Glass fabrication and product consistency testing of lanthanide borosilicate glass for plutonium disposition

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Abstract

The Department of Energy Office of Environmental Management (DOE/EM) plans to conduct the Plutonium Disposition Project at the Savannah River Site (SRS) in Aiken, SC, to disposition excess weapons-usable plutonium. A plutonium glass waste form is a leading candidate for immobilization of the plutonium for subsequent disposition in a geologic repository. The objectives of this present task were to fabricate plutonium-loaded lanthanide borosilicate (LaBS) Frit B glass and perform testing to provide near-term data that will increase confidence that LaBS glass product is suitable for disposal in the proposed Federal Repository. Specifically, testing was conducted in an effort to provide data to Yucca Mountain Project (YMP) personnel for use in performance assessment calculations. Plutonium-containing LaBS glass with the Frit B composition with a 9.5 wt% PuO_2 loading was prepared for testing. Glass was prepared to support glass durability testing via the ASTM product consistency testing (PCT) at Savannah River National Laboratory (SRNL). The glass was characterized with X-ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS) prior to performance testing. This characterization revealed some crystalline PuO_2 inclusions with disk-like morphology present in the as-fabricated, quench-cooled glass. A series of PCTs was conducted at SRNL with varying exposed surface area and test durations. Filtered leachates from these tests were analyzed to determine the dissolved concentrations of key elements. The leachate solutions were also ultrafiltered to quantify colloid formation. Leached solids from select PCTs were examined in an attempt to evaluate the Pu and neutron absorber release behavior from the glass and to investigate formation of alteration phases on the glass surface. A series of PCTs was conducted at 90 °C in ASTM Type 1 water to compare the Pu LaBS Frit B glass durability to current requirements for high level waste (HLW) glass in a geologic repository. The PCT (7-day static test with powdered glass) results on the Pu-containing LaBS Frit B glass at SA/V of $\approx 2000\ m^{-1}$ showed that the glass was very durable with an average normalized elemental release value for boron of 0.013 g/m^2. This boron release value is $\approx 640\times$ lower than normalized boron release from current environmental assessment (EA) glass used for repository acceptance. The PCT-B (7-, 14-, 28- and 56-day, static test with powdered glass) normalized elemental releases were similar to the normalized elemental release values from PCT-A testing, indicating that the LaBS Frit B glass is very durable as measured by the PCT. Normalized plutonium releases were essentially the same within the analytical uncertainty of the ICP-MS methods used to quantify plutonium in the 0.45 μm-filtered leachates and ultra-filtered leachates, indicating that colloidal plutonium species do not form under the PCT conditions used in this study.
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1. Introduction

The Department of Energy Office of Environmental Management (DOE/EM) plans to conduct the Plutonium Disposition Project at the Savannah River Site (SRS) to disposition excess weapons-usable plutonium. Vitrification appears to be a viable option for the disposition of the plutonium. An important part of the vitrification approach is to reduce the attractiveness of the plutonium by fabricating a plutonium glass form and immobilizing the Pu form within the high level waste (HLW) glass prepared in the defense waste processing facility (DWPF). This process is referred to as the 'can-in-canister' approach [1]. This requires that the current Pu Disposition Project schedule is consistent with DOE/EM plans for immobilizing HLW in the DWPF. Therefore, several inputs are needed to provide confidence that the Pu Disposition Project will meet the project schedule. Key inputs are near-term data that will increase confidence that lanthanide borosilicate (LaBS)

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glass product is suitable for disposal in the Federal Repository.

The Product Consistency Test (PCT) and short-term immersion tests at various temperatures and pHs were identified as means to provide some of the near term LaBS glass performance data [2]. This report describes results of the PCT. Immersion tests on monolithic Pu Frit B LaBS glass specimens are described elsewhere [3]. The PCT is a static test method in which known masses of crushed glass and ASTM Type 1 purified water are reacted for a desired duration [4]. The PCT Method-A test is conducted under specific test conditions: $90 \pm 2\,°C$; 7 days $\pm 2\%$; -100 to $+200$ mesh-size glass; ASTM Type 1 water/glass mass ratio of $10.0 \pm 0.5\,cm^3/g$. The PCT Method-B allows for varying the test conditions (temperature, duration, and glass/water mass ratio are commonly varied). Under PCT conditions, components that are released from the glass as it dissolves accumulate in the solution throughout the test and affect the corrosion rate through solution feedback effects. The primary feedback effects are through the effects of dissolved silica and increased pH. Orthosilicic acid concentration and pH have been found to show the most profound effects on corrosion rates of alkali borosilicate waste glasses, as discussed by Ebert [3]. The extent of degradation under these tests conditions can be compared with that of other waste forms.

The 7-day PCT results are used as a measure of product consistency acceptance in the DOE/EM waste acceptance product specifications (EM-WAPS) [5]. These specifications were developed by DOE/EM for the high level waste form Producers as the basis for their Waste Acceptance programs. The EM-WAPS are the technical specifications that the waste form Producers are required to meet in order to ensure acceptance of their vitrified HLW into the Civilian Radioactive Waste Management System. The current acceptance criterion is that the PCT-A response must be less than the response of the environmental assessment (EA) benchmark glass [6], after normalizing the glass compositions. One acceptable method of demonstrating that the acceptance criteria is met, is to ensure that the mean PCT results for a waste type are at least two standard deviations below the mean PCT results of the EA glass [5]. The average rate in the PCT-A test, based on the amount of boron released over 7 days, is used to determine the maximum rate calculated by the HLW glass degradation model in alkaline solutions. The standard 7-day PCT in demineralized water (PCT-A) was conducted in this task to demonstrate compliance with the waste acceptance criterion and determine the value of the k_E rate parameter for comparison with the defense HLW glass degradation model [2]. Longer-term PCT results were needed for static test results that can be used to verify the applicability of the degradation model. A primary focus of this effort was in the use of the PCT-B to study the formation and stability of colloids and to study alteration phases formed on the glass surface.

Glass formulation development was previously conducted at SRNL (formerly the Savannah River Technology Center, SRTC) in support of the Plutonium Immobilization Program (PIP) [7–9]. Two frit compositions were developed for LaBS glass. Frit A employed only gadolinium as a neutron absorber, whereas Frit B used both gadolinium and hafnium as neutron

absorbers with hafnium replacing zirconium in the frit composition. Boron is not relied upon as a neutron absorber because it is released from the waste form faster than plutonium and can become separated from plutonium as the waste form degrades. Both frits were used to make LaBS glasses for testing; however, the majority of previous performance testing was conducted with the Frit A composition. Due to the additional neutron absorbers present in the Frit B formulation, this frit became the reference composition at the culmination of PIP glass testing in 1997 [9]. PCT results for the LaBS Frit A compositions have been previously published [7,10], while only limited, unpublished PCT durability testing was performed on the LaBS Frit B composition.

