ^{90}Sr be present in a quantity that is less than 20 Ci/m^3. Hence, the concentration of ^{90}Sr in the AP-101 glass easily meets the requirement because it is about 100 times less concentrated.

No ^{99}Tc was observed in the AP-101 glass. However, a conservative maximum concentration can be calculated from the expected concentration if all of the ^{99}Tc present in the waste was contained in the AP-101 glass. If so, assuming that the density of the glass is 2.7g/cc, the glass contains 1.06E-3 Ci/m^3 of ^{99}Tc. The requirement is that the glass contains less than 1.0E-1 Ci/m^3 ^{99}Tc. Again, the requirement is met by a wide margin.

The activity of ^{137}Cs measured in the glass is 2.48E-4 µCi/g of glass. This reported measured value is 2.70 times the expected value. Using the same conservative density (2.7 g/cc), AP-101 glass contains 6.7E-4 Ci/m^3 of ^{137}Cs, which is obviously much less than the maximum requirement of 3 Ci/m^3. [2.2.2.8 Radionuclide Concentration Limitations clause *Section C* from *WTP Contract- DE-AC27-01RV1413 Modification No. M033]* However, note that Waste Treatment and Immobilization Plant Unit Operation

– iii - Cs Removal (also from *Section C* from *WTP Contract- DE-AC27-01RV1413 Modification No. M033*): This operation removes ^{137}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, ^{137}Cs will be further removed, to achieve a 0.3 Ci/m^3 in the ILAW product, to facilitate the maintenance concept established for the ILAW melter system. Hence our target is actually 0.3 Ci/m^3 in the ILAW product.

Table 6.4. Expected and Measured Radionuclide Content in µCi/g of AP-101 Glass

Isotope	Expected[(a)] µCi/g	Measured[(b)] µCi/g	Ratio[(c)]
		Radiochemical	
^{60}Co	2.36E-3	2.29E-3	0.97
^{63}Ni	2.39E-3	3.19E-3*	1.33
^{90}Sr	6.20E-2	6.22E-2*	1.00
$^{106}RuRh$	6.92E-4	3.46E-4	0.50
^{125}Sb	1.45E-3	1.3E-3	0.897
$^{126}SnSb$	2.54E-4	2.82E-4	1.11
^{137}Cs	9.2E-5	2.48E-4	2.70
^{151}Sm	8.98E-4	7.43E-4*	0.827
^{238}Pu	2.8E-6	3.16E-6*	1.13
^{239}Pu	2.00E-5	2.18E-5*	1.09
^{241}Am	1.16E-4	1.23E-4	1.06
Total U (µg/g)	1.26	55.5(d) 36(e)	28.50 – 43.30[(f)]
Total Alpha	8.7E-5	1.46E-4	1.68

(a) Calculated values based on the amounts in the pretreated AP-101.
(b) Measured for AP-101 ILAW. Values marked with an * are the lower of two duplicate values that had a large RPD, see Table 6.3. For the comparisons made in this table, it was recommended that the lower of the two analytical values be used (L. Greenwood—personal Communication).
(c) The measured value divided by the expected value.
(d) Measured by ICP-MS.
(e) Measured by KPA.
(f) The glass was shown to have considerably higher uranium content, believed to be due to natural uranium in the zircon batch material plus some depleted uranium.

It is also a requirement that the TRU concentration in the glass be less than 0.10 µCi/g (100 nCi/g). The sum total given in Table 6.5 is 6.48×10^{-4} µCi/g or 0.648 nCi/g. Hence, the requirement is met by a wide margin. To make a conservative estimate of the total activity of all of the TRU radioisotopes, those that are reported as "less than" were included in the estimate at their "less than" value. The 0.648 nCi/g total is expected to be greater than the actual total for the glass. Gross alpha is 5.9 nCi/g, which is well below the 0.1 µCi/g limit.

Table 6.5. Measured or Calculated Activity (in μCi/g) of TRU Isotopes in the AP-101 Glass[a]

TRU Isotope	Activity μCi/g
^{236}Pu	3.0E-6
^{237}Np	4.5E-5
^{238}Pu	3.7E-6
$^{239}Pu + ^{240}Pu$	3.15E-5
^{241}Pu	4.0E-4
^{242}Pu	4.0E-6
^{244}Pu[b]	5.2E-7
^{241}Am	1.54E-4
^{242}Cm	2.0E-6
^{243}Am	3.0E-6
$^{243}Cm + ^{244}Cm$	1.68E-6
Maximum Total TRU Activity	6.48E-4

(a) The values are based on mass spectrometry or direct radiological determination. MS values were used when radiological data were not available. Where the data gave only an upper limit, that value was used instead of the measured amount.

(b) Additional measured values for ^{244}Pu are 2.96×10^{-2} μg/g by ICP MS mass and the specific activity of 1.759×10^{-5} μCi/μg.

6.4.1 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 6.6 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.

Table 6.6. Measured Dose Rates of ILAW Glasses at Contact

Sample ID	Weight, g	Uncorrected		Corrected	
		Beta mr/g	Gamma mr/g	Beta mr/g	Gamma mr/g
AP-101[(a)]	1.949	0.77	-	69	-
AZ-101[(b)]	13.392	0.48	0.04	17	1.05
AN-107[(c)]	10.922	0.15	0.07	1	0.29
AW-101[(d)]	11.208	0.56	0.06	30	1.07

(a) AP-101 is described in RPP-WTP-092(this report)
(b) AZ-101 is described in RPP-WTP-106
(c) AN-107 is described in WTP-RPT -003
(d) AW-101 is described in WTP-RPT -003

6.5 Crystalline and Noncrystalline Phases

The AP-101 glass sample was completely amorphous. Figure 6.2 shows SEM images of different areas of the sample. All are crystal-free. The light spots on the surface are particles of dust. Table 6.7 lists EDS composition measurements taken at different areas. The results are nearly identical, except #3 (the middle area, 4 mm from the top of the melt) with a significantly lower Na content. As an outlier, #3 was not included in the average. Table 6.8 compares the EDS-measured compositions with inductively coupled plasma (ICP) and target fractions normalized to EDS-detectable components. Fractions of low-atomic-mass elements (Na, Mg. Al) tend to be underestimated by EDS, whereas fractions of high-atomic-mass elements (K, Ca, Ti, Fe, Zn) tend to be overestimated (the differences are below 5 mass%, but the relative difference can be high for minor components, such as K).

