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Plutonium Feed Impurity Testing in Lanthanide Borosilicate (LaBS) Glass

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ABSTRACT

A vitrification technology utilizing a lanthanide borosilicate (LaBS) glass is a viable option for dispositioning excess weapons-useable plutonium that is not suitable for processing into mixed oxide (MOX) fuel. A significant effort to develop a glass formulation and vitrification process to immobilize plutonium was completed in the mid-1990s. The LaBS glass formulation was found to be capable of immobilizing in excess of 10 wt % Pu and to be tolerant of a range of impurities. A more detailed study is now needed to quantify the ability of the glass to accommodate the anticipated impurities associated with the Pu feeds now slated for disposition.

The database of Pu feeds was reviewed to identify impurity species and concentration ranges for these impurities. Based on this review, a statistically designed test matrix of glass compositions was developed to evaluate the ability of the LaBS glass to accommodate the impurities. Sixty surrogate LaBS glass compositions were prepared in accordance with the statistically designed test matrix. The heterogeneity (e.g. degree of crystallinity) and durability (as measured by the Product Consistency Test – Method A (PCT–A)) of the glasses were used to assess the effects of impurities on glass quality.

INTRODUCTION

In the aftermath of the Cold War, the United States has identified an excess of up to 50 metric tons (MT) of weapons-useable plutonium. The Department of Energy (DOE) was to construct both a Mixed Oxide Fuel Fabrication Facility (MFFF) and a Plutonium Immobilization Program (PIP) facility to disposition this material. In April 2002, DOE decided not to construct the PIP facility and to solely proceed with the construction of the MFFF facility with a focus only on the disposition of weapons-grade plutonium to meet the non-proliferation agreement between Russia and the United States. This action resulted in up to 13 metric tons of DOE-Office of Environmental Management (DOE-EM) owned, weapons-useable, plutonium-bearing materials having no clear disposition path.

Vitrification utilizing a lanthanide borosilicate (LaBS) glass appears to be a viable option to disposition excess weapons-useable plutonium that is not suitable for processing into mixed oxide (MOX) fuel. A significant effort to develop a glass formulation and vitrification process to immobilize plutonium was completed in the mid-1990s to support the PIP. The LaBS glass formulation was found to be capable of immobilizing in excess of 10 wt% Pu and to be very tolerant of impurities [1-2]. Thus, this waste form could be suitable for the disposition of plutonium owned by the DOE-EM that may not be well characterized and that may contain high levels of impurities. However, the relative tolerance of the glass composition to the various impurities associated with current Pu feeds slated for disposition needs to be studied.

The present study focuses on the development of a composition envelope that describes the solubility of various impurities in the LaBS glass. To define this envelope, a series of glass compositions was selected, fabricated and characterized to evaluate the solubility of various impurity elements and their effects on crystallization and durability. To facilitate laboratory experiments, the glasses were formulated with Hf as a surrogate for Pu. Pu glass testing will be performed on select compositions for comparison with the results of the surrogate testing. Concurrent with the glass formulation studies, melter testing is being conducted to evaluate the effects of impurities on processing [3].

EXPERIMENTAL DETAILS

Development of the Impurity Test Matrix

A detailed analysis of the anticipated Pu feeds to be immobilized in waste glass was provided by Moore and Allender [4]. The projected impurity types and concentrations described in that report were used as the basis for defining the compositions of the glasses to be fabricated for this study.

The report by Moore and Allender projected the concentrations of more than 70 possible elements as impurities in the Pu feed. This list was reduced to seventeen elements based on several criteria. First, all of the elements with a best estimate maximum concentration of 18,000 $\mu\text{g/g}$ and above were included. Impurities that had relatively low concentrations and would be expected to have little impact on glass chemistry were excluded (e.g. the solubility of silicon in the glass should not be an issue and Si was removed from the impurity list). Next, sulfur and lead were included since these elements are known to typically have low solubility in the LaBS glass. Finally, selenium and cesium were included again due to low solubility being expected for these elements in LaBS glass.