2. Experimental

Glass-forming frit was fabricated for testing at SRNL by mixing reagent grade chemicals in the proportion given in Table 1 for the Frit B formulation scaled to produce a 300 g batch of frit. The previous Frit A formulation is also shown for comparison. Oxide chemicals were used for all components except for boron. Boric acid was used to provide the necessary B_2O_3 content in the frit. The frit batch was melted at $1500\,°C$ in Pt/Rh crucibles. After nominally 2 h at temperature, the crucible was removed from the furnace at temperature and the molten glass poured on a steel plate. The "cullet" pieces were collected for subsequent grinding. The cullet was ground in an automated agate mill and sieved to collect the fraction that was -325 mesh ($<45\,\mu m$). Two batches of Frit B were prepared using this method. After the frit was melted and ground, samples from both batches were analyzed using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) to verify the composition. The frit samples were prepared in duplicate using a sodium peroxide/sodium hydroxide (Na_2O_2/NaOH) fusion with HCl uptake. The peroxide fusion dissolution allows for the analysis of all elemental concentrations of interest (Al, B, Gd, Hf, La, Nd, Si, and Sr). The resulting solutions were analyzed in duplicate using the ICP-AES. Plutonium oxide material was produced at the Savannah River Site (SRS) and was obtained from a standard that was previously used for calorimetry testing. Before using the PuO_2 to fabricate glass, a 0.0256 g sample of the PuO_2 was dissolved in a 24.7 mL mixture of 8 M HNO_3/0.05 M KF for analyses. The dissolution was performed in a radiochemical glovebox by heating and stirring the PuO_2 in a glass beaker until it became fully dissolved. The resulting PuO_2 solution was analyzed by gamma spectroscopy and liquid scintillation counting to determine the actinide isotopic distribution, and ICP-AES to assess presence of any inactive, gross elemental impurities. Radioanalytical analyses indicated full recovery of the Pu and that the material was primarily Pu-239 with levels of other Pu isotopes, i.e., Pu-240, consistent with weapons-grade plutonium. Pu-241 and its daughter decay product Am-241 were both analyzed to be only 0.2 wt% of the PuO_2 material. The only inactive elemental species above 1 wt% determined from dissolution of the PuO_2 were Al, B, Ce and Na at respective levels of 1.3, 2, 1.1 and 3.2 wt%. The Al, B and Na likely result from acid corrosion of the glass beaker used to dissolve the PuO_2. Based on the full Pu recovery from the radioanalytical data and lack of any other significant levels

Table 1
LaBS glass compositions used in previous and current testing

Oxide	Frit A (mass %)	Frit B (mass %)
Al_2O_3	21.5	21.3
B_2O_3	11.7	11.6
Gd_2O_3	8.6	12.8
HfO_2	–	6.6
La_2O_3	12.4	8.1
Nd_2O_3	12.8	8.2
SiO_2	29.2	28.9
SrO	2.5	2.5
ZrO_2	1.3	–

of inactive elements found, it was decided to proceed with Pu glass fabrication using this well-characterized, pure PuO_2 material.

Once the composition of the frit was verified via chemical analysis, the frit was weighed into the appropriate amount to produce a nominal 100 g of glass with a 9.5 wt% PuO_2 loading. The frit was placed in a plastic bottle for introduction into the SRNL shielded cells facility (SCF), where the appropriate quantity of PuO_2, which had been previously transferred from a glovebox to the SCF, was weighed and added to the bottle containing the frit via remote handling. Remote handling of the weapons-grade Pu material for this study was not required by personnel radiation exposure considerations, which are discussed in detail by Meyers et al. [9]. However, glass fabrication and durability testing were performed in the SRNL SCF in order to utilize the existing high temperature furnace and PCT oven. The bottle containing frit and PuO_2 was capped and the mixture manually mixed for a few minutes using the rotation afforded by the manipulator arm. The mixture of frit and PuO_2 was placed in an open Pt/Rh crucible for melting. The Pt/Rh crucible was placed in a high temperature, resistively heated elevator furnace (CM Furnaces, Inc.) and the furnace was ramped to the melting temperature of 1500 °C using a ramp rate of 10 °C/min. The crucible melt was held at temperature for 4 h and promptly removed from the furnace and quenched by placing the crucible in a pan of water. Upon cooling, the glass monolith in the bottom of the crucible, which appeared homogeneous when visually examined, was manually removed from the crucible by "hammering" the crucible, resulting in nominally 99% of the glass recovered from the crucible as various size pieces. A total of four separate 100 g batches of plutonium-loaded glass were fabricated in this manner. In an effort to enhance homogenization of the glass, all of the various size pieces resulting from the four original melt/quenches were remelted a second time in a larger open Pt/Rh crucible with the same heating schedule and again quenched in water. This final remelted and quenched batch of Pu Frit B glass, which also appeared homogeneous when visually examined in the crucible, was again hammered out of the larger crucible and the glass pieces were used for all follow-on analyses and performance testing in this study. This also made it impractical to distinguish where the piece of glass originated with respect to the crucible melt. This precluded the ability to quantify the degree of stratification of PuO_2 within the glass melt. Previous analyses by Vienna et al. [11] identified stratification of PuO_2 in plutonium-loaded LaBS glasses fabricated in relatively small static crucible melts. In that testing, it was noted that co-grinding of the frit and PuO_2 and/or manual stirring of the melt during processing improved the incorporation of PuO_2 into the glass. Neither of those measures were attempted in this work. It should be noted that the PCT utilizes ground glass obtained from a bulk sample so the Pu distribution in the glass pieces used for the PCT would be expected to be representative of the bulk glass.

Samples of the powdered Pu glass were characterized to provide confidence that the glass was of acceptable quality to proceed with leach testing. X-ray diffraction (XRD) and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS) were used for this assessment. Specifically, the analyses were used to examine for the presence of crystalline species and other heterogeneities in the glass. The density of the glass was measured in duplicate by a water displacement method using a 50-mL pycnometer with a built in thermometer. The glass fraction that corresponded to the >100 mesh fraction from the PCT glass preparation, was used for the density measurements. The pycnometer was calibrated with ASTM Type 1 water prior to use. The density of the glass was necessary to calculate the mass of glass to be used in the PCT to ensure that the specified surface area was used in the testing. Since the density of the Pu LaBS glass is nominally 30–40% higher than a typical borosilicate HLW glass, it is necessary to utilize a greater mass of Pu LaBS glass to achieve a comparative glass surface area to HLW glass.

The PCT is an ASTM Standard Test (ASTM 1285-02) for leaching nuclear waste forms. With regard to glass it is a crushed glass static leach test performed in sealed vessels at 90 °C using ASTM Type 1 water. The ASTM Type 1 water was prepared using a Barnstead Nanopure Infinity™ ultrapure water system capable of filtering the water to at least 18 MΩ cm. Two types of PCTs were used to evaluate the durability of the Pu LaBS glass prepared with Frit B. One was the PCT-A test and the other, PCT-B.

The PCT-A test has a strict protocol and was designed to specifically be used to evaluate whether the chemical durability and elemental release characteristics of a nuclear waste glass have been consistently controlled during production. The test, which is performed in stainless steel vessels (Parr Instruments Corp.)

with 10.0 ± 0.5 mL of ASTM water per gram of glass, includes appropriate blanks and standards (EA glass and the Approved Reference Material-1 (ARM-1) glass [12]) as prescribed by the ASTM procedure. The PCT-A test was applied to triplicate samples of the Pu LaBS Frit B glass.

The PCT-B allows the researcher more flexibility. Different PCT-B tests were applied to the Pu LaBS glass with all tests conducted at 90 °C using ASTM Type 1 water. PCT-A tests in Teflon® vessels (Savillex Corp.) were used instead of stainless steel. They were performed to test the effect of vessel material on the results. Tests in steel vessels at slightly differently glass to water ratios than the PCT-A test were performed to test the effect of two different ratios of surface area to leachant volume (SA/V). PCT-B tests in Teflon® vessels at 90 °C at significantly higher SA/V for 7, 14, 28 and 56 days were conducted to investigate effects of higher SA/V. All PCT filtrates in this study were initially filtered through a 0.45 μm syringe filter. For all but one of the PCT tests, the 0.45 μm filtered leachates were also filtered through microfilters to assess whether colloids formed during the leaching a 90 °C. This ultrafiltration used high-flow Biomax-PB polyether sulfone membrane filters that are 30,000 nominal molecular weight limit (NMWL). These filters are listed as 'Ultrafree-CL Centrifugal Filter Units' from Millipore Corp. This ultrafiltration requires a centrifuge to force the leachate through the filter. The protocol for the PCT-A allows the use of only a 45 μm filter. Nalgene® 0.45 μm syringe filters (25-mm surfactant-free cellulose acetate membrane) were used with 20-mL latex-free Luer-LOK™ syringes in the PCT-A.

