

Vitrification and testing of a Hanford high-level waste sample. Part 1: Glass fabrication, and chemical and radiochemical analysis

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Abstract

The Hanford radioactive tank waste will be separated into low-activity waste and high-level waste that will both be vitrified into borosilicate glasses. To demonstrate the feasibility of vitrification and the durability of the high-level waste glass, a high-level waste sample from Tank AZ-101 was processed to glass, analyzed with respect to chemical composition, radionuclide content, waste loading, and the presence of crystalline phases and then tested for leachability. The glass was analyzed with inductively coupled plasma-atomic emission spectroscopy, inductively coupled plasma-mass spectrometry, γ -energy spectrometry, α -spectrometry, and liquid scintillation counting. The WISE Uranium Project calculator was used to calculate the main sources of radioactivity to the year 3115. The observed crystallinity and the results of leachability testing of the glass will be reported in Part 2 of this paper.

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1. Introduction

Radioactive waste currently stored in underground tanks at Hanford will be treated for geologic disposal: the waste will be separated into the high-level waste (HLW) and low activity waste fractions and both will be immobilized in the form of glasses [1]. The primary objective of this study was to demonstrate that glass, made from a HLW sample, met the acceptance, regulatory, and de-listing specifications concerning chemical and radionuclide composition, waste loading, crystallinity, and leachability [2–6]. The source of the HLW sam-

ple was the Hanford Tank AZ-101 and $3.8 \times 10^3 \text{ m}^3$ capacity, containing 64 Mg of nonvolatile HLW components. Mineral additives were mixed with the waste to obtain a processable glass with properties required for the repository and to achieve the highest waste loading compatible with the glass-property constraints and waste-processing uncertainties.

To select glass-forming and modifying ingredients, glass must be carefully formulated for each waste. Glass components are subjected to the mass balance represented by the equation

$$Ww_i + (W - 1)a_i = g_i \quad (i = 1, 2, \dots, N), \quad (1)$$

where w_i , a_i , and g_i are the i th component mass fraction in the nonvolatile portion of HLW, additive mix, and HLW glass, respectively, W is the waste loading, and N is the number of glass components. The task is to

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determine the a_i values, i.e., the proportions in which the mineral additives are mixed with the waste. Ideally, the resulting glass should have maximum waste loading and optimum processing properties, and it must satisfy regulatory requirements.

The problem of glass formulation and its solution have been described in several reports [7–10]. Briefly, if the key glass properties are known as functions of glass composition, Eq. (1) relates a_i s and W to the property values; consequently, the optimum additive mix composition, the maximum waste loading, and the target glass composition can be determined with an optimization software.

Because the functions relating glass properties to glass composition are based on a limited number of data and are subject to uncertainties, it is necessary to verify the results by fabricating the glass in the laboratory and measuring its key properties. Glass formulation is then adjusted to correct for the differences between the estimated and actual property values. This glass development work is done with nonradioactive simulants. The final step is making the glass from the real waste following procedures that closely simulate the conditions of the large-scale process.

The simulated AZ-101 HLW was developed and tested in the Vitreous State Laboratory (VSL) [11]. According to the VSL recipe, AZ-101 HLW sludge was to be blended with the Cs and Tc eluates in the proportions corresponding to the tank inventories at which the HLW blend is expected to be vitrified. Because the required volumes of eluates were not available, corrective chemicals were used to compensate for the deficit [12]. The melter feed was then prepared with the modified recipe and vitrified. The chemical and radiochemical analyses of the HLW glass are described in the following sections. The results of crystallinity and leachability studies will be reported in Part 2 of this paper.

The main objectives [2,4] of chemical analysis were to identify and quantify inorganic components present in the HLW glass at >0.5 mass% and to ensure that the waste loading was consistent with the minimum concentration of waste-component limits. For radiochemical analysis, the main objectives were to identify and quantify radionuclides with half lives ($t_{0.5}$) > 10 years and activities >0.05% of the total radioactive inventory as indexed to the years 2015 and 3115 [4]; it was also required to determine the total and fissile U and Pu content and isotope fractions in a canister into which the HLW glass is going to be poured in the vitrification plant.

2. Procedure

2.1. Glass formulation

The sample of pretreated AZ-101 HLW sludge was mixed with Cs and Tc ion exchange eluates from the

pretreatment of low-activity waste from Tank AZ-101 and Tank AP-101. Analytical laboratories provided the compositions of waste sludges and eluates in terms of concentrations of individual elements or anions [13].

Note: Waste glass is commonly formulated in terms of glass components that are conventionally defined as oxides and halides [10]. Though this convention does not reflect all details of glass structure, it greatly simplifies glass-formulation calculations. It is customary to represent each oxide by its prevalent valence and treat the halides as elements. Selecting the most prevalent oxide forms gives a close approximation of the actual oxygen content of the glass. An accurate account of oxygen in the glass is not possible since the oxidation–reduction state of the glass varies during vitrification and depends on the actual feed makeup (such as additions of reducing agents) and melter operation (bubbling). Accounting for halides as halogens means that the cations associated with halogens are represented at oxides; this error is considered minor because of small fractions of halogens in borosilicate HLW glasses. Although some components are actually highly volatile (chlorides and bromides), it is assumed that they are retained in the glass as long as they are present in minuscule concentrations. All waste components except NO_x , and CO_x , and iodine are considered nonvolatile, even though some fraction of some components (Cl, Br, SO_x , and Tc) may volatilize during melting, and traces of N and C are retained in the glass. Finally, some metallic oxides (PdO and Ag_2O) can get reduced to metals at elevated temperatures, ascend to the melt surface in oxygen bubbles, and alloy with Pt–Rh crucible walls. These reactions were disregarded because of the tiny fractions of these oxides in the glass (≤ 0.1 mass%).