Table I lists the impurities that were chosen using these criteria. For each of the elements in this table, an interval of possible concentrations is given. This interval represents the possible concentration of the indicated element as an impurity in the feed. The lower limits were defined by rounding the best estimate concentration for 50% of the projected feeds to either zero or, in the case of chlorine, to 5000 $\mu\text{g/g}$. The upper limits were defined by the greater of either the best estimate maximum concentration or the best estimate concentration for 98% of the projected feeds. These values were rounded to the nearest thousand $\mu\text{g/g}$. The concentration values were then converted to mass fractions of the Pu feed, as listed in Table I.

The chemical form of each of these impurity elements in the feed was not necessarily known, but there were some restrictions that were imposed on the approach used in developing the test matrix for this study. The first restriction imposed was a constraint on the overall mass of impurities in the feed. Moore and Allender provide total impurity concentration data for 2200 containers of the anticipated Pu feed based on Prompt Gamma Analysis and chemical estimates from laboratory samples [4]. Using these data, the total mass of the impurities was set to 35% of the overall Pu feed stream. This value was chosen to represent a worst case impurity concentration based on the data provided by Moore and Allender. Thus, on a mass basis, a design point for the study had to satisfy the constraint that the sum of the mass fractions of all of the impurities of that design point had to add to 0.35.

An additional restriction on the composition of the impurities making up a design point was required to address the issue of charge balance for that design point. If each of the

impurities of Table I were converted to an oxide as a result of the vitrification process and if the feed were batched in these oxides to introduce the appropriate concentrations of all of the elements of Table I, then there would be no need for a charge balance restriction. However, for Cl, F, and S this is not the case, and the batching of the impurities that involve one or more of these elements imposed a constraint of the amounts of other impurities of Table I that had to be present to provide a charge balance for the impurity concentration.

Table I. Impurities and Their Possible Concentrations as Mass Fractions in the Feed

Element	Lower Limit	Upper Limit
Cl	0.05	0.35
Ta	0	0.315
Mg	0	0.35
K	0	0.11
Fe	0	0.08
Na	0	0.096
F	0	0.195
Ca	0	0.048
Ga	0	0.09
Ni	0	0.04
Cr	0	0.038
Cu	0	0.02
S	0	0.005
C	0	0.005
Pb	0	0.006
Se	0	0.005
Cs	0	0.005

Keeping in mind the restrictions identified above, the problem of finding feasible combinations of the impurities was considered as a mixture problem [5]. Statistical software such as JMP Version 6.0.2 is available to assist in working with such problems [6]. Using tools associated with JMP, a matrix of 60 impurity combinations was developed to facilitate the impurity testing to assess individual and interactive effects. The 60 impurity concentrations were combined with HfO₂ as a surrogate for PuO₂ to form the feed material. The feed was then combined with LaBS Frit X (Table II) at a mass ratio of 14% feed to 86% frit. A 14% feed value represented a nominal upper bound for “waste loading” projected for Pu vitrification operations.

Table II. Chemical composition of LaBS Frit X

Component	wt%
Al ₂ O ₃	10.00
B ₂ O ₃	13.00
Gd ₂ O ₃	13.50
HfO ₂	7.00
La ₂ O ₃	19.00
Nd ₂ O ₃	15.00
SiO ₂	20.00
SrO	2.50

Glass fabrication and characterization

Each glass was batched from the appropriate amounts of reagent metal oxides, carbonates, sulfates, fluorides and chlorides. The batches were thoroughly mixed and melted in Pt/Rh crucibles at 1450 °C for 1 hour. The glass was then quenched by pouring onto a stainless steel plate. The resulting glass patty and the remaining contents of the crucible were ground to a fine powder using a ring pulverizer to further aid in mixing. The glass powder was subsequently re-melted at 1450 °C for one hour and quenched. Samples of each of the glasses were heat treated to simulate cooling inside a high level waste glass canister. This heat treatment allows for the identification of any crystalline phases that may form during slow cooling within the canister.