Ultrafiltration of the Pu glass leachates for this study used the Millipore ultrafilters described above in a Thermo IEC Centra CL2 centrifuge unit that was fit with a #221 rotor. This rotor is a six-place fixed trunniun swinging bucket design with nominal 3500 rpm maximum speed capability. The ultrafilters were pre-wetted with ASTM Type 1 water. Pre-wetting involved adding ≈2 g of water to the filter and centrifuging for 5 min on the maximum RPM setting. This typically pre-wetted the filter with <0.03 g of water. The pre-wetted ultrafilters were then wetted with some of the Pu glass syringe-filtered leachates from the initial 1500 and 2000 m^{-1} PCTs, followed by another 5 min of centrifuging. These ultrafiltered PCT leachates were analyzed by ICP-MS. The objective of these "filter preconditioning steps" was to minimize potential sorbing of plutonium on the filter when the actual samples were filtered. The ultrafilters were then finally used to ultrafilter the higher ≈20,000 m^{-1} SA/V PCT leachates that had been initially syringe-filtered, and these ultrafiltered leachates were also analyzed by ICP-MS.

Table 2 shows a summary of the various PCTs performed on the Pu Frit B LaBS glass. The first three tests are PCT-A conditions. The blank tests performed with ASTM Type 1 water are also included for comparison. All other tests are PCT-B including two blank tests performed for the longest duration of 56 days. All tests were performed remotely in the shielded cells facility of SRNL. A wrench and holder system was used to manually tighten the steel PCT vessels. A mechanical 'capping station' supplied by CEM Corp. was used to tighten the Teflon® vessels. This model #920030 capping station provided a nominal 5–10 ft/lb torque to tighten the Teflon® vessels. The average mass loss at 90 °C from the steel vessels and from the Teflon® vessels was the same at ≈0.010 g/day. Note that all the tests except for the PCT-B tests at the high SA/V for 28 days and 56 days met the ASTM PCT requirement that leachate mass loss is <5%. The last column of Table 2 also shows that only about 50% of the original starting leachant was recovered from the high ≈20,000 m^{-1} tests. This was mainly due to the fact that there was very little amount of free liquid volume in these high SA/V PCT-B tests. In the PCT-A tests the leachate was collected at the end of the test by decanting the free liquid from the PCT vessel into a clean specimen bottle by remote handling in the shielded cells facility. That bottle was then transferred to a radiochemical hood for syringe filtration. However, in the PCT-B tests at high SA/V, the leachate was decanted directly into a syringe that was pre-fit with a filter. The PCT-B tests at high SA/V were thus directly syringe-filtered in the SCF by remote handling. The PCT procedure recommends that Teflon® vessels not be used for PCT-B tests for radioactive glass waste forms with radiation doses exceeding 1E+05 rad of beta or gamma radiation [13], due to potential radiolytic degradation of the Teflon® vessel and subsequent release of F^- and HF into the test solution [14]. Limited analysis for F^- in these PCT-B tests in Teflon® vessels was attempted using Ion-Chromatography Analysis (IC-Anions) to investigate potential release of F^- from leaching these mainly alpha-emitting, Pu (predominately Pu-239) Frit B glasses.

Table 2
Summary of PCT-A and PCT-B tests performed on Pu Frit B LaBS glass

PCT method	Vessel type and ID[a]	Sample ID	Glass mass (g)	Leachant mass (g)	Ratio leachant to glass	SA/V (m⁻¹)	PCT duration (days)	Mass loss	% leachate mass loss	Avg. leachate mass loss per day	Mass leachate filtered	% ratio: filtered/starting
PCT-A	S-203	Pu-1	1.773	17.756	10.01	1505	7	0.069	0.4	0.010	13.987	79
PCT-A	S-253	Pu-2	1.778	17.734	9.97	1511	7	0.121	0.7	0.017	12.947	73
PCT-A	S-255	Pu-3	1.725	17.262	10.01	1506	7	0.053	0.3	0.008	13.054	76
PCT-A	S-210	Blank-1	NA	17.838	NA	NA	7	0.135	0.8	0.019	15.417	86
PCT-A	S-250	Blank-2	NA	17.839	NA	NA	7	0.099	0.6	0.014	15.348	86
PCT-A	S-261	Blank-3	NA	17.932	NA	NA	7	0.055	0.3	0.008	15.046	84
PCT-B	S-258	Pu-4	2.341	16.763	7.16	2104	7	0.098	0.6	0.014	12.904	77
PCT-B	S-B31	Pu-5	2.213	15.981	7.22	2087	7	0.058	0.4	0.008	11.777	74
PCT-B	S-461	Pu-6	2.232	16.135	7.23	2084	7	0.036	0.2	0.005	11.685	72
PCT-B	T-172	Pu-7	1.801	18.064	10.03	1502	7	0.085	0.5	0.012	14.56	81
PCT-B	T-146	Pu-8	1.83	18.29	9.99	1508	14	0.153	0.8	0.011	14.651	80
PCT-B	T-156	Pu-B-7	6.984	5.093	0.73	20663	7	0.062	1.2	0.009	2.762	54
PCT-B	T-133	Pu-B-7-rep	6.992	5.079	0.73	20743	7	0.1	2.0	0.014	2.086	41
PCT-B	T-110	Pu-B-14	6.995	5.063	0.72	20818	14	0.114	2.3	0.008	2.591	51
PCT-B	T-107	Pu-B-28	7.018	5.136	0.73	20590	28	0.265	5.2	0.009	2.445	48
PCT-B	T-129	Pu-B-56	6.995	5.093	0.73	20695	56	0.502	9.9	0.009	2.14	42
PCT-B	T-74	Blank-1	NA	5.053	NA	NA	56	0.542	10.7	0.010	3.927	78
PCT-B	T-143	Blank-2	NA	5.068	NA	NA	56	0.486	9.6	0.009	3.945	78

[a] S for steel vessels; T for Teflon® vessels.

All of the leachates resulting from leaching of the radioactive Pu-glass were measured for the following elements. Using ICP-AES the leachates were analyzed for B, Si, Sr and Al. Using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) the leachates were analyzed for Pu isotopes, La, Nd, Gd, and Hf. The ICP-AES instrument has a nominal instrument detection limit of about 0.01 mg/L and a 10% uncertainty in analyses of most elements. The ICP-MS instrument has a nominal instrument detection limit of about 0.01 μg/L and a 20% uncertainty in analyses. The pH of the leachates was also measured. An Accumet pH meter was used for the low SA/V PCT leachates along with certified buffer solutions. Small drops of the higher SA/V PCT leachates were put onto pH indicator paper to estimate the pH of these leachates due to the limited amount of these leachates. After the leach tests were completed and the leachates were removed for analysis, the vessels containing the damp powder glass residues were dried overnight in an oven at 90 °C. The dry glass powders were emptied from the vessels and some ASTM-1 rinse water was added to the vessels to rid any remaining glass powders. The rinsed vessels were dried, acid-stripped with 1 vol.% nitric acid and the acid rinse solutions analyzed for all glass components.

3. Results

The two batches of Frit-B were analyzed for use prior to plutonium glass fabrication. Samples of the frit were digested in duplicate and measurements were made using ICP-AES on the duplicates. All frit elements for both batches of the LaBS frit batch were found to be within ±10% of the targeted values. The sum of oxides for the duplicate measurements on the two frit batches ranged from 97.5 to 99.2 wt% indicating good elemental recovery from the analyses.

To conduct the PCT a glass is ground, sieved and washed. This provides a material with a consistent surface area that is free of fines for subsequent leach testing. It also provides a significant amount of material surface area for physical examination. A portion of the sieved, washed (unleached) Pu LaBS glass was submitted for XRD and SEM/EDS analyses to evaluate for the presence of crystallinity or heterogeneities in the glass. The results shown in Figs. 1 and 2 indicate that there was some small fraction of crystalline PuO_2 in the glass. Fig. 1 XRD analysis showed the presence of crystalline PuO_2 in the ground glass sample. The SEM/EDS analysis of the ground glass confirmed that specific grains contain PuO_2 crystal inclusions with disk-like morphologies (Fig. 2(a) and (b) SEM) that are primarily comprised of Pu (Fig. 2(c) EDS). Recent pressurized unsaturated flow (PUF) testing on plutonium-bearing LaBS glass indicated the potential separation of Pu from Gd during glass dissolution [15]. Post-test analysis of the LaBS glass from a 6-year PUF test showed a region where Pu had apparently accumulated in a Pu-bearing disk-like phase that had become separated from the Gd neutron absorber. The disk-like Pu phases identified in that work had identical morphology to the phase found in the current as-fabricated Pu LaBS Frit B glass observed in this study. This suggests that the apparent PuO_2 separation observed in the PUF test was not due to glass leaching but was a result of glass fabrication.