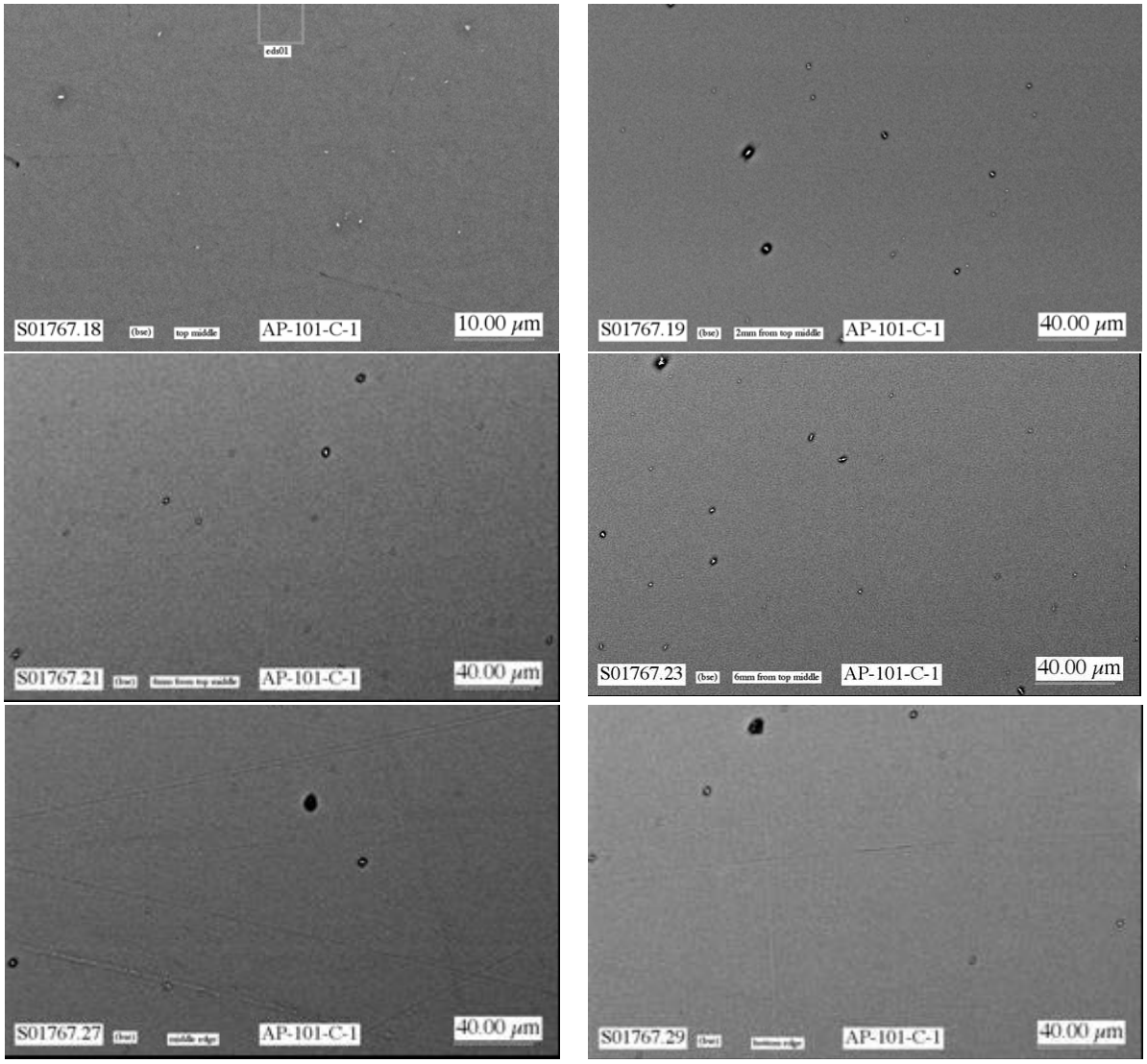

Figure 6.2. SEM Micrographs of AP-101 Melt Subjected to CCC Heat Treatment (#18 is from the top middle area; #19 is the middle area, 2 mm from top; # 21 is the middle area, 4 mm from top, #23 is the middle area, 6 mm from top, #27 is from the middle ridge area, and #29 is from the bottom ridge area)

Table 6.7. EDS Composition (in atomic fractions) of AP-101 Glass Subjected to CCC Heat Treatment

#	O	Na	Mg	Al	Si	K	Ca	Ti	Fe	Zn
1	0.517	0.135	0.009	0.030	0.224	0.029	0.011	0.009	0.023	0.013
2	0.519	0.135	0.008	0.030	0.224	0.029	0.011	0.008	0.023	0.013
3	0.535	0.116	0.009	0.030	0.225	0.029	0.011	0.009	0.023	0.013
4	0.522	0.136	0.009	0.030	0.221	0.029	0.011	0.008	0.023	0.012
5	0.518	0.136	0.009	0.030	0.223	0.029	0.011	0.009	0.023	0.013
6	0.521	0.136	0.008	0.030	0.221	0.029	0.011	0.008	0.022	0.013
7	0.522	0.136	0.008	0.030	0.220	0.029	0.011	0.009	0.023	0.013
8	0.515	0.138	0.009	0.030	0.224	0.029	0.011	0.008	0.023	0.013
Average	0.521	0.134	0.009	0.030	0.223	0.029	0.011	0.008	0.023	0.013

Table 6.8. EDS Composition (in mass fractions) of AP-101 Glass Subjected to CCC Heat Treatment

	EDS	ICP	Target	Δ	Δ_{rel}
Na_2O	0.169	0.216	0.214	-0.047	-0.218
MgO	0.014	0.018	0.017	-0.005	-0.246
Al_2O_3	0.061	0.065	0.066	-0.003	-0.052
SiO_2	0.535	0.519	0.513	0.016	0.031
K_2O	0.055	0.033	0.044	0.022	0.661
CaO	0.025	0.023	0.023	0.001	0.058
TiO_2	0.027	0.025	0.023	0.002	0.074
Fe_2O_3	0.073	0.067	0.064	0.006	0.094
ZnO	0.042	0.034	0.034	0.008	0.231
Δ the difference between EDS and ICP mass fraction of an oxide. Δ_{rel} the relative difference [$\Delta_{rel} = 1 - x_i(\text{EDS})/x_i(\text{ICP})$].					

6.6 PCT

Results of the analyses of 7-day PCT solutions from testing the CCC-treated AP-101 glass are summarized in Table 6.9. Concentrations of elements were measured for AP-101 glass and for LRM standard glass, both in triplicate. Normalized elemental releases for the key elements are listed in Table 6.10. The measured normalized releases of the standard glass are in good agreement with reported values, except for lithium. This, however, is irrelevant for AP-101 data because AP-101 does not contain lithium. As expected, normalized boron and sodium releases are identical and their values, 0.65 g/m^2, are fairly below the limit of 2.0 g/m^2.