As stated above, the HLW for vitrification is a blend of the HLW sludge with intermediate HLW streams (Cs and Tc eluates) from low-activity waste pretreatment. Converting analytical data for these wastes to compositions in terms of glass components, we obtain the j th glass component mass per unit mass of HLW (c_j) and per unit volume of i th eluate (c_{ij}). The mass fractions of the nonvolatile portions of the individual waste streams are then calculated using the formulas

$$h_j = \frac{c_j}{\sum_{j=1}^G c_j} \quad (2)$$

and

$$e_{ij} = \frac{c_{ij}}{\sum_{j=1}^G c_{ij}}, \quad (3)$$

where h_j , and e_{ij} are the j th glass component mass fraction in the nonvolatile portions of the pretreated HLW sludge and the i th eluate, respectively, and G is the number of nonvolatile components present in the HLW blend.

The blended HLW composition in terms of glass components is then

$$w_j = Hh_j + \sum_{i=1}^E B_i e_{ij}, \tag{4}$$

where w_j is the j th glass component mass fraction in the nonvolatile portion of the blended HLW, H is the fraction of glass components in the blended HLW from the HLW sludge, B_i is the fraction of glass components in the blended HLW from the i th eluate, and E is the number of eluates (four different eluates were blended with the AZ-101 HLW sample).

By Eqs. (2) and (3), $\sum_{j=1}^G h_j = 1$, and $\sum_{j=1}^G e_{ij} = 1$. Because of the total mass balance

$$H + \sum_{i=1}^E B_i = 1, \tag{5}$$

we also have $\sum_{j=1}^G w_j = 1$.

Table 1 shows the compositions of the dry AZ-101 HLW and the eluates in terms of glass components (as oxides and halogens). To obtain w_j from Eq. (4), the B_i values are expressed as functions of the proportions at which the intermediate wastes are blended with the HLW sludge:

$$B_i = \frac{b_i e_i}{\sum_{j=1}^G c_j + \sum_{i=1}^E b_i e_i}, \tag{6}$$

where $e_i = \sum_{j=1}^G c_{ij}$ is the total mass of glass components per a unit mass of HLW, and $b_i = V_i/M$ is the i th eluate blending volume; here V_i is the i th eluate volume to be mixed with the mass M of dry HLW.

The available mass of the AZ-101 dry sludge was $M = 66.5$ g. Both the required volumes (based on the tank inventory) of eluates and those available for this task are listed in Table 2, which also summarizes eluate properties and lists the e_i and B_i values, both originally required and availability-based. By Eq. (5), $H = 0.9841$ when available amounts of eluates are used.

The amounts of corrective chemicals needed to compensate for the lack of eluates can be determined by having the composition, the blending data, and the glass composition designed at VSL [11], shown in Table 3 as the ‘HLW Glass I’. The corrective addition, based on the missing amounts of eluates, is listed in Table 3. Being nonradiative, the corrective chemicals are conveniently added to the melter feed with the mineral additives. The waste loading, $W = 0.3175$, as determined at the VSL, is now divided into two parts, one due to the actual waste blend and the other due to the corrective chemicals:

$$Ww_j = (W - S)d_j + Ss_j, \tag{7}$$

where S is the loading fraction of corrective chemicals, and s_j and d_j are j th component mass fractions in the nonvolatile portion of the corrective chemical mix and

Table 1
Compositions of pretreated AZ-101 HLW sample and the Cs and Tc eluates in g/kg^a

	HLW	Eluates			
		AZ-101	AP-101, Cs	AZ-101, Cs	AP-101, Tc
Ag ₂ O	1.21				
Al ₂ O ₃	236.61	11.45		23.74	
B ₂ O ₃	0.37	79.68	20.68	248.30	400.47
BaO	2.11	0.18	1.91		
BeO	0.09				
Bi ₂ O ₃	0.21				
Br					59.43
CaO	13.17	22.61	25.81		
CdO	20.77	1.04	1.56		
Ce ₂ O ₃	7.70				
Cl	0.88			2.13	0.76
CoO	0.20				
Cr ₂ O ₃	4.19	10.41	32.96		1.00
CuO	0.92	1.77		1.21	
F	0.49			2.61	2.68
Fe ₂ O ₃	362.77	4.26	6.64		
K ₂ O	3.02	66.92			69.49
La ₂ O ₃	8.54				
Li ₂ O	0.31				
MgO	3.20				
MnO ₂	10.64				
MoO ₃	0.10				
Na ₂ O	92.19	574.55	739.60	367.30	396.04
Nd ₂ O ₃	6.27				
NiO	15.95	1.22		1.35	
P ₂ O ₅	12.94				1.40
PbO	2.33	3.32			
PdO	3.32				
Rh ₂ O ₃	0.79				
Ru ₂ O ₃	2.48				
SO ₃	2.52		170.84	4.11	14.20
SiO ₂	35.01	108.01		349.26	54.52
SnO ₂	5.73				
SrO	5.06				
TiO ₂	0.37				
UO ₂	26.31	114.58			
Y ₂ O ₃	0.61				
ZnO	0.43				
ZrO ₂	110.17				

^a MnO₂, SnO, Ru₂O₃, and UO₂ are VSL-reported oxides; in Section 3, glass composition is expressed in terms of MnO, SnO₂, RuO₂, and UO₃.

the actual waste blend, respectively. By rearranging Eq. (7), we have

$$S = W \frac{w_j - d_j}{s_j - d_j}. \tag{8}$$

The actual value of S , shown in the first row of Table 3, was obtained for $j \equiv \text{Na}_2\text{O}$ as the major waste component.

Table 2
Cs and Tc eluates

Tank		AP-101	AZ-101	AP-101	AZ-101
		¹³⁷ Cs	¹³⁷ Cs	⁹⁹ Tc	⁹⁹ Tc
Eluate					
Density	g/mL	1.017	1.012	0.996	0.998
Solid content	mass%	0.34 ± 0.02	0.48 ± 0.05	0.06 ± 0.02	0.1 ^a
Glass components content	mass%	0.4 ± 0.2	0.19 ± 0.07	0.3 ± 0.2	
Glass components concentration (<i>c_i</i>)	g/L	1.980	1.464	1.035	0.745
Cs/Tc radioactivity	MBq/mL	28.3	481	0.0154	0.138
Required blending volume (<i>b_i</i>)	L/kg	7.146	4.048	4.364	2.897
Total required volume (<i>V_i</i>)	mL	475	269	290	193
Available volume (<i>V_i</i>)	mL	171	235	75	127
Actual blending volume (<i>b_i</i>)	L/kg	2.573	3.537	1.132	1.914
Required blending mass fraction (<i>B_i</i>)		0.0172	0.0072	0.0055	0.0026
Actual blending mass fraction (<i>B_i</i>)		0.0063	0.0064	0.0014	0.0018
Required radioactivity	GBq	13.5	129	0.0045	0.0265
Actual radioactivity	GBq	4.84	113	0.0012	0.0175

^a Estimated value.