Visual examination of the PuO_2 source material indicated that it was finely divided and similar to the sized frit used to make the glass (i.e., −325 mesh (<45 μm)). However, to ensure that the crystalline PuO_2 inclusions observed in the quenched glass were not a result of large particle size starting material, SEM analysis was conducted on a sample of the PuO_2. The analysis indicated
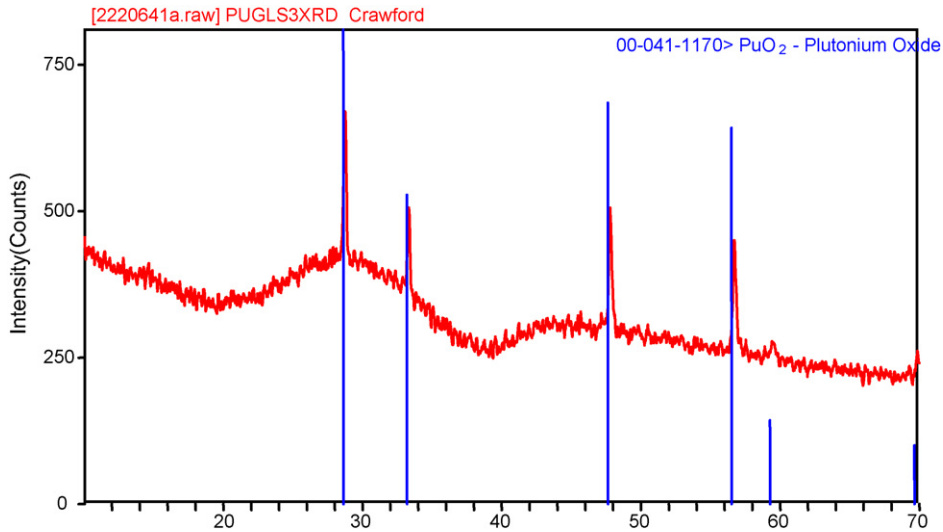
Fig. 1. XRD pattern of Pu LaBS Frit B glass ground, sieved, washed non-leached sample indicating presence of PuO_2 crystalline phase.
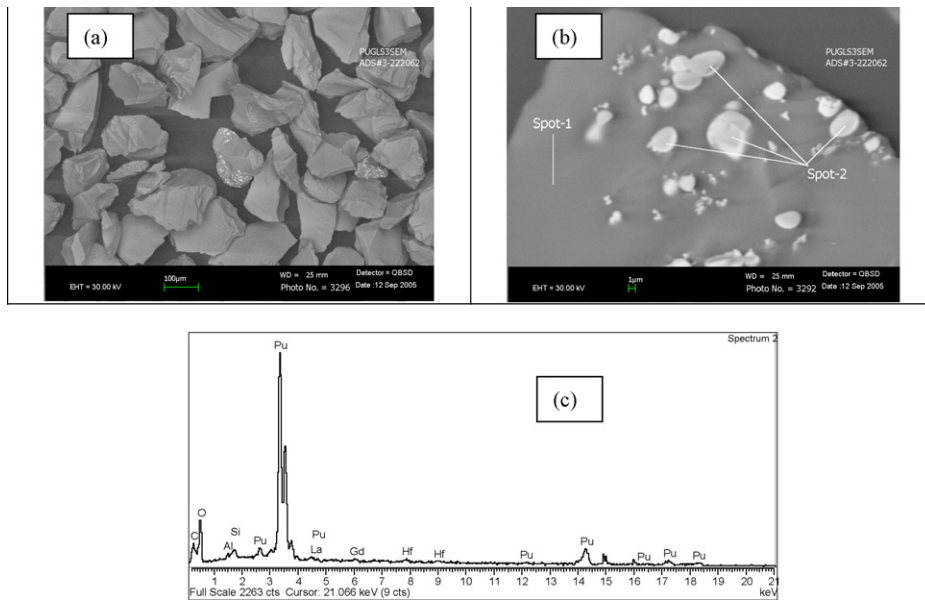

Fig. 2. SEM micrographs showing PuO_2 crystals in the ground, sieved, washed non-leached Pu LaBS Frit B glass on 100 μm scale (a) and on 1 μm scale (b). EDS (c) indicates crystalline PuO_2 phases (spot 2 inclusions shown in (b)) are primarily Pu-containing.

that the PuO_2 was comprised of very fine crystallites (nm-scale) that formed larger agglomerates. Fig. 3 shows the SEM images of the PuO_2 source material. Based on this observation, it is evident that large particle size PuO_2 starting material was not the cause of the crystalline PuO_2 in the glass. It was more likely that after dissolution of PuO_2 in the melt, enriched areas of PuO_2 were formed in the melt (via stratification due to density differences), and that the PuO_2 precipitated from the enriched
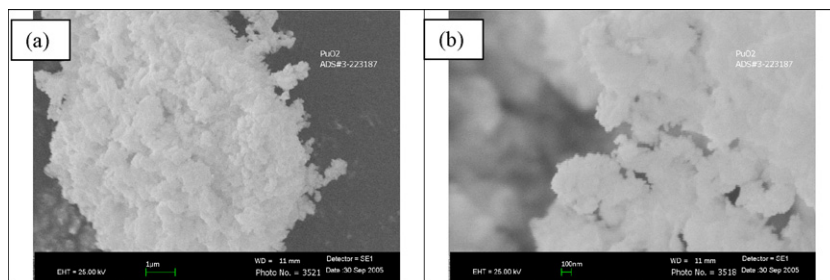

Fig. 3. SEM micrographs of PuO_2 source material showing the fine crystallite size on (a) 1 μm scale and (b) 0.1 μm scale.

Table 3
Average concentrations (ppm) of B, Si, Li and Na, and the final pH from the 90 °C PCT based on triplicate PCT-A tests and blanks

Sample ID	B	Si	Li	Na	pH[b]
Blanks	<0.11	<0.54	<0.05	<0.39	6.9
ARM-1[a]	18.8	65.8	14.6	39.5	10.4
EA glass	628	928	184	1683	12.0
Pu LaBS glass Frit B	0.18	<0.54	NP[c]	NP	7.2

[a] Control chart ranges for ARM-1 glass [16]: B, 13–23 ppm; Si, 49–73 ppm; Li, 11–16 ppm; and Na, 29–44 ppm.
[b] Initial pH of the leach water was also 6.9.
[c] NP, not present in the glass.

phase, such as the Pu-rich crucible bottom, to form the disk-like morphology in the glass. Re-melting of the glass was not sufficient to homogenize the PuO_2 in these enriched areas.

Duplicate samples of >100 mesh ground glass were used to determine the density of the Pu glass. The density determined was 3.57 ± 0.01 g/cm³. The temperature range at which the measurements were made was 28.3–28.8 °C, but since the density variation with temperature for glass is relatively low, this value can be considered relatively constant at ambient temperatures. This density value was used to calculate the mass of glass needed to ensure that the specified surface area was used in the PCT.