Table 6.9. 7-Day PCT Solution Analysis (concentrations in mg/L) of AP-101 Glass Subjected to CCC Heat Treatment

Element	AP-101-C-90[a]			LAW-TP121-LRM-90[a]		
B	39.8	40.3	39.4	26.1	26.4	25.8
Li	0.01	0.009	0.01	0.088	0.088	0.088
Na	177	179	175	163	165	162
Si	87.4	88.5	87.4	85.2	86.1	85.2
Al	6.58	6.58	6.69	15.40	15.60	15.50
Ba	0.00	0.00	0.00	0.001	0.00	0.00
Ca	0.29	0.29	0.30	0.40	0.16	0.37
Cd	0.00	0.00	0.00	0.234	0.226	0.217
Co	0.00	0.00	0.00	0.009	0.008	0.009
Cr	0.061	0.074	0.058	0.378	0.379	0.386
Cu	0.008	0.008	0.018	0.013	0.012	0.013
Fe	0.927	0.903	1.080	2.91	2.86	2.93
K	23.6	23.9	23.3	4.0	3.9	3.6
La	0.000	0.000	0.000	0.028	0.026	0.024
Mg	0.35	0.32	0.42	0.120	0.110	0.094
Mn	0.020	0.010	0.009	0.157	0.145	0.149
Mo	0.025	0.026	0.025	0.253	0.257	0.247
Ni	0.068	0.067	0.070	0.561	0.567	0.558
P	0.337	0.349	0.329	0.759	0.780	0.745
Pb	0.030	0.024	0.000	0.216	0.209	0.200
Sb	0.054	0.055	0.083	0.045	0.040	0.040
Sr	0.00	0.00	0.00	0.002	0.000	0.000
Ti	0.122	0.128	0.149	0.156	0.157	0.158
V	0.061	0.061	0.061	0.007	0.006	0.006
W	0.082	0.075	0.079	0.000	0.000	0.000
Y	0.000	0.000	0.000	0.005	0.004	0.005
Zn	0.786	0.770	0.889	0.049	0.066	0.048
Zr	0.23	0.23	0.275	1.72	1.75	1.73

(a) Analyses were performed in triplicate.

Table 6.10. Normalized 7-Day PCT Releases in g/m^2 of AP-101 Glass Subjected to CCC Heat Treatment

	AP-101[a]				LAW-TP121-LRM-90[a]					
	1	2	3	Average	1	2	3	Average	Reported[b]	Δ_{rel}[c]
B	0.65	0.66	0.64	0.65	0.52	0.53	0.52	0.525	0.593	-0.11
Li	---	---	---	---	0.07	0.07	0.07	0.075	0.213	-0.65
Na	0.65	0.65	0.64	0.65	0.55	0.55	0.54	0.549	0.572	-0.04
Si	0.21	0.21	0.21	0.21	0.17	0.17	0.17	0.168	0.166	0.01

(a) Analyses were performed in triplicate.
(b) Values reported in WSRC-TR-99-00095.
(c) Δ_{rel} = Average/Reported – 1(LRM only).

6.7 TCLP

A TCLP test was performed, and leachates were analyzed for antimony, arsenic, barium, beryllium, chromium, cadmium, lead, mercury, nickel, selenium, silver, thallium, vanadium, and zinc. The only elements detected in the TCLP leachates via ICP-AES were barium, chromium, mercury, and zinc, which were detected at 0.32 mg/L-TCLP, 0.007 mg/L-TCLP, 0.00083 mg/L-TCLP, and1.2 mg/L-TCLP respectively, all significantly less than the UTS (Table 6.11). No QC problems were noted. Due to the very low UTS limit for thallium, this element was analyzed by ICP-MS. These results indicate that thallium is also well below the UTS. Boron was detected at 1.15 mg/L-TCLP but a UTS level is not specified.

Table 6.11. Analytical Results for TCLP Inorganic Constituents of Potential Concern (CoPC).

Note that the ICP-AES (ICP-MS for Tl) values are indicated to be simply less than the UTS when not detected, but when they are detected (> MDL), and less than UTS, the value is reported followed by "J".

CAS#	Constituent	Symbol	Required for LDR	UTS[(a)] mg/L-TCLP	ICP-AES[(b)] mg/L-TCLP (ave. of two)	MDL[(c)] mg/L
7440-36-0	Antimony	Sb	X	1.15	0.028 U	0.028
7440-38-2	Arsenic	As	VIT	5.0	0.045 U	0.045
7440-39-3	Barium	Ba	VIT	21	0.32 J	0.002
7440-41-7	Beryllium	Be	X	1.22	0.0002 U	0.0002
7440-42-8	Boron	B	n/a	n/a	1.3	0.012
7440-43-9	Cadmium	Cd	VIT	0.11	0.009 J	0.006
18540-29-9	Chromium	Cr	VIT	0.6 total	0.015 J	0.004
7439-92-1	Lead	Pb	VIT	0.75	0.035 U	0.034
7439-97-6	Mercury	Hg	VIT	0.025	0.000092 J	0.000045
7440-02-0	Nickel	Ni	X	11	0.015 J	0.014
7782-49-2	Selenium	Se	VIT	5.7	0.042 U	0.042
7440-22-4	Silver	Ag	VIT	0.14	0.005 U	0.004
7440-28-0	Thallium	Tl	X	0.20	0.00016J	0.000013
7440-62-2	Vanadium	V	n/a	1.6	0.003 U	0.003
7440-66-6	Zinc	Zn	n/a	4.3	1.3 J	0.005

(a) UTS = Universal Treatment Standard, 40 CFR 268.48.
(b) Average of sample and duplicate; Hg was measured with CVAA; Tl was measured with ICP-MS.
(c) MDLs were determined with dilute acidified water (2% HNO_3) per ASO-QAP-001 and adjusted by the average sample processing factor (~1.01).
"J" = estimated value that is greater than the MDL and less than the EQL.
"U" =Undetected. Analyte was analyzed but not detected (e.g., no measurable instrument response), or response was less than the 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.

6.8 Property Comparison of Actual and Simulated AP-101 Glass

Table 6.12 through Table 6.15 list physical, chemical, and rheological properties for actual and simulated AP-101 waste, melter feed, and glass. As Table 6.12 and Table 6.13 show, the actual and simulated wastes have similar pH values, and the actual and simulated melter feed have similar bulk densities. Regarding the rheological properties, the two values listed in Table 6.15, one for the yield stress and one for the consistency, are in good agreement. The VSL glass data (Muller and Pegg 2003) comes from their report summarized in Appendix E.

Table 6.16 and Table 6.17 specify the property similarity criteria between actual and simulated LAW and LAW melter feed for the simulated material to be a "verified" representative of the real waste or melter feed. The last columns in these tables indicate the type of application for the simulant. Bulk density, yield stress, and consistency comparisons for the melter feed are provided in Table 6.13 and Table 6.15.