The mass of glass, M_G , to be made from $M = 66.5$ g of AZ-101 dry sludge was determined as follows. The glass contains $W - S$ glass components from the blended waste that contains H glass components from AZ-101 HLW. Hence,

$$M_G = \frac{M}{(W - S)H} \sum_{j=1}^G c_j = 173 \text{ g.} \quad (9)$$

This glass, though nearly identical in chemistry to the Waste Treatment Plant (WTP) anticipated formulation, is, by Table 2, 17.5% lower in radioactive component loading.

Table 4 lists batch chemicals containing glass-forming and modifying additives plus corrective chemicals for 173 g glass. Uranium oxide was added to the mix to match an updated AZ-101 composition. The extremely minor components that would make <0.02 mass% in glass (BaO, Br, CdO, Cl, CuO, F, Fe₂O₃, NiO, P₂O₅, and PbO) and SO₃ were deleted from the corrective chemicals. Although Al₂O₃ was not deleted from the list of additives, an alumina source is not included in Table 4 because, as Table 5 shows, the silica sand contains 0.14 mass% Al₂O₃ as an impurity, more than the amount of Al₂O₃ from missing eluates. As a result, the final glass, denoted as 'HLW Glass II' in Table 3, is 0.05 mass% higher in Al₂O₃ than the glass designed at VSL.

2.2. Glass fabrication

The HLW melter feed was melted in a hot cell. The pretreated sludge was emptied into a 2-L stainless steel vessel, stirred vigorously for 25 min with a magnetic stir bar, and heated to reduce its volume. The Cs and Tc eluates were added to the boiling sludge, while heating and

stirring continued for 3 h. The blended HLW was stirred and kept warm for an additional 1 h. The additives (Table 4) were premixed in an agate milling chamber for 4 min, and the mix was added to the blended HLW. To evaporate nearly all of the water, the resulting melter feed slurry was heated for 4.2 h on a hot plate and vigorously stirred, first with a magnetic stirrer until it became too thick and then manually with a stainless steel spatula. When the slurry dried into hard chunks of melter feed, it was transferred to a 200-mL Pt10%Rh crucible and placed in an oven preheated at 200 °C. Drying continued for 2.2 h while the temperature was gradually increased to 300 °C. The crucible was then placed into a furnace at 600 °C and calcined for 1 h.

The calcined feed was ground in an automated alumina grinder for 10 min and passed through a 40-mesh sieve. Grinding and sieving was repeated until all calcined feed passed through the 40-mesh sieve. The calcine was added back to the crucible and melted at 1150 °C for 2.5 h; it was covered with a lid after 0.5 h once the gas-evolving reactions were complete. The melt was then poured onto a stainless steel plate.

All glass (total of 162.95 g) was stored in a clean stainless steel container. Of this amount, 0.40 g remained attached to crucible walls; the rest of the glass (162.55 g) was usable. The 10-g difference between the calculated and actually prepared glass was due to process losses, such as the transfer of dry feed from the stainless steel beaker to the platinum crucible, feed removal from stirring tools, and grinding and sieving the calcine.

2.3. Chemical analysis

The chemical composition of the AZ-101 HLW glass was measured in duplicate along with an analytical stan-

Table 3
Composition of blended AZ-101 HLW, additives, corrective chemicals, and HLW glass (in mass fractions)^a

Glass component	Blended AZ-101	Mineral additives	Corrective chemicals	HLW Glass I	HLW Glass II
Loading fraction	0.3122	0.6825	0.0053		
Ag ₂ O	0.0012			0.0004	0.0004
Al ₂ O ₃	0.2330		0.0132	0.0728	0.0733
B ₂ O ₃	0.0021	0.1538	0.1341	0.1064	0.1063
BaO	0.0021		0.0002	0.0007	0.0007
BeO	0.0001			0.0000	0.0000
Bi ₂ O ₃	0.0002			0.0001	0.0001
Br	0.0001		0.0031	0.0000	0.0000
CaO	0.0133		0.0161	0.0042	0.0042
CdO	0.0205		0.0008	0.0064	0.0064
Ce ₂ O ₃	0.0076			0.0024	0.0024
Cl	0.0009		0.0006	0.0003	0.0003
CoO	0.0002			0.0001	0.0001
Cr ₂ O ₃	0.0044		0.0086	0.0014	0.0014
CuO	0.0009		0.0014	0.0003	0.0003
F	0.0005		0.0008	0.0002	0.0002
Fe ₂ O ₃	0.3571		0.0031	0.1115	0.1116
K ₂ O	0.0035		0.0473	0.0013	0.0013
La ₂ O ₃	0.0084			0.0026	0.0026
Li ₂ O	0.0003	0.0549		0.0376	0.0376
MgO	0.0032			0.0010	0.0011
MnO ₂	0.0105			0.0033	0.0033
MoO ₃	0.0001			0.0000	0.0000
Na ₂ O	0.1003	0.1245	0.5241	0.1191	0.1187
Nd ₂ O ₃	0.0062			0.0019	0.0019
NiO	0.0157		0.0011	0.0049	0.0049
P ₂ O ₅	0.0127		0.0001	0.0040	0.0040
PbO	0.0023		0.0022	0.0007	0.0007
PdO	0.0033			0.0010	0.0010
Rh ₂ O ₃	0.0008			0.0002	0.0002
Ru ₂ O ₃	0.0024			0.0008	0.0008
SO ₃	0.0036		0.0110	0.0012	0.0011
SiO ₂	0.0357	0.6374	0.1575	0.4470	0.4468
SnO	0.0056			0.0018	0.0018
SrO	0.0050			0.0016	0.0016
TiO ₂	0.0004			0.0001	0.0002
UO ₂	0.0266		0.0747	0.0087	0.0087
Y ₂ O ₃	0.0006			0.0002	0.0002
ZnO	0.0004	0.0293		0.0201	0.0201
ZrO ₂	0.1084			0.0338	0.0338
Sum	1.0000	1.0000	1.0000	1.0000	1.0000