The PCT-A test was performed on Pu Frit B glass and the average concentrations in ppm of B, Si, Li and Na, in the final filtered leachates after the tests are shown in Table 3. Averages of the final pH values of the leachates are also presented. The concentrations were corrected for the acidification dilutions of the leachates as required by the ASTM procedure. The results for the blanks indicated that contamination of the leachates from possible impurities in the water or impurities on the stainless steel vessels was negligible. Per the ASTM procedure, the results for the standard ARM-1 glass were compared to a control chart based on results for previous PCTs on this standard glass. As shown in Table 3, the results for the ARM-1 glass were between the lower and upper control limits [16], indicating that the test conditions were properly controlled. A multi-element solution standard containing B, Si, Li, and Na in the concentration range of 10–80 mg/L was submitted for analysis in parallel with the leachates. The measured results agreed within 10% or less of the known values indicating that the ICP-AES analyses were sufficiently accurate. Since no impurities were determined in the blanks, and the standard ARM-1 results were within the lower and upper bounds of historical PCTs, and analysis of multi-element standard solutions were within the nominal 10% uncertainty of the analytical instrumentation, the results of the PCT-A test performed in steel vessels on the radioactive Pu LaBS Frit B glass were considered acceptable. Note that the final leachate pH for the Pu Frit B LaBS glass was near neutral and lower than the EA and ARM-1 glass leachate pHs. This is expected since the LaBS glass contains no alkali, i.e., Na or K, to cause significant increase in the solution pH.

Normalized mass losses are the best indication of the durability of a glass in a PCT. Normalization accounts for the concentration of an element in the glass. The normalized release is a measure of the total mass of glass dissolved in a PCT based

on a specific element in the glass. Per the ASTM PCT procedure [4], the normalized concentration is the grams of glass dissolved per liter of leachate (g/L) based on a specific element calculated from the following equation as

$$NC_i = \frac{c_i(\text{sample})}{f_i}, \tag{1}$$

where NC_i is normalized concentration for leached glass based on element i, in grams of glass dissolved per liter of leachate, $c_i(\text{sample})$ the concentration of element i in g/L in the leachate, and f_i the fraction of element i in the unleached glass (unitless).

Using the as-batched target elemental fractions in the LaBS Pu Frit B glass, the normalized concentration results were determined from Eq. (1) above and presented in Table 4. Based on normalized concentration for B, the leachability of the Pu LaBS glass (NC(B) = 0.018 ± 0.001 g/L) is orders of magnitude less than that for the reference value for EA glass (NC(B) = 16.7 ± 1.2 g/L), and clearly less than the reference EA (NC(B) − 2(S.D.)), or 14.3 g/L. On this basis it meets the criterion for durability in the EM-WAPS [5]. Table 4 also shows the current data is also comparable with data obtained from previous LaBS Frit B PCT-A testing performed at SRNL on Pu Frit B glasses that contained either impurities or uranium. Normalized releases for B and Sr were nearly equal indicating congruent dissolution based on these two elements. Note that all the other normalized concentrations for Pu, La, Nd, Gd and Hf were much lower than those based on B and Sr. The average NC(Pu) was 4.2E−03 g/L, which was only slightly higher than NC_i values for La, Nd, Gd and Hf on the order of 10^{-4} g/L. Comparison of the EA normalized concentrations from the PCT-A test performed in this study with normalized EA concentrations from the published study [6] indicate that the normalized EA concentration data in this study are within the average ± 1 standard deviation of the published values for B, Na, Li and Si.

Following the PCT-A testing, a sample of leached glass was obtained from the 7-day exposure tests for analysis. The sample was dried overnight in the PCT oven to facilitate handling. A sample of the dried glass was placed on an aluminum stub for SEM analysis. The SEM results presented in Fig. 4 show no evidence of alteration phase formation on the glass surface; however, the crystalline PuO_2 disk-like inclusions were again evident on some glass grains.

The density of the Pu LaBS glass is greater than a Sodium Borosilicate (NaBS) glass such as a typical DWPF glass. A typical DWPF glass has a density of nominally 2.58 g/cm³ while the Pu LaBS glass fabricated from Frit B has a measured density of 3.57 g/cm³. Consequently in a PCT-A with a ratio of 10 mL of leachant per gram of glass, there would be less surface area of glass exposed to the leachant with the higher density glass. To correct for this, triplicate PCT-B tests, labeled as Pu-4–Pu-6 in Table 2, were performed with Pu LaBS glass where the SA/V of about 2000 m⁻¹ is comparable to a PCT-A test with a DWPF glass. Consequently for the PCT with Pu LaBS glass, 7.23 mL of leachant ($10 \times (2.58/3.57)$) was used per gram of Pu LaBS glass. These were not PCT-A tests because the ASTM procedure specially states that for a PCT-A test the ratio of leachant volume to mass of glass has to be 10.0 ± 0.5 cm³/g of sample.

Table 4
Average normalized concentration (g glass/L) PCT-A results for Pu FRIT B and EA glass based on triplicate tests

Element	Measured Pu LaBS (g/L) (S.D., %R.S.D.)	Previous Pu LaBS (g/L)[a] (7.4 wt% impurities)	Previous Pu LaBS (g/L)[a] (6 wt% UO_3)	Measured EA (g/L) (S.D., %R.S.D.)	Published EA (g/L) (S.D., %R.S.D.)
B	0.018 (0.001, 7.1)	0.014	0.020	18.0 (0.2, 1)	16.7 (1.2, 7.3)
Na	NP[b]	NP	NP	12.5 (0.3, 2.3)	13.3 (0.9, 6.8)
Li	NP	NP	NP	9.4 (0.1, 2.0)	9.6 (0.7, 7.7)
Si	<0.015	0.013	0.016	4.1 (0.3, 2.3)	3.9 (0.4, 9.6)
Sr	0.016 (0.001, 7.0)	0.017	0.021	NP	NP
Pu-239	0.0042 (0.0004, 10)	0.0035	0.0044	NP	NP
La	0.00069 (0.00015, 22)	0.0018	0.0012	NP	NP
Nd	0.00018 (0.00009, 27)	0.0007	0.0002	NP	NP
Gd	0.00080 (0.000030, 38)	[c]	[c]	NP	NP
Hf	0.00012 (0.000007, 57)	[c]	[c]	NP	NP
pH	7.20 ± 0.07	Not reported	Not reported	12.0	11.9

[a] Previous unpublished SRNL (formerly SRTC) PCT-A results from 1997 Pu Frit B testing – leachate analysis only, no acid strip.
[b] NP, not present in the glass.
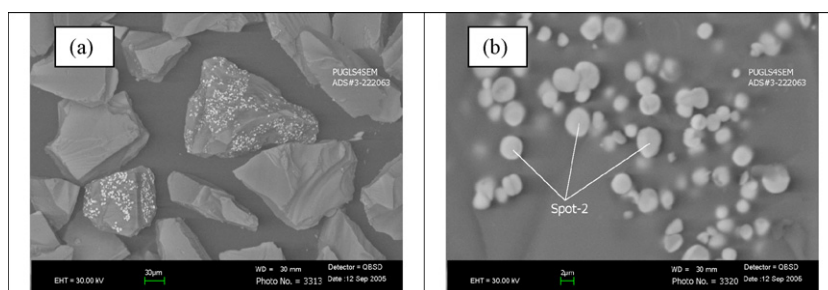[c] Analytes determined to be less than ICP-MS detection limits.

Fig. 4. SEM micrographs of 7-day leached Pu LaBS glass showing crystalline PuO_2 but no observable alteration phase formation on (a) 30 μm scale and (b) 2 μm scale.