Table 6.12. Properties of Actual and Simulant AP-101 Waste at 8M Na at 25°C

Property	Actual (PNWD)	Simulant (VSL)[(a)] (Muller and Pegg 2003)
pH	>14	13.56
Density, g/mL	1.399	1.39
(a) Temperature not specified; it is assumed that the values were obtained at room temperature.		

Table 6.13. Properties of Actual and Simulant AP-101 Melter Feed Prepared from 8 M Na Pretreated Waste at 25°C (Bredt et al. 2003) (VSL data private communication and Appendix B from Muller and Pegg 2003)

Property	Actual (PNWD)	Simulant (VSL)[a]
pH	12.5[b]	11.39
Median volume particle size (PS) (μm)[c]	9.2	n/a
95% volume particle-size distribution (PSD), D_{95} (μm)[c]	20.2	n/a
Bulk density (g/mL)	1.742	1.76
Supernatant liquid density (g/mL)	1.39	n/a
Settled solids (vol%)	60.3	n/a
Centrifuged solids density (g/mL)	2.11	n/a
Centrifuged solids (vol%)	49.3	n/a
Centrifuged solids (wt%)	59.6	n/a
Total solid (wt%)	65.3	n/a
Undissolved solids (wt%)	37.7	n/a
Newtonian viscosity at 25°C (cP)	39.9	~40
Newtonian viscosity at 40°C (Pa·s)	27	n/a
Yield stress at 25° (Pa)	ND	<0.1
Shear strength at 40°C (Pa)	79[e]	n/a
Glass components[d] (wt%)	53.76	n/a

(a) Glass formulated to LAWA126.
(b) Ambient temperature (~23°C).
(c) Particle size analysis performed on melter feed prepared from 6M Na pretreated waste.
(d) Glass components are oxides and halogens present in the glass.
(e) Yield strength of melter feed prepared from 6M Na pretreated waste was 790 Pa.
n/a = not available.
ND = not detected.

Table 6.14. Properties of Actual and Simulant AP-101 Glass

Property	Actual (PNWD)	Simulant (VSL) (Muller and Pegg 2003)
Waste loading in glass (mass fraction)	0.24695	0.2468
Na_2O mass fraction in waste oxides	0.74607	0.7479
Na_2O mass fraction in glass	0.1842	0.18462
Density (g/mL)	n/a	2.687 (LAWA126) 2.679 (PNLA126CC)

Table 6.15. Comparison of Rheological Properties Between AP-101 Actual Waste and Simulant Melter feed

Property	PNWD (actual at 8 M)	VSL (simulant at 8 M) (Muller and Pegg 2003)
Yield stress from rheogram (Pa)	~0 at 25°C ~0 at 40°C	~0 (<0.1) at 25°C
Consistency (cP)	39.9 at 25°C 27.0 at 40°C	~40 (at RT?)[(a)]
Shear strength (Pa)	79 at 40°C	n/a
(a) Temperature not specified; it is assumed the values were obtained at room temperature (RT).		

Table 6.16. Summary of Verification Criteria for Pretreated LAW[(a)]

Property	Criterion	Application
Viscosity	±20%	Pumping
Density	± 0.05 g/mL	Mixing and pumping
(a) Simulant verification criteria, Poloski, WTP-RPT-075c, Rev. A, March 2003.		

Table 6.17. Summary of Verification Criteria for LAW Melter Feed[(a)]

Property	Criterion	Application
Slurry density	± 5%	Mixing and pumping
Maximum settled solids shear strength at 40°C	±50%	Plant upset conditions
Particle density	± 0.1 g/mL	Mixing
Interstitial liquid density	± 0.05 g/mL	Mixing
Particle size (D_{95})	± 20%	Mixing
Interstitial liquid viscosity	± 20%	Mixing
Consistency index	± 30%	Pumping and settling
Yield stress	± 35%	Pumping and settling
Total oxides	± 10%	Melter mass balance
Total solids	± 10%	Melter mass balance
(a) Simulant verification criteria, Poloski, WTP-RPT-075c, Rev. A, March 2003.		

Table 6.18 compares the TCLP results for PNWD Actual and VSL Simulant AP-101 Waste Glass. The PNWD Actual AP-101 Waste Glass was quenched from melt while the VSL Simulant AP-101 Waste Glass was given a CCC heat treatment. The results for the two glasses indicate that their response to the TCLP was quite similar and that the VSL simulated AP-101 LAW glass met the UTS limits for inorganic hazardous constituent concentrations (for the elements measured) of the LDR regulations for Washington state and RCRA.

Table 6.18. Comparison of TCLP Results between AP-101 Actual and Simulant Glass in mg/L

Element	UTS	Actual Quenched (PNWD)	Simulated CCC(VSL) (Muller and Pegg 2003)
Antimony	1.15	<2.8E-2	n/a
Arsenic	<0.25	<3.6E-2	<5.0E-2
Barium	21.00	0.32 J	0.61
Beryllium	1.22	<2.0E-4	n/a
Boron	na	1.15	n/a
Cadmium	0.11	<3.8E-3	<3.0E-3
Chromium	0.60	7.0E-3 J	7.0E-3
Lead	0.75	<2.3E-2	<2.4E-2
Mercury	0.025	8.3E-4 J	n/a
Nickel	11	<1.3E-2	<8.0E-3
Selenium	5.70	<3.6E-2	<5.3E-2
Silver	0.14	<5.0E-3	<3.0E-3
Thallium	0.20	2.13E-4 J	n/a
Vanadium	1.6	<3.9E-3	n/a
Zinc	4.30	1.2 J	1.64

"J" = estimated value that is greater than the MDL and less than the EQL.
na = not applicable
n/a = not available

7.0 Conclusions

The primary objective for vitrifying the LAW sample AP-101 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 leachability. A pretreated tank supernatant was prepared as a melter feed for vitrification. The analyzed composition of the pretreated AP-101 waste was used by CUA VSL to formulate a target glass composition (LAW-A126). The supernatant tank sample, i.e., AP-101, was processed through pretreatment chemical-separation processes, and the decontaminated supernatant was converted to LAW glass after adding glass-former chemicals.