^a MnO₂, SnO, Ru₂O₃, and UO₂ are VSL-reported oxides; in the rest of this paper, glass composition is expressed in terms of MnO, SnO₂, RuO₂, and UO₃.

standard reference glass (ARG-1) [14] and low-activity test standard reference material (LRM) [15]. Three methods were used to solubilize the glass: a Na₂O₂–NaOH fusion in a Zr crucible, a KOH–KNO₃ fusion in a Ni crucible, and acid digestion [13]. Cation analysis was performed with inductively coupled plasma-atomic emission spectroscopy (ICP-AES). A portion of the Na₂O₂–NaOH fusion samples was taken for radiochemical analysis and inductively coupled plasma-mass spectrometry (ICP-MS) analysis. Corrections to the waste-glass analysis based on standard glass analyses and blanks were

performed in six steps [16]: (1) analyte screening, (2) blank correction, (3) nondetect replacement, (4) relative standard deviation computation, (5) bias correction, and (6) normalization.

Fusions procedures were done with an ~0.10-g sample and acid digestion with a 0.2-g sample; the crucible content was then diluted to 100 mL. Before analysis by ICP-AES, the sample prepared by the fusion processes was diluted five-fold; the ICP-AES results were adjusted for all laboratory processing factors and instrument dilutions.

Table 4
Chemical additives for 173 g glass

Chemical	Mass (g)
Na ₂ B ₄ O ₇ · 10H ₂ O	48.460
CaCO ₃	0.013
Cr ₂ O ₃	0.006
K ₂ CO ₃	0.060
Li ₂ CO ₃	16.076
Na ₂ CO ₃	11.907
SiO ₂	75.179
U ₃ O ₈	0.067
ZnO	3.443
Total	155.211

Table 5
Mass fractions of impurities in batch chemicals

	Lithium carbonate	Sodium carbonate	Silica	Zinc oxide
Al ₂ O ₃			0.0014	
CaO			0.0001	
CdO				0.0001
Cl	0.0001	0.0002		
Fe ₂ O ₃	0.0004		0.0002	
MgO	0.0010		0.0001	
TiO ₂			0.0001	

For fusion processes, two process blanks, two laboratory-control samples (~0.1 g of LRM and ARG-1 glasses) and a duplicate were prepared with the samples. For the digestion procedure, a process blank, matrix spike, laboratory-control samples (~0.2 g of LRM and ARG-1 glasses), and duplicate were prepared with the

samples. Recovery values were listed for all analytes included in the spike that were measured at or above the estimated quantitation level. A matrix spike was prepared using the acid-digestion sample.

2.4. Radiochemical analysis

The radiochemical composition was obtained with γ -energy spectrometry (GEA), α -spectrometry, and liquid scintillation counting on a sample of AZ-101 HLW glass solubilized with a Na₂O₂–NaOH fusion. For GEA, duplicate samples and blanks were directly aliquoted from fusion solutions. Daily control counts and weekly background checks were measured for each γ -detector to ensure the detector performance. Detection limits were calculated for all isotopes of interest, i.e., ⁶⁰Co, ⁹⁵Nb, ¹¹³Sn, ¹²⁵Sb, ¹²⁶Sn/Sb, ¹³⁴Cs, ¹³⁷Cs, ¹⁴⁴Ce, ¹⁵²Eu, ¹⁵⁴Eu, ¹⁵⁵Eu, ²³²Th, and ²⁴¹Am. The samples were counted for extended counting times to obtain lower detection limits. For ⁹⁰Sr activity, Sr was chemically separated from duplicate samples, and the ⁹⁰Sr activities were measured with an LB4100 gas proportional counter. A ⁸⁵Sr tracer was added to each sample to determine the chemical yield by γ -counting. For ⁶³Ni activity, Ni was chemically separated from the sample, and the ⁶³Ni activity was measured with liquid scintillation counting on a Packard 2550. Pu and Am/Cm were separated sequentially, precipitation plated for counting, and counted with α -spectrometry. A ²⁴²Pu tracer was used to determine the Pu yields. For Am/Cm, an ²⁴³Am tracer was used to determine the Am/Cm yields. The activity of ¹⁵¹Sm was measured in an Am–Cm α -counting mount by liquid scintillation counting. Because

Table 6
Radioisotopes with $t_{0.5} > 10$ years, the N/N_0 values at $t = 11$ and 1111 years,^a and the principal daughter products

	$t_{0.5}$ (years)	N/N_0 (2015)	N/N_0 (3115)	Significant daughter radioisotopes	$t_{0.5}$ (years)
⁹⁰ Sr	28.5	7.7×10^{-01}	2.7×10^{-12}	Short lived	
⁹⁹ Tc	2.13×10^5	1.0	1.0		
¹³⁷ Cs	30	0.78	1.0×10^{-11}	Short lived	
¹⁵¹ Sm	90	0.92	2.2×10^{-04}		
²³³ U	1.59×10^5	1.0	1.0	²²⁹ Th	7.3×10^3
²³⁴ U	2.45×10^5	1.0	1.0	²³⁰ Th	7.7×10^4
²³⁵ U	7.04×10^8	1.0	1.0	Short lived	
²³⁶ U	2.34×10^7	1.0	1.0	²³² Th	1.4×10^{10}
²³⁸ U	4.47×10^9	1.0	1.0	Short lived	
²³⁷ Np	2.14×10^6	1.0	1.0	²³³ Pa → ²³³ U	0.07; 1.59×10^5
²³⁸ Pu	87.7	0.92	1.7×10^{-04}	²³⁴ U	2.45×10^5
²³⁹ Pu	2.41×10^4	1.0	0.97	²³⁵ U	7.04×10^8
²⁴⁰ Pu	6.56×10^3	1.0	0.89	²³⁶ U	2.34×10^7
²⁴¹ Pu	14.4	0.59	1.3×10^{-23}	²³⁷ U → ²³⁷ Np	0.02; 2.14×10^6
²⁴² Pu	3.76×10^5	1.0	1.0	²³⁸ U	4.47×10^9
²⁴¹ Am	432.7	0.98	0.17	²³⁷ Np	2.14×10^6
²⁴² Am	141	0.95	4.6×10^{-03}	²⁴² Cm → ²³⁸ Pu → ²³⁴ U	0.45; 87.7; 2.45×10^5
²⁴³ Cm	28.5	0.77	2.7×10^{-12}	²³⁹ Pu	2.41×10^4

^a $t = 0$ at 2004.