In the PCT, the glass is carefully sieved through standard mesh size sieves so that the surface area of the glass is reproducible from test to test. The exposed surface area of the glass in a PCT has been estimated by assuming that the particles are spherical and that the distribution of particle sizes is Gaussian [4]. The size of the holes in the 100 and 200 mesh sieves are 0.149 mm and 0.074 mm, respectively. Thus the diameter of the spheres range between these two values with an average value of 1.12E−04 m. Based on these assumptions the exposed surface area in a PCT with the Pu LaBS glass was calculated using equations from Ref. [4] to be 0.015 m²/g of sieved glass. Since the density of the Pu LaBS glass was 3.57 g/cm³ this gave a SA/V for the PCT-A tests of 1500 m⁻¹. Per the ASTM PCT procedure [4], the normalized release in terms of grams of glass leached per square meter for PCT-A is calculated using the following equation:

$$NL_i = \frac{c_i(\text{sample})}{((f_i)(\text{SA}/V))}, \qquad (2)$$

where NL_i is normalized release based on element i, in grams of glass leached per square meter of glass exposed in the PCT, c_i(sample) is the concentration of element i in g/L in the leachate, and f_i is the fraction of element i in the unleached glass (unitless), and SA/V is the surface area of the glass divided by the leachate volume in units of m²/L. Note that the SA/V for the Pu LaBS glass of 1500 m⁻¹ expressed in terms of m²/L is 1500 m⁻¹ × [(1 m²/L)/1000 m⁻¹] = 1.5 m²/L.

Normalized release results from Eq. (2) for the PCTs performed at different SA/V of either 1500 m⁻¹ or 2100 m⁻¹ in steel vessels are shown in Table 5 along with NL_i values for the EA glass. The NL_i values for EA glass were calculated from published PCT-A NC_i values [6] and the measured EA glass density of 2.7 g/cm³ [17]. Results indicate that for the most part the normalized releases in both series of SA/V tests on the Pu Frit B glass were the same based on identical elements, and the final leachate pHs were nearly the same. The NL(B) values from either Pu Frit B SA/V test (0.012–0.013 g/m²) are much less than NL(B) for EA glass of 8.3 ± 0.6 g/m². Per the EM-WAPS [5], both NL(B) values for Pu Frit B glass are clearly less than the reference EA average (NL(B) − 2(S.D.)), or 7.1 g/m².

The NL_i PCT results for PCT-B tests in Teflon® vessels for 7 and 14 days at the two different SA/V of 1500 m⁻¹ and 21,000 m⁻¹ are shown in Table 6 along with analyzed F⁻ concentrations. The 7-day PCT data are shown in the first two data rows (Pu-7 and Pu-B-7) and the 14-day PCT data are shown in the latter two rows (Pu-8 and Pu-14). The 7-day PCT data at SA/V of 20,700 m⁻¹ was the average of duplicate tests that were performed at different times. As was shown in the previous section for comparison of 7-day PCT normalized release in steel at 1500 m⁻¹ and 2100 m⁻¹, these data presented in Table 6 also indicate that for the most part the normalized releases in all four series of tests were very similar. This is obvious from comparing the NL(B) releases (in the range of 6.5E−3 to 1.6E−2 g/m²) and also from comparing the NL(Pu)

Table 5

Average normalized releases (g glass/m^2) in PCT tests at SA/V of 1500 and 2100 m^{-1} in steel vessels[a]

Element	Pu Frit B (g/m^2) (S.D., %R.S.D.) SA/V ≈ 1500 m^{-1}	Pu Frit B (g/m^2) (S.D., %R.S.D.) SA/V ≈ 2100 m^{-1}	Published EA (g/m^2) (S.D., %R.S.D.) SA/V = 2000 m^{-1}
B	1.2E−02 (8.5E−04, 7.1)	1.3E−02 (9.1E−04, 7.0)	8.3 (0.6, 7.3)
Na	NP[b]	NP	6.7 (0.5, 6.8)
Li	NP	NP	4.8 (0.4, 7.7)
Si	<9.8E−03	<7.0E−03	2.0 (0.2, 9.6)
Sr	1.1E−02 (7.7E−04, 7.0)	1.0E−02 (2.2E−04, 2.2)	NP
Pu-239	2.8E−03 (2.8E−04, 10)	2.4E−04 (1.8E−04, 7.5)	NP
La	4.6E−04 (9.9E−05, 22)	1.9E−04 (1.1E−04, 60)	NP
Nd	1.2E−04 (3.2E−05, 27)	1.0E−04 (4.8E−05, 48)	NP
Gd	5.3E−05 (2.0E−05, 38)	5E−05 (8E−06, 16)	NP
Hf	8E−06 (2E−06, 57)[c]	4E−06[c]	NP
pH	7.20 ± 0.07	7.38 ± 0.13	11.9

[a] Results are averages of triplicate tests. The tests at SA/V at ≈1500 m^{-1} were PCT-A tests whose results are presented in Table 4 on a normalized g/L basis.

[b] NP, not present in the glass.

[c] Concentrations in the leachates were so low that only one significant figure was presented in the ICP-MS results.

releases (in the range of 1.2E−3 to 3.7E−3 g/m^2). Fluoride analysis of these leachates indicates that less than 0.7 mg/L F$^-$ was present in the 7- to 14-day PCTs at 1500 m^{-1}. This F$^-$ concentration is similar to the PCT procedure suggested upper F$^-$ concentration limit of 0.5 mg/L for cleaning of new or used Teflon® vessels [4]. The measured upper limit F$^-$ concentration is higher than the IC-Anion instrument detection limit of 0.2 mg/L due to the ≈3.4× dilution factor used in preparing the filtered leachates for analysis. Similar fluoride analysis on the higher SA/V, 21,000 m^{-1} PCT leachates indicated less than detectable F$^-$ levels of <5 mg/L. The higher values for the F$^-$ upper limits in these higher SA/V tests are due to the limited volume of leachate available for analysis as discussed below for the long-term, higher SA/V PCTs in Teflon®. These leachates required dilution factors of 20× or higher.

Comparisons can also be made between the normalized release of the PCT-A results performed in triplicate steel vessels (Pu-1–Pu-3) at a water to glass ratio of 10× and the single similar PCT that was performed in a Teflon® vessel (Pu-7). Table 7 shows these normalized filtered leachate data to be very similar indicating that the vessel material has insignificant influence on the filtered leachate concentrations over the 7-day test. The normalized B and Sr values were essentially the same in the triplicate steel versus the single Teflon® vessel.

Table 8 shows normalized releases for all of the PCTs at SA/V ratios near 21,000 m^{-1}. No PCT blanks were performed for the 7–28-day tests, and two blanks were included for the 56-day duration. Fluoride anion analysis was performed on highly diluted filtered leachates from these tests and these results are

also shown in the last column of Table 8. Normalized releases for boron, silicon, strontium increase as the leach time increased through 56 days. Normalized release values can be expressed as normalized rates, NR$_i$, by dividing by the leach time duration [4]. In comparing these data to monolithic immersion tests on Pu Frit B glasses, Ebert has noted that the PCT normalized release for B and Si increase nearly linearly between 7 and 56 days with a corresponding normalized rate NR(B) ≈ 2.8E−4 g/(m^2 day) and for NR(Si) ≈ 1.4E−4 g/(m^2 day) [3]. These normalized rates from 7 to 56 days are slightly lower than the respective 7-day normalized rates for B, Si or Sr for the ≈21,000 m^{-1} tests from Table 8 (NR$_i$ in the range of 6E−4 to 1.3E−3 g/(m^2 day)) or from the 1500–2000 m^{-1} tests from Table 5 (NR$_i$ in the range of 1.2E−3 to 1.7E−3 g/(m^2 day)). Normalized releases for B, Si and Sr were nearly congruent and also higher than for the other elements in the glass (La, Nd, Gd, Hf and Pu). This indicates that the degradation rate of the glass matrix as determined by the release of B, Si and Sr, generally bound the release of La, Nd, Gd, Hf and Pu. For any given test duration shown in Table 8, the NL(Pu) values on the order of 10^{-3} g/m^2 are slightly higher than those for NL(La), NL(Nd), NL(Gd) on the order of 10^{-5} to 10^{-4} g/m^2, and higher than NL(Hf) on the order of 10^{-6} to 10^{-5} g/m^2. Relatively similar dissolution behavior of the neutron absorbers Gd and Hf and the fissile Pu is important with respect to whether the contents of a degraded waste package will ever reach a critical configuration [9]. Blank-corrected data for the 56-day PCT are similar to uncorrected data for most elements except for Si, which showed relatively high Si levels in the dilution-corrected