The chemical composition of each of the study glasses was measured by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). Samples were prepared via two methods: a peroxide fusion dissolution was used for measurement of B concentrations and a lithium metaborate dissolution was used for measurement of the other cation concentrations. Ion Chromatography (IC) was employed to measure the concentration of the anions in each glass. Samples of the quenched and slowly cooled versions of each glass were analyzed for the presence of any crystalline phases by X-ray diffraction (XRD).

The PCT-A [7] was used to measure the durability of samples of each glass, both quenched and slowly cooled. Samples of each glass were ground to a size fraction of -100 to +200 mesh and placed in stainless steel vessels with de-ionized water following the test procedure. The vessels were sealed and placed in an oven at 90 °C for 7 days. The leachates were then removed from each vessel, filtered, and analyzed via ICP-AES. Normalized elemental release values were calculated using the ICP-AES leach solution data and measured glass composition data.

RESULTS AND DISCUSSION

The results of the chemical composition measurements for each of the study glasses are summarized in Figure 1. A plot is shown for each of the elements (converted to an oxide) that was varied in the glass compositions (i.e., the anticipated impurity elements and the Pu surrogate Hf).

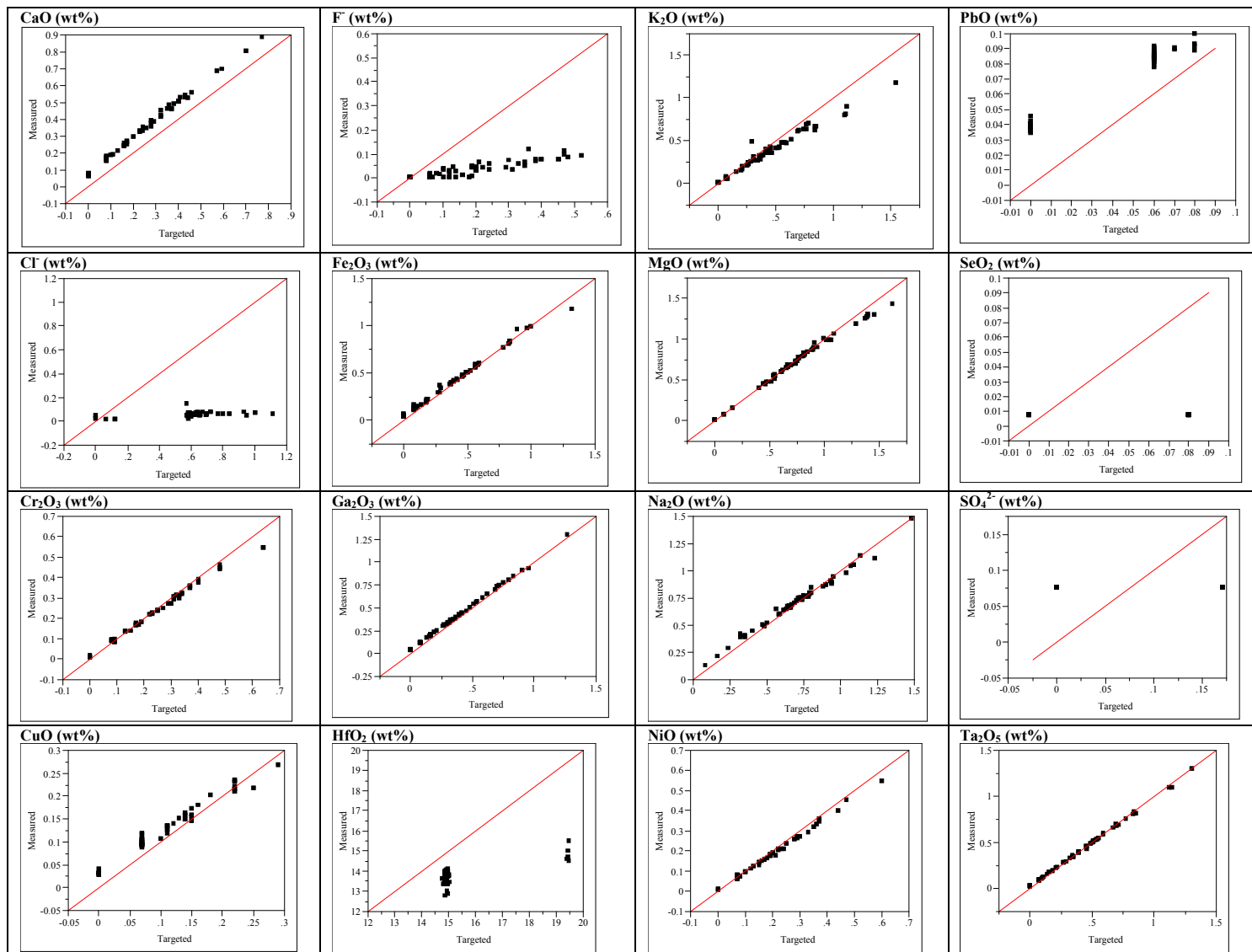


Figure 1. Measured versus Targeted Concentrations for Select Analytes in the Study Glasses

The measured CaO and PbO concentrations were consistently higher than the targeted values. The measured Cr₂O₃ and Fe₂O₃ concentrations are very close to the targets except for the one highest targeted value for each of these components. The measured Cl⁻, F⁻, SeO₂ and SO₄²⁻ concentrations are well below their target values for all of the study glasses. This is likely due to volatilization of these species during melting of the glass batch. It should be noted that SeO₂ and SO₄²⁻ were tested at two