The 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% were identified and quantified*.
   The AP-101 LAW glass contains 11 constituent oxides with concentration >0.5 mass%. These oxides are as follows (with best analytical estimates in mass%): SiO_2 (44.72), Na_2O (18.62), B_2O_3 (9.93), Fe_2O_3 (5.73), Al_2O_3 (5.56), ZnO (2.92), K_2O (2.83), ZrO_2 (2.73), TiO_2 (2.18), CaO (2.00), and MgO (1.59). [2.2.2.6.1 Chemical Composition Qualification clause *Section C* from *WTP Contract: DE-AC27-01RV1413 Modification No. M033]*

2. *Key radionuclides were 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 6.3 and allows the values reported to be indexed to any date desired. [2.2.2.7 Radiological Composition Documentation clause *Section C* from *WTP Contract: DE-AC27-01RV1413 Modification No. M033]*

3. *The activities of radionuclides in the ILAW product are as follows: ^{137}Cs <3 Ci/m^3, ^{90}Sr<20 Ci/m^3, ^{99}Tc <0.1 Ci/m^3, and transuranic (TRU) <100 nCi/g*.
   The AP-101 LAW glass contains ^{90}Sr, ^{99}Tc, ^{137}Cs, and TRU at levels considerably below the contract limits as shown in the Table 7.1. [2.2.2.8 Radionuclide Concentration Limitations clause *Section C* from *WTP Contract- DE-AC27-01RV1413 Modification No. M033]* Note Waste Treatment and Immobilization Plant Unit Operation: specifies "In addition, ^{137}Cs will be further removed, to achieve a 0.3 Ci/m^3 in the ILAW product, to facilitate the maintenance concept established for the ILAW melter system."

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

Radionuclide	Contract Limit	Based on Measured Value	Ratio –Contract Limit to Measured Value
^{90}Sr	20 Ci/m^3	1.93E-1 Ci/m^3	~ 100
^{99}Tc	0.1 Ci/m^3	1.06E-3 Ci/m^3	~ 100
^{137}Cs	3 Ci/m^3	6.7E-4 Ci/m^3	~ 450
TRU	100 nCi/g	6.48E-1 nCi/g	~ 150

4. *The fraction of Na_2O from LAW for Envelope A in the glass is >14 mass%.*

   The measured Na_2O mass fraction in the AP-101 LAW glass is 18.62 mass%. Hence, the AP-101 LAW glass meets the task specification concentration. [2.2.2.2 Waste Loading: The loading of waste sodium from Envelope A in the ILAW glass shall be greater than 14 weight percent based on Na_2O. The loading of waste sodium from Envelope B in the ILAW glass shall be greater than 3.0 weight percent based on Na_2O. The loading of waste sodium from Envelope C in the ILAW glass shall be greater than 10 weight percent based on Na_2O. 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_2O.]

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

   The AP-101 glass was found to be completely amorphous. [2.2.2.6.3 Crystalline Phase Identification: 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 g/m^2 (at 90^{o}C).*

   The measured mass loss based on the normalized releases of boron, sodium, and silicon (the AP-101 glass does not contain any lithium) are 0.65 g/m^2, 0.65 g/m^2, and 0.21 g/m^2 respectively. These values are well below the limit of 2.0 g/m^2. [2.2.2.17.2 Product Consistency Test: 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 test was used to demonstrate that the release of hazardous inorganics met the UTS for the Land Disposal Restrictions).*

   The AP-101 LAW glass passed the TCLP test and qualifies for land disposal. [2.2.2.20 Dangerous Waste Limitations: The ILAW product shall be acceptable for land disposal under the State of Washington Dangerous Waste Regulations, WAC 173-303, and RCRA LDR in 40 CFR 268.]

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

Chemistry and Radiochemistry Summary for AP-101 Glass

Appendix A: Chemistry and Radiochemistry Summary for AP-101 Glass

Table A.1. ICP-AES Chemistry Summary for ARG-1 and LRM Glass

	Ave. K&Na Fusions for ARG-1 (μg/g)	Ave. K&Na Fusions for ARG-1 as Oxides (μg/g)	ARG-1 as Mass Fractions	Ave. K&Na Fusions for LRM (μg/g)	Ave. K&Na Fusions for LRM as Oxides (μg/g)	LRM as Mass Fractions
Ag_2O	0	0	0.0000	0	0	0.0000
Al_2O_3	23155	43752	0.0456	46755	88346	0.0928
B_2O_3	24975	80420	0.0837	23025	74141	0.0779
BaO	714	797	0.0008	0	0	0.0000
BeO	0	0	0.0000	0	0	0.0000
Bi_2O_3	0	0	0.0000	0	0	0.0000
CaO	9050	12663	0.0132	2785	3897	0.0041
CdO	0	0	0.0000	1320	1508	0.0016
CeO_2	0	0	0.0000	0	0	0.0000
Co_2O_3	0	0	0.0000	0	0	0.0000
Cr_2O_3	674	985	0.0010	1224	1789	0.0019
CuO	0	0	0.0000	0	0	0.0000
Fe_2O_3	91850	131320	0.1368	9492.5	13572	0.0143
K_2O	18700	22526	0.0235	9700	11685	0.0123
La_2O_3	0	0	0.0000	65	76	0.0001
Li_2O	12800	27555	0.0287	420	904	0.0009
MgO	4387.5	7276	0.0076	605	1003	0.0011
MnO_2	13582.5	17538	0.0183	475	613	0.0006
MoO_3	0	0	0.0000	670	1005	0.0011
Na_2O	75600	101907	0.1061	138445	186621	0.1960
Nd_2O_3	0	0	0.0000	0	0	0.0000
NiO	7900	10054	0.0105	1375	1750	0.0018
P_2O_5	1390	3185	0.0033	2220	5087	0.0053
PbO		0	0.0000	1200	1293	0.0014
SiO_2	228675	489181	0.5094	258425	552822	0.5806
SnO_2	0	0	0.0000	0	0	0.0000
SrO	26	31	0.0000	2.25	3	0.0000
ThO_2	0	0	0.0000	0	0	0.0000
TiO_2	5712.5	9529	0.0099	574.5	958	0.0010
UO_2	0	0	0.0000	0	0	0.0000
V_2O_3	110	162	0.0002	0	0	0.0000
Y_2O_3	0	0	0.0000	0	0	0.0000
ZnO	220	274	0.0003	0	0	0.0000
ZrO_2	840	1135	0.0012	3755	5072	0.0053
		960289	1.0000		952144	1.0000