Table 6

Average normalized releases (g glass/m^2) in PCT-B tests at SA/V of 1500 and 21,000 m^{-1} in Teflon® vessels

Sample ID	SA/V (m^{-1})	B (g/m^2)	Si (g/m^2)	Sr (g/m^2)	La (g/m^2)	Nd (g/m^2)	Gd (g/m^2)	Hf (g/m^2)	Pu (g/m^2)	F^{-}[a] (mg/L)
Pu-7	1,502	1.6E−02	<9.8E−03	1.0E−02	2.2E−03	6.9E−04	4.2E−04	<2.6E−06	3.7E−03	<0.7
Pu-B-7[b]	20,700	6.7E−03	4.4E−03	8.8E−03	2.1E−04	8.8E−05	6.4E−05	<7.3E−06	1.2E−03	<4
Pu-8	1,508	6.5E−03	1.0E−02	8.7E−03	5.4E−06	<4.2E−06	<4.2E−05	<2.6E−06	2.6E−03	<0.7
Pu-B-14	20,818	7.2E−03	<4.4E−03	8.5E−03	7.9E−05	8.9E−05	3.7E−05	1.3E−05	1.2E−03	<5

[a] Fluoride anion analysis from filtered leachates, see text.

[b] Average of Pu-B-7 and Pu-B-7-rep.

Table 7
Average normalized releases (g glass/m^2) in PCT-A tests at SA/V of 1500 in steel (Pu-1–Pu-3) and Teflon® (Pu-7) vessels

Sample ID	SA/V (m^{-1})	B (g/m^2)	Si (g/m^2)	Sr (g/m^2)	Al (g/m^2)	La (g/m^2)	Nd (g/m^2)	Gd (g/m^2)	Hf (g/m^2)	Pu (g/m^2)
Pu-1–Pu-3	1500	1.2E−02	<9.8E−03	1.1E−02	<1.0E−03	4.7E−04	1.2E−04	6.3E−05	6.2E−06	3.0E−03
Pu-1–Pu-3 S.D.	1500	8.5E−04	NA	7.7E−04	NA	9.9E−05	3.3E−05	1.7E−05	5.3E−06	2.9E−04
Pu-7	1502	1.6E−02	<9.8E−03	1.0E−02	<1.0E−03	2.2E−03	6.9E−04	4.2E−04	<2.6E−06	3.7E−03

Table 8
Average normalized releases (g glass/m^2) in PCT tests at SA/V of 21,000 m^{-1} in Teflon® vessels from 7 to 56 days

Sample ID	SA/V (m^{-1})	B (g/m^2)	Si (g/m^2)	Sr (g/m^2)	La (g/m^2)	Nd (g/m^2)	Gd (g/m^2)	Hf (g/m^2)	Pu (g/m^2)	F^{-} [b] (mg/L)
Pu-B-7 [a]	20,700	6.7E−03	4.4E−03	8.8E−03	2.1E−04	8.8E−05	6.4E−05	<7.3E−06	1.2E−03	<4
Pu-B-14	20,818	7.2E−03	<4.4E−03	8.5E−03	7.9E−05	8.9E−05	3.7E−05	1.3E−05	1.2E−03	<5
Pu-B-28	20,590	1.2E−02	6.3E−03	1.0E−01	2.9E−05	1.6E−05	2.4E−05	7.9E−06	1.0E−03	<6
Pu-B-56	20,695	2.0E−02	1.1E−02	1.3E−02	3.1E−05	5.2E−05	3.4E−05	5.9E−06	2.1E−03	d
Pu-B-56 [c]	20,695	1.5E−02	3.1E−03	1.3E−02	7.3E−06	2.6E−05	2.1E−05	5.9E−06	2.0E−03	d

[a] Average of Pu-B-7 and Pu-B-7-rep.
[b] Fluoride anion analysis from filtered leachates, see text.
[c] Blank-corrected Pu-B-56 NL$_i$ values.
[d] Insufficient sample, see text.

blanks (7.7–11.1 mg/L) versus the Pu Frit B dilution-corrected leachate of 26.7 mg/L. Future long-term Pu LaBS glass PCTs will include blanks for each individual time duration and contain sufficient volume in order to minimize dilution before analysis.

Leachate volume limitations from these high SA/V tests prevented pH measurement with a pH meter. However, droplets of the leachates were contacted with pH indicator paper and all of the leachates were determined to be near neutral pH, similar to the low SA/V 7-day PCT result leachate pHs. Fluoride analysis indicates less than 4–6 mg/L values in the 7-, 14- and 28-day leachates. For the 56-day leachate and 56-day blanks, there was insufficient sample available for F^{-} analysis after ICP-AES and ICP-MS analyses. Previous leach testing of fully radioactive HLW monolithic glass specimens in Tuff ground water in Teflon® vessels has shown higher glass dissolution after about 28 days in Teflon® vessels versus similar tests in stainless steel vessels [14]. As indicated above, the NL(B) values shown in Table 8 appear to increase linearly from 7 to 56 days, i.e., there is no observed acceleration of glass dissolution through the 56 days. Since boron is soluble in the leachates it is a good measure of overall glass dissolution. On this basis it does not appear that any enhanced leaching of the Pu Frit B glass occurred. Future long-term Pu LaBS glass PCTs are planned to be performed in steel vessels to mitigate any concerns associated with potential F^{-} contamination of leachates and enhanced leaching from performing PCTs on radioactive glasses in Teflon® vessels.

Table 9 compares the normalized releases for the filtered versus the ultrafiltered leachates from the PCT-A and PCT-B tests. The ultrafiltered leachates were only analyzed by ICP-MS due to volume limitations on the amount of ultrafiltered product. Comparison of the plutonium normalized releases showed that ultrafiltering did not have a significant influence on the amount of plutonium present in the filtered products. The last column of Table 9 showed that filtered
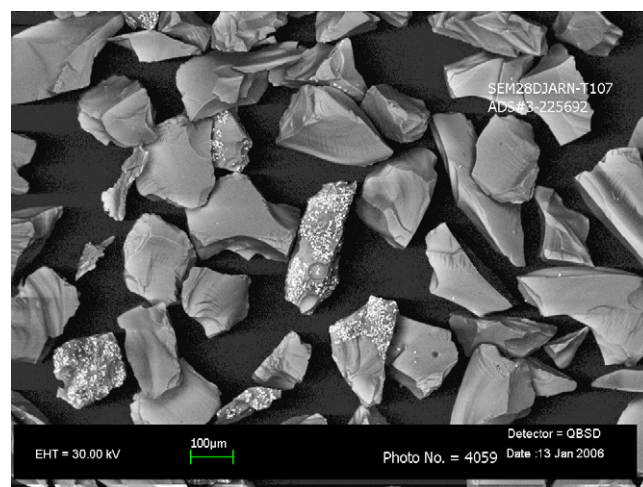

Fig. 5. SEM micrographs of 28-day leached Pu LaBS glass showing crystalline PuO$_2$ inclusions and no observable alteration phase formation.

and ultrafiltered leachates had nearly the same normalized release values. Comparison of the PCT-A normalized Pu release for filtered versus ultrafiltered (Pu-1–Pu-3 data) showed that the average normalized release for Pu is the same for filtered and ultrafiltered to within two standard deviations. The normalized release rates for filtered and unfiltered samples calculated from the PCT-B data at SA/V of 2100 m^{-1} (Pu-3–Pu-6 data) were within one standard deviation. The 7- and 14-day PCT-B normalized Pu release filtered and ultrafiltered data at SA/V of ≈21,000 m^{-1} were nearly identical. Ultrafiltration normalized release for the 7- and 14-day PCT-B at SA/V of 1500 m^{-1}, as well as the ultrafiltration normalized release for the 28- and 56-day PCT-B did show slightly lower values when compared to the analogous filtered normalized releases. However, these differences were likely within the analytical uncertainty of the ICP-MS analyses that are reported at ±20%.