^{90}Y , the ^{90}Sr 's daughter, is chemically separated with the Am–Cm fraction, several weeks of decay were required to avoid interference with β -counting.

For ICP-MS, AZ-101-HLW glass was prepared with Na_2O_2 –NaOH fusion (both with and without iodine option), KOH– KNO_3 fusion, and acid digestion. The prepared samples and batch quality control samples were analyzed with ICP-MS. The final results were corrected for laboratory preparation and for dilutions performed during analyses. The concentrations of the Pu isotopes were determined with a ^{239}Pu calibration standard. Since minor Pu isotope standards were not available, the quality control checks for ^{239}Pu were taken to represent the quality control check for the other Pu isotopes. The isotope concentrations of the U isotopes were determined with ^{238}U from a natural U calibration standard. Because minor U isotope standards were not available, the quality control checks for ^{238}U were taken to represent the other U isotopes. The instrument detection limit

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

The radioactive decay and future activities were determined with the WISE Uranium Project calculator [17]. Table 6 lists the $t_{0.5}$ values of the main isotopes and their remaining fractions, N/N_0 , in years 2015 and 3115; here N_0 and N are the number of radioisotope atoms at the present time and after the elapsed time, t .

3. Results

3.1. Chemical composition

Table 7 lists the results of glass-sample analyses, and Table 8 lists the reported and analyzed compositions of

Table 7
ICP-AES data (in mg element/g glass) for AZ-101 HLW glass sample composition

	Na_2O_2 –NaOH fusion ^a				KOH– KNO_3 fusion ^b				Acid digestion ^c		
	Blank		AZ-101-HLW		Blank		AZ-101-HLW		Blank	AZ-101-HLW	
Ag	0.00	0.00	0.18	0.05	0.00	0.07	0.12	0.07	0.00	0.05	0.05
Al	0.33	0.26	49.50	51.20	1.47	0.67	49.00	48.10	0.00	44.80	44.20
B	0.00	0.00	33.50	34.60	0.12	0.00	34.30	33.60	0.00	31.80	29.60
Ba	0.00	0.00	0.65	0.69	0.02	0.04	0.67	0.65	0.00	0.71	0.70
Bi	0.00	0.00	0.29	0.23	0.25	0.20	0.46	0.33	0.00	0.12	0.13
Ca	4.30	3.00	7.41	7.30	0.00	0.78	3.80	3.60	0.00	3.45	3.43
Cd	0.00	0.00	6.28	6.44	0.00	0.00	6.32	6.27	0.00	6.35	6.33
Ce	0.00	0.00	0.19	0.18	0.00	0.00	0.93	0.64	0.00	0.69	0.68
Cr	0.07	0.00	0.91	0.92	0.07	0.06	0.91	0.89	0.00	0.93	0.93
Cu	0.05	0.00	0.34	0.34	0.11	0.13	0.43	0.43	0.00	0.30	0.30
Fe	2.54	0.59	83.80	86.20	0.90	0.33	88.10	84.50	0.02	88.00	87.00
K	32.00	20.00	15.00	6.70					0.00	0.27	0.25
La	0.00	0.00	2.57	2.70	0.00	0.00	2.60	2.62	0.00	2.70	2.68
Li	0.13	0.11	17.60	18.30	0.18	0.36	17.40	16.70	0.00	17.90	17.70
Mg	0.00	0.00	0.90	0.88	0.35	0.34	0.46	0.93	0.00	0.78	0.79
Mn	0.00	0.00	2.21	2.27	0.17	0.20	2.50	2.40	0.00	2.34	2.32
Na					8.47	13.90	94.60	87.90	0.10	85.00	84.60
Nd	0.00	0.00	1.96	2.06	0.00	0.00	1.80	2.00	0.00	1.95	1.94
Ni	0.37	0.00	4.18	4.25					0.00	4.38	4.35
P	0.54	0.24	3.75	2.61	1.20	0.63	2.50	2.33	0.00	2.13	2.13
Pb	0.00	0.00	0.77	0.73	0.24	0.30	0.46	0.84	0.00	0.63	0.61
Rh	0.00	0.00	0.92	0.72	0.00	0.00	1.39	0.30	0.00	0.21	0.22
Si	1.20	0.00	213.00	219.00	1.80	0.00	212.00	211.00			
Sn	1.50	0.00	2.50	1.90	0.00	0.00	2.32	1.40	0.00	0.81	0.86
Sr	0.12	0.09	1.68	1.76	0.00	0.00	1.64	1.58	0.00	1.69	1.68
Ti	0.00	0.00	0.13	0.15	0.00	0.00	0.12	0.15	0.00	0.14	0.14
U	0.00	0.00	9.70	8.80	0.00	0.00	9.28	7.60	0.00	5.43	5.43
Y	0.00	0.00	0.17	0.18	0.00	0.00	0.23	0.17	0.00	0.17	0.17
Zn	0.00	0.00	16.20	16.60	0.00	0.00	15.90	16.00	0.01	15.70	15.60
Zr					0.00	0.00	28.20	27.70	0.00	29.30	29.20

^a Na and Zr fractions are not obtained with Na_2O_2 –NaOH fusion.

^b K and Ni fractions are not obtained with KOH– KNO_3 fusion.

^c Si fraction is not obtained with acid digestion.