Table A.2. Radiochemistry Summary for AP-101 Glass

Radio-nuclide	Measured Radiation	Measured Activity µCi/g			One-Sigma Error %		RPD %	Spike Recovery %	
		Proc. Blank	Initial	Duplicate	Initial	Duplicate		Blank	Matrix
^{51}Cr	γ	---	<9.0E-5	---	---	---	---	---	---
^{59}Fe	γ	---	<3.0E-5	---	---	---	---	---	---
^{60}Co	γ	---	2.29E-3	---	2	---	---	---	---
^{63}Ni	β	<9.0E-5	4.73E-3	3.19E-3	4	4	39	90	94
^{79}Se	β	---	<4.8E-4	---	---	---	---	---	---
^{88}Y	γ	---	<2.0E-5	---	---	---	---	---	---
^{90}Sr	β	7.57E-3	6.22E-2	8.05E-2	5	5	26	93	99
^{95}Nb	γ	---	<2.0E-5	---	---	---	---	---	---
^{95}Zr	γ	---	<2.0E-5	---	---	---	---	---	---
^{99}Tc[(a)]	γ	---	Not measured	---	---	---	---	---	---
^{103}Ru	γ	---	<2.0E-5	---	---	---	---	---	---
^{106}RuRh	γ	---	3.46E-4	---	9	---	---	---	---
^{113}Sn	γ	---	<2.0E-5	---	---	---	---	---	---
^{125}Sb	γ	---	1.3E-3	---	3	---	---	---	---
^{126}SnSb	γ	---	2.82E-4	---	3	---	---	---	---
^{134}Cs	γ	---	<2.0E-5	---	---	---	---	---	---
^{137}Cs	γ	---	2.48E-4	---	4	---	---	---	---
^{144}Ce	γ	---	<7.0E-5	---	---	---	---	---	---
^{151}Sm	β	<4.0E-4	7.43E-4	1.06E-3	10	9	35	78	46
^{152}Eu	γ	---	<3.0E-5	---	---	---	---	---	---
^{154}Eu	γ	---	---	---	---	---	---	---	---
^{155}Eu	γ	---	---	---	---	---	---	---	---
^{232}Th	γ	---	<2.0E-5	---	---	---	---	---	---
^{237}Np	MS	---	---	---	---	---	---	---	---
^{236}Pu	α	<2.0E-6	<3.0E-6	<3.0E-6	---	---	---	---	---
^{238}Pu	α	<9.0E-7	3.2E-6	4.3E-6	35	27	30	---	---
^{239}Pu + ^{240}Pu	α	1.69E-5	2.18E-5	4.11E-5	13	8	61	109	107
^{241}Pu	β	<3.0E-4	<4.0E-4	<3.0E-4	---	---	---	104	84
^{242}Pu	α	---	<4.0E-6	---	---	---	---	---	---
^{241}Am	α	0.9.84E-6	1.21E-4	1.24E-4	5	5	2	98	95
^{242}Cm	α	<5.0E-6	<2.0E-6	<2.0E-6	---	---	---	---	---
^{243}Am	α	---	<3.0E-6	---	---	---	---	---	---
^{243}Cm + ^{244}Cm	α	<5.0E-6	<3.0E-6	1.7E-6	---	40	---	---	---
Total α	α	---	1.46E-4	1.71E-4	---	---	---		
Total U	ICP-AES	<50 µg/mL		---	---		---	---	---

(a) ICP-MS did not detect any Tc in the sample.

Appendix B

ICP Mass Spectrometry Summary for AP-101 Pretreated Waste

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

Table B.1. ICP Mass Spectrometry Summary for AP-101 Pretreated Waste. Note radioisotope activities for calculating μCi/g from μg/g came from Browne and Firestone (1986).

Element	Concentration μg/g (*μCi/g)	±1 Sigma	MDL μg/g
Tc-99 (μCi/g)	3.07E-4*	1.74E-5 (μCi/g)	1.63E-5 (μCi/g)
Tc-99 (dup)	3.24E-4*	1.78E-5 (μCi/g)	1.62E-5 (μCi/g)
Rb	2.55	4.62E-2	9.04E-4
Rb (dup)	2.60	1.04E-1	9.0E-4
Pd	3.10E-2	4.98E-3	2.63E-3
Pd (dup)	3.38E-2	1.05E-2	2.95E-3
Ru	2.12	8.39E-2	1.61E-3
Ru (dup)	2.18	2.91E-2	1.80E-3
Rh	1.00	3.72E-2	7.17E-4
Rh (dup)	1.03	1.51E-2	8.03E-4
I-129 (μCi/g)	1.54E-4*	5.7E-6 (μCi/g)	5.1E-6 (μCi/g)
I-129 (dup)	1.74E-4*	4.39E-6 (μCi/g)	4.97E-6 (μCi/g)
Cs	<2.01E-3	---	<2.01E-3
Cs (dup)	<2.01E-3	---	<2.01E-3
Pr	2.00E-3	4.73E-4	3.06E-4
Pr (dup)	1.73E-3	1.37E-4	3.43E-4
Pt	2.63E-2	4.12E-4	5.47E-4
Pt (dup)	6.47E-3	2.05E-3	5.12E-4
Ta	5.28E-3	7.71E-4	7.73E-4
Ta (dup)	4.10E-3	1.66E-3	7.24E-4
U	8.91E-1	9.8E-3	6.44E-5
U (dup)	8.95E-1	1.28E-2	5.45E-5
U-233	1.05E-6*	3.39E-7 (μCi/g)	2.80E-8 (μCi/g)
U-233 (dup)	8.57E-7*	2.07E-7 (μCi/g)	2.37E-8 (μCi/g)
U-234	4.35E-7*	1.29E-7 (μCi/g)	9.93E-8 (μCi/g)
U-234 (dup)	4.95E-7*	9.06E-8 (μCi/g)	8.40E-8 (μCi/g)
U-235	1.66E-8*	3.0E-10 (μCi/g)	2.05E-10 (μCi/g)
U-235 (dup)	1.68E-8*	2.67E-10 (μCi/g)	1.74E-10 (μCi/g)
U-236	3.63E-8*	1.61E-9 (μCi/g)	6.19E-10 (μCi/g)
U-236 (dup)	3.07E-8*	1.58E-9 (μCi/g)	5.24E-10 (μCi/g)
U-238	2.97E-7*	5.3E-11 (μCi/g)	3.1E-11 (μCi/g)
U-238 (dup)	2.98E-7*	4.0E-11 (μCi/g)	2.6E-11(μCi/g)