concentration levels and volatility reduced the concentrations in the glass to below the analytical detection limit for all glasses (hence, the appearance of two data points in the plots in Figure 1). The measured HfO₂ concentrations were below their target values for all of the study glasses. It is likely that for HfO₂, the solubility limit in the glass was exceeded and some of the HfO₂ batch material remained in the bottom of the crucibles after pouring the glasses. The measured K₂O concentrations are very close to the target values up to a concentration of about 0.48 wt %, after which the measured concentrations fall below the target values. The measured MgO concentrations are very close to the target values up to a concentration of about 1.1 wt %, after which the measured concentrations fall below the target values. The measured CuO, Ga₂O₃, Na₂O, NiO, and Ta₂O₅ concentrations generally fall very close to their target values across the ranges of concentrations targeted in this study for each of these components.

The XRD results showed that all but two of the quenched glasses were X-ray amorphous. Two of the quenched glasses formulated with 4% impurities in the simulated Pu feed contained some crystalline HfO₂. This is not surprising, as the target HfO₂ concentration in these glasses was ~19.5 wt %. For the slowly cooled glasses, 3 of the 5 glasses with 4% impurities in the simulated Pu feed contained some crystalline HfO₂. This was confirmed by Scanning Electron Microscopy (SEM) as shown in Figure 2. The HfO₂ crystallites appear brighter in this backscattered electron image due to their higher average atom mass, and Energy Dispersive Spectroscopy (EDS) confirmed that the concentration of Hf in this crystallites was much higher than the surrounding glass matrix. The basis for the use of HfO₂ as a surrogate for PuO₂ in borosilicate glasses from a solubility perspective has been documented [8]. Therefore, insolubility of HfO₂ at these concentrations is not unexpected since the solubility limit of PuO₂ in LaBS glass was found to be 13.4 wt % [1].