Table 8
ICP-AES data, in mg element/g glass, for standard reference glasses^a

	ARG-1					LRM				
	Reported [14]		Na ₂ O ₂ –NaOH fusion	KOH–KNO ₃ fusion	Acid digestion	Reported [15]		Na ₂ O ₂ –NaOH fusion	KOH–KNO ₃ fusion	Acid digestion
	Mean	STD				Mean	STD			
Ag			0.06	0.05	0.01			0.00	0.05	0.00
Al	25.03	0.116	25.20	26.50	25.00	50.33	0.630	53.80	54.80	52.70
B	26.93	0.124	26.10	27.00	26.40	24.38	0.453	25.40	26.20	23.90
Ba	0.79	0.009	0.75	0.76	0.81	0.01	0.009	0.01	0.02	0.01
Bi			0.22	0.29	0.11			0.00	0.25	0.03
Ca	10.22	0.064	14.20	10.80	10.60	3.86	0.021	7.78	4.20	3.74
Cd	0.00	0.000	0.00	0.00	0.00	1.40	0.026	1.46	1.59	1.51
Ce			0.00	0.00	0.00			0.00	0.00	0.00
Cr	0.64	0.007	0.66	0.69	0.67	1.30	0.034	1.36	1.42	1.37
Cu	0.03	0.001	0.09	0.21	0.04	0.00	0.000	0.00	0.15	0.00
Fe	97.92	0.511	94.50	97.50	97.50	9.65	0.294	10.40	10.60	10.30
K	22.50	0.133	44.20		22.90	12.29	0.066	24.00		12.20
La	0.00	0.000	0.00	0.00	0.01	0.17	0.004	0.14	0.12	0.09
Li	14.91	0.070	15.10	14.50	15.50	0.51	0.019	0.60	0.65	0.49
Mg	5.19	0.030	5.43	5.70	5.64	0.60	0.024	0.74	1.00	0.70
Mn	14.60	0.076	14.40	15.10	15.20	0.62	0.031	0.62	0.79	0.63
Na	85.31	0.171		90.30	85.60	148.59	1.847		165.00	154.00
Nd			0.22	0.19	0.00			0.00	0.00	0.00
Ni	8.25	0.047	8.01		8.43	1.49	0.102	1.53		1.54
P	0.96	0.048	1.30	1.80	1.26	2.36	0.786	2.32	2.99	2.33
Pb	0.00	0.000	0.23	0.38	0.03	0.93	0.074	1.10	1.20	0.90
Rh			0.00	0.00	0.00			0.00	0.00	0.00
Si	223.90	0.734	226.00	230.00		253.35	3.515	269.00	272.00	
Sn			1.30	1.00	0.32			1.40	0.94	0.09
Sr	0.03	0.008	0.15	0.04	0.03	0.00	0.000	0.14	0.03	0.02
Ti	6.89	0.042	6.24	6.19	6.81	0.60	0.024	0.59	0.62	0.60
U			0.00	0.00	0.00			0.00	0.00	0.00
Y			0.00	0.00	0.01			0.00	0.00	0.02
Zn	0.16	0.129	0.23	0.22	0.19	0.00	0.000	0.00	0.00	0.01
Zr	0.96	0.037		0.96	1.12	6.88	0.030		7.04	7.15

^a See Table 7 footnotes.

the standard reference glasses. The reported data were used to obtain the final adjusted normalized results for each of the two replicates in each of the three digestions. Unanalyzed and undetected components (Cl, CoO, F, PdO, RuO₂, and SO₃) were substituted by their assumed target values. Where concentrations were not obtained (Na and Zr with Na₂O₂–NaOH fusion, K and Ni with KOH–KNO₃ fusion, and Si with acid digestion), values were substituted with inverse variance weighted means of the concentrations from the other two methods before the final normalization. Table 9 summarizes the results for each sample-preparation method and the overall average. It also shows, in the last column, the composition of the nonradioactive simulant, HLW98-95, made and analyzed at VSL [11]. Finally, the last two rows present the sums of squared standard deviations, $\Sigma\sigma_{iA}^2$, for all constituents listed in the target composition and the squared error, $\Sigma(w_{iA} - w_{iT})^2$ where w_{iA} and w_{iT} are

the component analyzed and target mass fraction, respectively. The chemical constituents present at mass fractions >0.5 mass% (Na₂O, Fe₂O₃, B₂O₃, Al₂O₃, Li₂O, ZrO₂, ZnO, UO₃, and CdO) for which identification and quantitation is required [4], show reasonable agreement with the target (NiO, CaO, P₂O₅, MnO, and La₂O₃ had some mass fractions determined as >0.5 mass% by at least one ICP analysis). The details of quality control measurements are provided in Ref. [18].

The waste-loading fraction in the glass was obtained from component mass balances, rearranging modified Eq. (1) as

$$W_i = \frac{g_{iA} - a_i}{w_i - a_i}, \quad (10)$$

where W_i is the estimated waste loading based on i th component mass balance, and g_{iA} is the i th component

Table 9
Averaged best analytical estimates for AZ-101 HLW glass composition in mass fractions compared to target^a