Appendix C

ICP Mass Spectrometry Summary for AP-101 Glass

Appendix C: ICP Mass Spectrometry Summary for AP-101 Glass

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

Isotope	Na Fusion	Na Process Blank Fusion	K Fusion	K Process Blank Fusion	Average Amount	QC Status
^{99}Tc	4.93E-1	1.29	<1.875	<1.85	Non-Detect	Process Contaminated[(a)]
^{101}Ru	7.23	<7.09E-1	8.38	<9.08E-1	7.81	Good
^{102}Ru	4.27	<6.77E-1	5.36	<1.05	4.82	Good
^{103}Rh	2.46	<2.38E-1	2.27	<2.69E-1	2.37	Good
^{105}Pd	<7.11	<7.07	4.23	<1.40	4.23	K-fusion Best[(b)]
^{120}Sn	64.8	<14.8	70.3	<6.70	67.5	Ok[(c)]
^{121}Sb	4.20E-1	<0.2.96E-1	<7.90E-1	<7.78E-1	4.2E-1	Low LCS[(d)]
^{128}Te	<6.12	<6.06	<5.66	<5.58	<5.66	Good
^{129}I	<15.8	<15.8	---	---	<15.8	Good – low sensitivity[(e)]
^{182}W	86.6	<8.70	227	<19.1	227	K-fusion best
^{232}Th	22.8	<2.08	20.6	<1.67	21.7	Good
U-Total	58.2	<6.90E-1	52.8	<5.09E-1	55.5	Good
^{233}U	1.36E-1	<1.13E-2	<6.47E-3	<6.38E-3	<6.47E-3	Good
^{234}U	<8.3E-3	<8.26E-3	<8.38E-3	<8.26E-3	<8.3E-3	Good
^{235}U	2.31E-1	<1.07E-2	2.13E-1	<9.51E-3	2.22E-1	Good
^{236}U	<6.58E-3	<7.05E-3	<3.83E-3	<3.71E-3	<3.83E-3	Ok
^{237}Np	<5.19E-2	<5.16E-2	<5.68E-2	<5.60E-2	<5.19E-2	Good – low sensitivity
^{238}U	58	<6.90E-1	52.6	<5.01E-1	55.3	Good
^{239}Pu	<2.43	<2.41	<2.66	<2.61	<2.43	Good – low sensitivity
^{240}Pu	<5.75E-2	<5.72E-2	<6.29E-2	<6.20E-2	<5.75E-2	Good – low sensitivity
^{241}Pu/ ^{241}Am	<2.33E-2	<2.31E-2	<2.55E-2	<2.51E-2	<2.33E-2	Good – low sensitivity
^{242}Pu	<3.49E-2	<3.47E-2	<3.82E-2	<3.76E-2	<3.49E-2	Good – low sensitivity
^{244}Pu	<2.70E-2	<2.69E-2	<2.96E-2	<2.91E-2	<2.70E-2	Good – low sensitivity

(a) Process contaminated – Non-sample containing chemicals show as much Tc as the samples.
(b) K-fusion Best – Higher values and/or signal to noise ratio than the sodium fusion.
(c) Ok – One out of the four samples gave apparently poor results.
(d) Low LCS – The Montana soil laboratory control standard sample numbers for this isotope were about 50% of the expected level.
(e) Good – low sensitivity - indicates high sample dilution factors are the cause of the low sensitivity.

Table C.2. AP-101 Glass Uranium and TRU Inventory

U Isotope	ICP MS µg/g	Specific Activity µCi/µg	Measured or Calculated Activity, µCi/g
^{233}U	6.47E-3	9.64E-3	6.2E-5
^{234}U	8.38E-3	6.225E-3	5.2E-5
^{235}U	2.31E-1	1.922E-6	4.4E-7
^{236}U	6.58E-3	6.508E-5	4.3E-7
^{238}U	58	3.36E-7	1.95E-5
TRU Isotope			
^{236}Pu	---	---	3.0E-6
^{237}Np	---	---	4.5E-5
^{238}Pu	---	---	3.7E-6
$^{239}Pu + ^{240}Pu$	---	---	3.15E-5
^{241}Pu	---	---	4.0E-4
^{242}Pu	---	---	4.0E-6
^{244}Pu	2.96E-2	1.759E-5	5.2E-7
^{241}Am	---	---	1.54E-4
^{242}Cm	---	---	2.0E-6
^{243}Am	---	---	3.0E-6
$^{243}Cm + ^{244}Cm$	---	---	1.68E-6
Total Activity of TRU in AP-101 Glass			6.48E-4

Appendix D

From: The Catholic University of America LAW Glass Formulation LAWA126 (simulant AP-101) to Support Actual AP-101 Waste Testing [Muller IS, and IL Pegg. 2003. *The Catholic University of America LAW Glass Formulation to Support AP-101 Actual Waste Testing, Vitreous State Laboratory Final Report.* VSL-03R3470-2, Rev. 0, for Duratek, Inc. and Bechtel National Inc., Richland, WA.]

Appendix D: From: The Catholic University of America LAW Glass Formulation LAWA126 (simulated AP-101) to Support Actual AP-101 Waste Testing

Table D.1. Abbreviated from the Original VSL Batch Table*

Envelope Constituents	AP-101 as Given in PNNL 5.62 M Na		Glass		AP-101 wt% Pretreated	AP101 wt% in glass Pretreated	LAWA126 for this AP101	LAWA126 for AP101					Target Weight (g)
								Additives	Additives				
Element	Moles/L	mg/L ICP	Oxides	mol wt.	---	24.70%	24.70%	100.00%	75.30%	Source in Additives	Assay	Ratio	Additives
Al	2.57E-01	6940.0	Al_2O_3	101.96	5.48	1.354	5.651	5.71	4.30	Kyanite (Al2SiO5) 325 Mesh	0.990	0.5400	134.87
B	1.39E-03	15.0	B_2O_3	69.62	0.02	0.005	9.844	13.07	9.84	H3BO3	0.986	0.5630	297.42
Ca	1.92E-04	7.7	CaO	56.08	0.00	0.001	1.995	2.65	1.99	Wollanstonite NYAD 325 Mesh	0.993	0.4750	70.94
Cr	2.75E-03	143.0	Cr_2O_3	152.00	0.09	0.022	0.022	---	---	---	---	---	---
Fe	4.48E-05	2.5	Fe_2O_3	159.70	0.00	0.000	5.555	7.38	5.55	Fe2O3	0.998	1.0000	87.26
K	7.98E-01	31200.0	K_2O	94.20	15.72	3.881	3.881	---	---	---	---	---	---
Mg			MgO	40.30	0.00	0.000	1.481	1.97	1.48	Olivine (Mg2SiO4) 325 Mesh (#180)	0.990	0.4800	52.31
Na	5.62E+00	129300.0	Na_2O	61.98	74.75	18.46	18.462	---	---	---	---	---	---
Ni	1.35E-04	7.9	NiO	74.69	0.00	0.001	0.001	---	---	---	---	---	---
Si	4.88E-03	137.0	SiO_2	60.09	0.12	0.030	44.206	58.67	44.18	SiO2 (Sil-co-Sil 75)	0.997	1.0000	600.79
Ti			TiO_2	79.90	0.00	0.000	1.999	2.66	2.00	Rutile Sand Premium Airfloated	0.954	1.0000	35.17
U	2.15E-04	51.1	UO_2	270.00	0.02	0.006	0.006	---	---	---	---	---	---
Zn	8.56E-05	5.6	ZnO	81.39	0.00	0.001	2.963	3.93	2.96	ZnO	0.997	1.0000	49.86
Zr	1.53E-05	1.4	ZrO_2	123.22	0.00	0.000	2.999	3.98	3.00	Zircon ZrSiO4 (Flour) Mesh 325	0.990	0.6725	75.59
Cl	5.59E-02	1980.0	Cl	35.45	0.83	0.204	0.204	---	---	Sugar	---	---	107.2
F	1.53E-01	2900.0	F	19.00	1.21	0.299	0.299	---	---	Sum of Additives (g)	---	---	1404.211
PO_4	1.07E-02	1020.0	P_2O_5	70.97	0.32	0.079	0.079	---	---	Expected Glass yield (g)	---	---	1678.1
SO_4	4.20E-02	4030.0	SO_3	80.06	1.40	0.347	0.347	---	---	Number of moles of sodium used	---	---	10.000