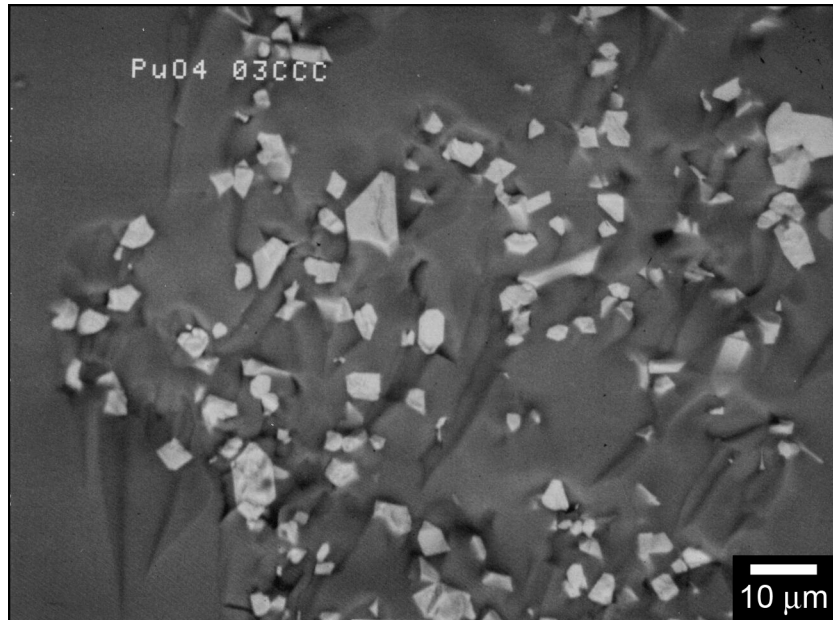


Figure 2. SEM micrograph of a LaBS glass fracture surface in an area containing undissolved HfO_2 (bright crystallites).

The results of the PCTs indicated that each of the study glasses was highly durable as compared to the Environmental Assessment (EA) glass, which is used as a benchmark for defense-related waste glasses destined for the U.S. federal repository [9]. Boron has been found to be released at the same maximum normalized concentration as some high-activity radionuclides, and is therefore typically used to gauge the performance of simulated waste glasses. The concentration of B in the PCT leachates was below the detection limit of the ICP-AES instrument for most of the study glasses. This is consistent with previous testing on a Pu-loaded LaBS glass without impurities where boron leachate values as measured by ICP-AES were also below detection limits [10]. The highest normalized release for boron measured in the study was 0.041 g/L, which is considerably smaller than that of the EA glass (16.695 g/L). The maximum normalized release rates among the 60 glasses for the other elements measured were also quite low: 0.005 g/L for Hf, 0.014 g/L for Gd, 1.229 g/L for Na and 0.090 g/L for Si. The normalized release rates for these elements were generally too small to attempt to correlate the results with the compositions of the test glasses. Note that the pH of the leachate solutions (typically ~ 8.0) were generally lower than that of typical high-level waste glasses developed for defense-related radioactive waste sludges (typically ~ 10.5), which may have had some influence on the PCT results.

CONCLUSIONS

Sixty surrogate glass compositions were developed through a statistical design approach to cover the anticipated ranges of concentrations for the dominant impurity species expected in the Pu feed. These glasses were fabricated and characterized in the laboratory to determine the degree of crystallization that occurred, both upon quenching and slow cooling, and to measure the durability of each glass. XRD and SEM results indicated that some crystalline HfO_2 remained in

some of the glasses with the lowest concentration of impurities. No other significant crystalline phases were identified. The PCT results showed that all 60 of the glass compositions tested were very durable (regardless of thermal heat treatment), with the highest normalized release for boron being 0.041 g/L. The normalized release rates for these elements were generally too small to attempt to correlate the results with the compositions of the test glasses. Overall, the LaBS glass system appears to be very tolerant of the impurities projected to be included in the Pu waste stream. There was evidence of volatility especially with the anion species. Corresponding melter process testing is underway to address handling of the volatile species.

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