	Na ₂ O ₂ –NaOH	KOH–KNO ₃	Acid digestion	Average	Target	HLW98-95 ^b
SiO ₂	0.4357	0.4421	0.4512	0.4430	0.4469	0.425
Na ₂ O	0.1084	0.1023	0.1066	0.1058	0.1187	0.118
Fe ₂ O ₃	0.1168	0.1210	0.1221	0.1200	0.1116	0.128
B ₂ O ₃	0.1018	0.1063	0.0942	0.1008	0.1063	0.106
Al ₂ O ₃	0.0856	0.0830	0.0784	0.0823	0.0733	0.064
Li ₂ O	0.0379	0.0360	0.0380	0.0373	0.0376	0.038
ZrO ₂	0.0374	0.0369	0.0380	0.0374	0.0338	0.039
ZnO	0.0204	0.0199	0.0195	0.0199	0.0201	0.019
UO ₃	0.0105	0.0100	0.0064	0.0090	0.0092	0.012
CdO	0.0073	0.0064	0.0067	0.0068	0.0064	0.009
NiO	0.0054	0.0054	0.0055	0.0054	0.0049	0.006
CaO	0.0048	0.0047	0.0048	0.0047	0.0042	0.004
P ₂ O ₅	0.0057	0.0033	0.0047	0.0045	0.0040	0.004
MnO	0.0029	0.0029	0.0030	0.0030	0.0027	0.005
La ₂ O ₃	0.0038	0.0044	0.0061	0.0047	0.0026	0.002
Ce ₂ O ₃	0.0002	0.0009	0.0008	0.0006	0.0024	0.003
Nd ₂ O ₃	0.0016	0.0023	0.0011	0.0017	0.0020	0.002
SnO ₂	0.0024	0.0022	0.0023	0.0023	0.0019	0.000
SrO	0.0020	0.0019	0.0020	0.0020	0.0016	0.002
Cr ₂ O ₃	0.0013	0.0012	0.0014	0.0013	0.0014	0.004
K ₂ O	0.0000	0.0003	0.0003	0.0002	0.0013	0.001
MgO	0.0014	0.0006	0.0013	0.0011	0.0011	0.001
SO ₃	0.0011	0.0011	0.0011	0.0011	0.0011	0.001
PdO	0.0010	0.0010	0.0010	0.0010	0.0010	0.001
RuO ₂	0.0008	0.0008	0.0008	0.0008	0.0007	0.000
BaO	0.0008	0.0004	0.0007	0.0006	0.0007	0.001
PbO	0.0004	0.0004	0.0004	0.0004	0.0004	0.001
Ag ₂ O	0.0002	0.0001	0.0001	0.0001	0.0004	0.000
Cl	0.0003	0.0003	0.0003	0.0003	0.0003	0.001
CuO	0.0002	0.0001	0.0003	0.0002	0.0003	0.001
F	0.0002	0.0002	0.0002	0.0002	0.0002	0.000
Rh ₂ O ₃	0.0010	0.0011	0.0003	0.0008	0.0002	0.000
TiO ₂	0.0002	0.0003	0.0002	0.0002	0.0002	0.000
Y ₂ O ₃	0.0002	0.0003	0.0002	0.0002	0.0002	0.000
Bi ₂ O ₃	0.0003	0.0002	0.0001	0.0002	0.0001	0.000
CoO	0.0001	0.0001	0.0001	0.0001	0.0001	0.000
10 ² Σσ _{iA} ²	0.597	0.697	0.412	0.0140		
10 ² Σ(w _{iA} – w _{TA}) ²	42.57	43.21	44.05	43.27		

^a See Table 7 footnotes.

^b Nonradioactive simulant [11].

analyzed mass fraction in glass. The a_i values are listed in Table 3; w_i was obtained from Eq. (7):

$$w_i = \frac{d_i(W - S) + s_i S}{W}, \quad (11)$$

where $W - S = 0.3122$, and $S = 0.0053$ (Table 3).

Table 10 summarizes the W_i values for 7 out of 10 components with the targeted $g_j \geq 0.005$. Na₂O was not included because, as Table 3 shows, its w_i and a_i values are close while the difference $w_i - a_i$ is in the denominator in Eq. (9); this would cause a large error in W_i . UO₃ was not included because of the ambiguity caused by the last-minute update of the waste composition and subsequent addition of U₃O₈ with the minerals. Finally, Al₂O₃ was

not included because its target fraction was exceeded because of a high alumina impurity in the silica sand. The last column in Table 10 shows the relative difference between W_i values and the target waste loading; its value ranges from 1.7% for Li₂O to 11.7% for B₂O₃, reflecting the difference between the measured and targeted fraction (Table 9). The measured waste loading can be defined either as an average value or as a weighted average

$$W_{wa} = \frac{\sum_{i=1}^m W_i g_{iA}}{\sum_{i=1}^m g_{iA}}, \quad (12)$$

where $m = 7$ is the number of components listed in Table 10; $W_{wa} = 0.3324$, a value 4.7 relative % higher than the

Table 10
Component mass balance-estimated waste loading of AZ-101 HLW glass

Glass component	w_i	a_i	g_{iA}^a	W_i^b	$W_i/W - 1$
SiO ₂	0.0377	0.6374	0.4430	0.3242	0.0211
Fe ₂ O ₃	0.3512	0.0000	0.1200	0.3417	0.0763
B ₂ O ₃	0.0043	0.1538	0.1008	0.3547	0.1172
Li ₂ O	0.0003	0.0549	0.0373	0.3230	0.0173
ZrO ₂	0.1066	0.0000	0.0374	0.3512	0.1060
ZnO	0.0004	0.0293	0.0199	0.3255	0.0252
CdO	0.0202	0.0000	0.0068	0.3364	0.0596
Average				0.3367	0.0604
Weighted average				0.3324	0.0468

^a The averaged best analytical estimate.

^b Calculated from Eq. (10), with g_i and a_i as listed in Table 3.

targeted 0.3175. With the waste loading of 0.3324, the total mass of AZ-101 HLW will be 193 Mg.

3.2. Radiochemical composition

The results of measured and calculated activities are summarized in Table 11, which lists averaged activity data for the radionuclides with $t_{0.5} > 10$ years and $>0.05\%$ of the total inventory. The γ -emitters found in the AZ-101 HLW glass were ⁶⁰Co, ¹³⁷Cs, ¹⁵⁴Eu, ¹⁵⁵Eu, and ²⁴¹Am; the β -emitters ⁹⁰Sr, ⁶³Ni, and ¹⁵¹Sm; and the α -emitters ²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu, ²⁴¹Am, ²⁴³Cm, and ²⁴⁴Cm. Of these radioisotopes, three had half-lives <10 years: ⁶⁰Co (5.27 years; 0.106 MBq/g), ¹⁵⁴Eu (8.81 years; 0.124×10^5 MBq/g), and ¹⁵⁵Eu (4.96 years; 0.111 MBq/g). The ²⁴¹Am activities determined by α spectroscopy were in good agreement with those determined by γ -energy analysis. No ¹²⁹I was detected in the glass by ICP-MS (iodine option). Excellent agreement exists between the directly measured ²³⁹⁺²⁴⁰Pu activity (0.131 MBq/g) and that calculated from ICP-MS data (²³⁹Pu activity and ²⁴⁰Pu activity sum to 0.135 MBq/g). The details of quality control measurements are reported in Ref. [18].