* Note that in their report [*The Catholic University of America LAW Glass Formulation to Support AP-101 Actual Waste Testing Vitreous State Laboratory Final Report, VSL-03R3470-2, Rev. 0.* Appendix A3. Batching Recipe for Feed LAWA126 Submitted for Actual Waste Testing (Various dilutions may be tested; the recipe is based on a total number of sodium moles, here for 8 moles, or 1 liter of 8 molar concentrate)] the batching table is set up for eight moles of sodium not 10. The numbers between the tables are consistent.

Appendix E

TCLP Results for AP-101 Envelope A Glass

Appendix E: TCLP Results for AP-101 Envelope A Glass

Test Plan Number:	TP-RPP-WTP-121 Rev. 0
Preparation Method:	RPG-CMC-110 Rev. 1/ RPG-CMC-139 Rev. 0/ RPG-CMC-101 Rev.0
Analysis Method:	RPG-CMC-211 Rev. 0 (ICPAES)
	RPG-CMC-201 Rev. 0 (Mercury)
	329-OP-SC01 Rev. 0 (ICP/MS)
Leach Date:	01/14/2004-01/15/2004
Spreadsheet Author/Date:	B.M. Oliver/2-10-04
Spreadsheet Reviewers/Date:	K.N Pool/4-30-04

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 AP-101 LAW 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 E.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 AP-101 LAW glass, for all analytes of interest and including QC performance (Table E.2 through E.4), is provided below.

E.2 Sample Analysis Results

Table E.1. TCLP Sample Results

CAS #	Constituent	Sample Result (mg/L)[1]	Duplicate Result (mg/L)[1]	MDL[1] (mg/L)	EQL[2] (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	0.29 J	0.35 J	0.002	21
7440-41-7	Beryllium	0.0002 U	0.0002 U	0.0002	1.22
7440-42-8	Boron	1.35	1.25	0.012	0.05
7440-43-9	Cadmium	0.011 J	0.006 U	0.006	0.11
18540-29-9	Chromium	0.020 J	0.010 J	0.004	0.6
7439-92-1	Lead	0.035 U	0.035 U	0.035	0.75
7439-97-6	Mercury	0.000064 J	0.00012 J	0.000045	0.025
7440-02-0	Nickel	0.015 J	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	0.00021J	0.00011J	0.000013[3]	0.20
7440-62-2	Vanadium	0.003 U	0.003 U	0.003	1.6
7440-66-6	Zinc	1.3 J	1.3 J	0.005	4.3

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

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

	PB Success Criteria: <EQL		LCS Success Criteria: 75%-125% Recovery		
Analyte	Success Criteria (EQL) mg/L	Prep Blank Results mg/L	Expected Spike Cone mg/L	LCS/BS Results mg/L	Recovery[(a)] (%)
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[(b)]
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

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

(a) LCS/BS recoveries have been corrected for contribution of analyte concentration in the preparation blank.
(b) No acceptance criteria provided for mercury analysis.

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 the process blanks was within the acceptance criteria of <EQL or ≤ 5% of the concentration in the samples.

Mercury Analysis

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

ICP-MS (Tl only)

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

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 multi-element 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

Table E.3. Matrix Spike (MS) Results

Matrix Spike Success Criteria: 75%-125%				
Analyte	**Expected Spike Conc. (mg/L)**	**Original Sample Results (mg/L)**	**Matrix Spike (mg/L)**	**Recovery (%)[(a)]**
Antimony	1.11	0.028 U	1.15	104
Arsenic	1.55	0.045 U	1.60 J	103
Barium	1.11	0.29 J	1.42 J	101
Beryllium	0.554	0.002 J	0.55 J	100
Boron	4.44	1.35	5.79	100
Cadmium	0.554	0.011 U	0.546	96
Chromium	1.11	0.020 J	1.19	105
Lead	0.665	0.035 U	0.692	104
Mercury	0.00131	0.000064 J	0.000714	54[(b)]
Nickel	2.22	0.015 U	2.36 J	106
Selenium	0.887	0.042 U	0.938	106
Silver	0.333	0.005 U	0.322	97
Thallium	1.552	0.00021J	1.64	105
Vanadium	1.11	0.003 U	1.07 J	96
Zinc	2.22	1.28 J	3.61 J	105

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

(a) MS recoveries have been corrected for contribution of analyte concentration in the preparation blank.
(b) No acceptance criteria provided for mercury analysis.

Two matrix spikes were prepared for the AP-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 spikes were prepared and analyzed. The 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

Table E.4. Post Spike Results

Post Spike Success Criteria: 75%-125%				
Analyte	**Expected Spike Conc (mg/L)**	**Sample (mg/L)**	**Post Spike (mg/L)**	**Recovery (%)[(a)]**
Antimony	1.25	0.028 U	1.29	103
Arsenic	1.25	0.045 U	1.29 J	103
Barium	0.25	0.30 J	0.40 J	102
Beryllium	0.05	0.002 J	0.05 J	95
Boron	1.00	1.36	1.74	106
Cadmium	0.25	0.01 J	0.249	97
Chromium	0.50	0.02 J	0.53 J	103
Mercury	0.00200	0.0000039 J	0.00209	105[(b)]
Lead	1.25	0.035 U	1.30	104
Nickel	0.50	0.015 J	0.53 J	105
Selenium	1.25	0.042 U	1.29	103
Silver	0.25	0.005 U	0.239	96
Thallium	0.005	0.00021 J	0.00399	76
Vanadium	0.50	0.003 U	0.47 J	95
Zinc	0.75	1.29 J	1.46 J	109

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

(a) PS recoveries have been corrected for contribution of analyte concentration in the preparation blank.
(b) No acceptance criteria provided for mercury analysis.

E.5.1 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 ≥ 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 AP-101 LAW glass sample. The post spike recovery was within the success criterion.

ICP-MS (Tl only)

The post spike recovery was within the success criteria.

E.5.2 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.6 Modifications to Procedures

No modifications were made to the test plan.

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