Table 9
Average normalized releases (g glass/m^2) in PCT-A and PCT-B tests comparing filtered vs. ultrafiltered

Sample ID	SA/V (m^{-1})	La (g/m^2)	Nd (g/m^2)	Gd (g/m^2)	Hf (g/m^2)	Pu (g/m^2)	% Diff. filtered vs. ultrafiltered (Pu)[c]
Pu-1–Pu-3	1,500	4.7E−04	1.2E−04	6.3E−05	6.2E−06	3.0E−03	11
Pu-1–Pu-3 S.D.	1,500	9.9E−05	3.3E−05	1.7E−05	5.3E−06	2.9E−04	
Pu-1–Pu-2 UF[a]	1,500	1.6E−05	<9.7E−05	<3.5E−04	<4.5E−05	2.6E−03	
Pu-1–Pu-2 UF S.D.[a]	1,500	8.0E−06	5.4E−08	2.0E−07	2.5E−08	2.0E−04	
Pu-4–Pu-6	2,100	1.9E−04	4.8E−05	3.1E−05	2.8E−06	2.5E−03	6
Pu-4–Pu-6 S.D.	2,100	1.1E−04	2.3E−05	6.2E−06	1.1E−06	1.8E−04	
Pu-4–Pu-6 UF	2,100	3.3E−04	3.0E−04	2.9E−04	2.0E−04	2.4E−03	
Pu-4–Pu-6 UF S.D.	2,100	2.9E−04	2.3E−04	8.2E−05	1.6E−04	2.3E−04	
Pu-7 (F)	1,502	2.2E−03	6.9E−04	4.2E−04	<2.6E−06	3.7E−03	6
Pu-7 (UF)	1,502	1.0E−03	2.6E−04	1.5E−04	<3.9E−05	3.4E−03	
Pu-8 (F)	1,508	5.4E−06	<4.2E−06	<4.2E−05	<2.6E−06	2.6E−03	10
Pu-8 UF	1,508	3.2E−05	<9.5E−05	<3.5E−04	<3.9E−05	2.4E−03	
Pu-B-7 (F)[b]	20,700	2.1E−04	8.8E−05	6.4E−05	<7.3E−06	1.2E−03	0
Pu-B-7 (UF)[b]	20,700	1.9E−04	6.8E−05	4.5E−05	<8.4E−06	1.2E−03	
Pu-B-14 (F)	20,818	7.9E−05	8.9E−05	3.7E−05	1.3E−05	1.2E−03	−4
Pu-B-14 (UF)	20,818	2.2E−05	1.4E−05	5.0E−06	6.9E−06	1.3E−03	
Pu-B-28 (F)	20,590	2.9E−05	1.6E−05	2.4E−05	7.9E−06	1.0E−03	16
Pu-B-28 (UF)	20,590	2.1E−05	1.2E−05	3.8E−05	6.9E−06	8.8E−04	
Pu-B-56 (F)	20,695	3.1E−05	5.2E−05	3.4E−05	5.9E−06	2.1E−03	8
Pu-B-56 (UF)	20,695	1.4E−04	1.1E−04	6.5E−05	6.4E−05	1.9E−03	

[a] Pu-3 was not ultrafiltered.
[b] Average of Pu-B-7 and Pu-B-7-rep.
[c] ((Filt. − UF)/Filt.) × 100.

Following the PCT-B testing, samples of leached glass were obtained from the 28- and 56-day exposure tests for analysis. The SEM results presented in Figs. 5 and 6 again showed no evidence of alteration phase formation on the glass surface; however, crystalline PuO$_2$ disk-like inclusions were evident on some glass grains. Thus the SA/V = 21,000 m^{-1} leached glass powder surfaces at 28 and 56 days were similar to unleached (Fig. 2) glass powder surfaces and 7-day, 1500 m^{-1} leached surfaces (Fig. 4). Using Eq. (39) from Ebert [3], the depth to which the glass dissolved in these tests can be estimated from the normalized release of Si and the Pu Frit B glass density. Calculations indicate that for normalized Si release in these tests, in the range of 0.006–0.011 g/m^2, and a measured Pu Frit B glass density of 3.57 g/m^3, estimated dissolution depths of only 0.0017–0.003 μm are expected. These depths are much less than the SEM micrograph scales shown in Fig. 4 (2–30 μm) and Figs. 5 and 6 (100 μm).

All data presented in Tables 3–9 pertain to leachate data only. In addition to filtered leachate analyses, all of the PCT steel and Teflon® vessels were acid-stripped in this study with 1 vol.% HNO$_3$ to analyze for potential leached species sorbed onto the inner surface of the leach vessels. For instance, certain radionuclides and redox sensitive species are attracted to steel [4]. The acid strip solutions were analyzed by ICP-AES and ICP-MS analyses. Enrichment of plutonium from the acid strip solutions versus any of the other glass elements was not observed. In fact, all of the acid strip solutions showed detectable amounts of all the elements in the glass. This observation along with the varying concentrations found in the acid strip solutions, indicates that

Fig. 6. SEM micrographs of 56-day leached Pu LaBS glass showing crystalline PuO$_2$ inclusions and no observable alteration phase formation.

trace levels of glass could have been present in the PCT vessels before acid stripping. This indicates that the vessels were not completely rid of leached powdered glass after the leach test and before the acid strip. Converting the analyzed amount of the glass elementals in the acid strip solutions to calculated glass amounts shows that indeed microgram quantities of glass were present in the combined strip solutions from the three successive acid strips of the vessels. Calculations for the Pu Frit B glass indicate that a single particle of >200 mesh to <100 mesh glass with density 3.57 g/m^3 and volume of 7.25E−13 m^3 [4], has average weight of 2.5 μg.

4. Conclusions and further testing

Plutonium-containing LaBS Frit B composition glass was fabricated, analyzed and leach tested in this task. Several conclusions can be drawn from the testing. A small amount of crystalline PuO_2 was present in the glass after static, crucible melt fabrication and quench-cooling. The crystalline particles had a disk-like morphology and likely formed after initial dissolution in the melt via stratification due to density differences, resulting in an enriched Pu phase that precipitated crystalline PuO_2. PCT-A results on the Pu-containing LaBS Frit B glass showed that the glass was very durable and was better than two orders of magnitude more durable from a boron release standpoint than the current environmental assessment (EA) glass used for repository acceptance. The normalized elemental release values for the 7-day PCT-B tests in either steel or Teflon® vessels were comparable with the PCT-A results in steel vessels, again indicating the relative good durability exhibited by this glass. In the long-term, 21,000 m^{-1} SA/V PCTs, normalized release rates for 7-day tests were higher than normalized release rates calculated from 7 to 56 days. Less than detectable concentrations of F^- through 28 days and an observed linear increase in NL(B) from 7 to 56 days suggest that there was no enhanced leaching of these Pu Frit B glasses in Teflon® vessels. All PCT results showed normalized release of B, Si and Sr to be nearly congruent, and higher than Pu and the neutron absorber Gd and Hf elements. Comparison of the initial syringe-filtered leachates to the ultrafiltered leachates indicated that normalized plutonium releases were essentially the same within the analytical uncertainty of the ICP-MS methods used to quantify plutonium in the leachates. These results indicated that colloidal plutonium species did not form under the PCT conditions used in this study. Future PCT-B testing should be conducted for longer durations on the Frit B composition and other candidate compositions (e.g., a Pu-Frit X glass that has been identified in other recent Pu glass formulation testing [18] at SRNL) to provide additional insight into colloid and alteration phase formation. Additional 7-day PCT studies in stainless steel vessels have recently been completed on Pu Frit X glass that was either quench-cooled or heat-treated. These results will be reported in a future report. The PCT results reported in this study, along with parallel testing of the Pu Frit B glass at Argonne National Laboratory (ANL) using Pu Frit B glass supplied by SRNL in monolith immersion testing and vapor hydration testing [3], can be utilized in the repository performance assessment [2].

Acknowledgements

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