The radioactivity of Tc eluates used was 18.7 MBq (Table 2); this would result in 108 MBq/kg of Tc radioactivity in the glass (for 173 g of glass produced). The measured Tc concentration in the glass, using ICP-MS, was 77 mg/kg, corresponding to the Tc radioactivity of 47.4 MBq/kg (Table 11); accordingly, 43.9% Tc was retained in the glass.

About 54 radioisotopes in the decay chains of the AZ-101 HLW radioisotopes were identified with the WISE Uranium Project calculator [17], including the waste isotopes themselves. As Table 11 shows, 2015 radioactivity of about 2.32 GBq/g will be dominated by fission products ⁹⁰Sr with its immediate daughter

Table 11
Half lives in years and averaged AZ-101 HLW glass activities in MBq/g, current and projected to 2015 and 3115

Radioisotopes and significant daughters	$t_{0.5}$	2004 ^c	2015 ^d	3115 ^d
⁶³ Ni	100	0.0910		
⁹⁰ Sr	29.1	921	714	
⁹⁰ Y	4.49×10^{-7}		714	
⁹⁹ Tc ^a	2.13×10^5	0.0474	0.0474	0.0474
¹³⁷ Cs	30.2	566	440	
^{137m} Ba	1.17×10^{-4}		440	
¹⁵¹ Sm	90.0	15.2	14.0	0.0218
²³¹ Pa	3.28×10^4			0.0111
²³⁴ U ^a	2.45×10^5	7.73×10^{-5}		
²³⁵ U ^a	7.04×10^8	3.37×10^{-6}		
²³⁶ U ^a	2.34×10^7	7.40×10^{-6}		
²³⁸ U ^a	4.46×10^9	6.18×10^{-5}		
²³⁷ Np ^a	2.14×10^6	1.51×10^{-3}		0.0111
²³⁸ Pu	87.7	0.0162		
²³⁹ Pu ^a	2.41×10^4	0.105		0.0266
²⁴⁰ Pu ^a	6.54×10^3	0.0300		0.102
²⁴² Pu ^a	3.76×10^5	6.03×10^{-6}		
²⁴¹ Am	432	2.64	2.59	0.445
²⁴³ Cm	29.1	0.0104 ^b		
²⁴⁴ Cm	18.1			
Sum		2992	2325	0.665

^a Activities are based on ICP-MS data.

^b The sum of ²⁴³Cm and ²⁴⁴Cm activities.

^c Measured activities of radioisotopes with $t_{0.5} > 10$ years.

^d Calculated activities (only radioisotopes constituting $>0.05\%$ of the total activity are included).

⁹⁰Y and ¹³⁷Cs with its immediate daughter ^{137m}Ba. By 3115, the total activity will drop to 0.665 MBq/g; the fission products will essentially disappear except for ⁹⁹Tc, a radioisotope contributing a minuscule fraction of the overall activity at 2015; longer lived transuranic radioisotopes will dominate; and ²³¹Pa will become a reportable part of the radionuclide inventory.

Hanford HLW canisters will be 4.5 m high and 0.61 m in diameter and will contain approximately

Table 12
Mass and concentration of U and Pu per WTP canister

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

1.18 m³ of glass. With the estimated glass density of 2.71×10^3 kg/m³, the mass of glass in a canister is 3198 kg (fill tests resulted in 3.10–3.17 Mg of glass in HLW glass canisters [19]). As Table 12 shows, the total U in a WTP canister will be 16.2 kg (14 kg/m³), of which 99.1% will be ²³⁸U and 0.85% ²³⁵U; out of the total Pu mass of 160 g (136 g/m³), 93.1% will be ²³⁹Pu.

4. Conclusions

A sample of pretreated AZ-101 HLW sludge was mixed with Cs and Tc ion exchange eluates and mineral additives and converted to HLW glass; the glass was tested to demonstrate that the large-scale production will satisfy the processing and regulatory requirements. The main results concerning waste loading, chemical composition, and radionuclide content are as follows:

1. The waste loading fraction of AZ-101 HLW glass, 33.24 mass%, was slightly above the target of 31.22 mass%.
2. The glass composition was close to target, containing, on mass basis, 44.3% SiO₂, 12.0% Fe₂O₃, 10.6% Na₂O, 10.1% B₂O₃, 8.2% Al₂O₃, 3.7% Li₂O, 3.7% ZrO₂, 2.0% ZnO, 0.9% UO₃, and 4.5% of other components.
3. The following radionuclides with $t_{0.5} > 10$ years were identified in the glass: ⁶³Ni, ⁹⁰Sr, ⁹⁹Tc, ¹³⁷Cs, ¹⁵¹Sm, ²³⁴U, ²³⁵U, ²³⁶U, ²³⁸U, ²³⁷Np, ²³⁸Pu, ²³⁹Pu, ²⁴⁰Pu, ²⁴²Pu, ²⁴¹Am, ²⁴³Cm, and ²⁴⁴Cm. The 2004 and 2015 activity is mainly due to ⁹⁰Sr (61%) and ¹³⁷Cs (38%) with their immediate daughters, ⁹⁰Y and ^{137m}Ba; in 3115, the main sources of radioactivity will be ²⁴¹Am (67%), ²⁴⁰Pu (15%), ⁹⁹Tc (7%), and ²³⁹Pu (4%).
4. In a WTP canister containing 1.18 m³ of glass, the total mass of U will be 16.2 kg (137 g of ²³⁵U), and the total mass of Pu is 160 g (149 g of ²³⁹Pu). The concentration of Pu in the glass is 136 g/m³. The current isotope mass fractions of U are 0.0067% ²³⁴U, 0.84% ²³⁵U, 0.06% ²³⁶U, and 99.1% ²³⁸U; and those of Pu are 93.1% ²³⁹Pu, 7.21% ²⁴⁰Pu, and 0.08% ²⁴¹Pu.

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