DEVELOPMENT OF GLASS COMPOSITIONS TO IMMOBILIZE ALKALI, ALKALINE EARTH, LANTHANIDE AND TRANSITION METAL FISSION PRODUCTS FROM NUCLEAR FUEL REPROCESSING

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ABSTRACT

The Advanced Fuel Cycle Initiative (AFCI) waste management strategy revolves around specific treatment of individual or groups of separated waste streams. A goal for the separations processes is to efficiently manage the waste to be dispositioned as high level radioactive waste. The Advanced Fuel Cycle Initiative (AFCI) baseline technology for immobilization of the lanthanide (Ln) and transition metal fission product (TM) wastes is vitrification into a borosilicate glass. A current interest is to evaluate the feasibility of vitrifying combined waste streams to most cost effectively immobilize the wastes resulting from aqueous fuel reprocessing.

Studies showed that high waste loadings are achievable for the Ln only (Option 1) stream. Waste loadings in excess of 60 wt % (on a calcined oxide basis) were demonstrated via a lanthanide borosilicate (LaBS) glass. The resulting glasses had excellent relative durability as determined by the Product Consistency Test (PCT). For a combined Ln and TM waste stream glass (Option 2), noble metal solubility was found to limit waste loading. However, the measured PCT normalized elemental releases for this glass were at least an order of magnitude below that of Environmental Assessment (EA) glass. Current efforts to evaluate the feasibility of vitrifying combined Ln, TM, alkali (Cs is the primary radionuclide of concern) and alkaline earth (Sr is the primary radionuclide of concern) wastes (Option 3) have shown that these approaches are feasible. However, waste loading limitations with respect to heat load (Cs/Sr loading), molybdenum solubility and/or noble metal solubility will likely be realized and must be considered in determining the cost effectiveness of these approaches.

INTRODUCTION

The United States Department of Energy (DOE) Advanced Fuel Cycle Initiative (AFCI) is designed to demonstrate a proliferation-resistant integrated nuclear fuel cycle. This fuel cycle consumes transuranic (TRU) elements and supports growth of carbon-free international nuclear energy markets. Building on the knowledge gained over the last 60 years of nuclear science and engineering, the proposed recycling system is not only more sustainable than prior concepts, it will generate less waste and reduce thermal and long-lived radiation impacts on a geologic repository.

The AFCI waste management strategy revolves around specific treatment of individual or groups of separated waste streams. It is a goal for the separations processes to minimize the amount and radiotoxicity of waste to dispose. The waste streams will be separated by either of two set of processes; 1) UREX+ and/or 2) electrochemical. The UREX+ set of processes are nitric acid based solvent extraction processes. The electrochemical set of processes are performed in a chloride based molten salt and include dissolution of the less noble metals followed by electro-reduction.

An example UREX+ flowsheet is shown schematically in figure 1. The example UREX+ flowsheet highlights three (of many) waste streams that require immobilization:

- Separated cesium and strontium waste (Cs/Sr) in the CCD-PEG (or FPEX) raffinate, also contains barium and rubidium

- The raffinate from transuranic extraction (TRUEX) referred to as the transition metal fission product (TM) waste stream, and
- Trivalent actinide lanthanide separations by phosphorus-reagent extraction from aqueous complexes (TALSPEAK) product containing lanthanides and yttrium (Ln stream).

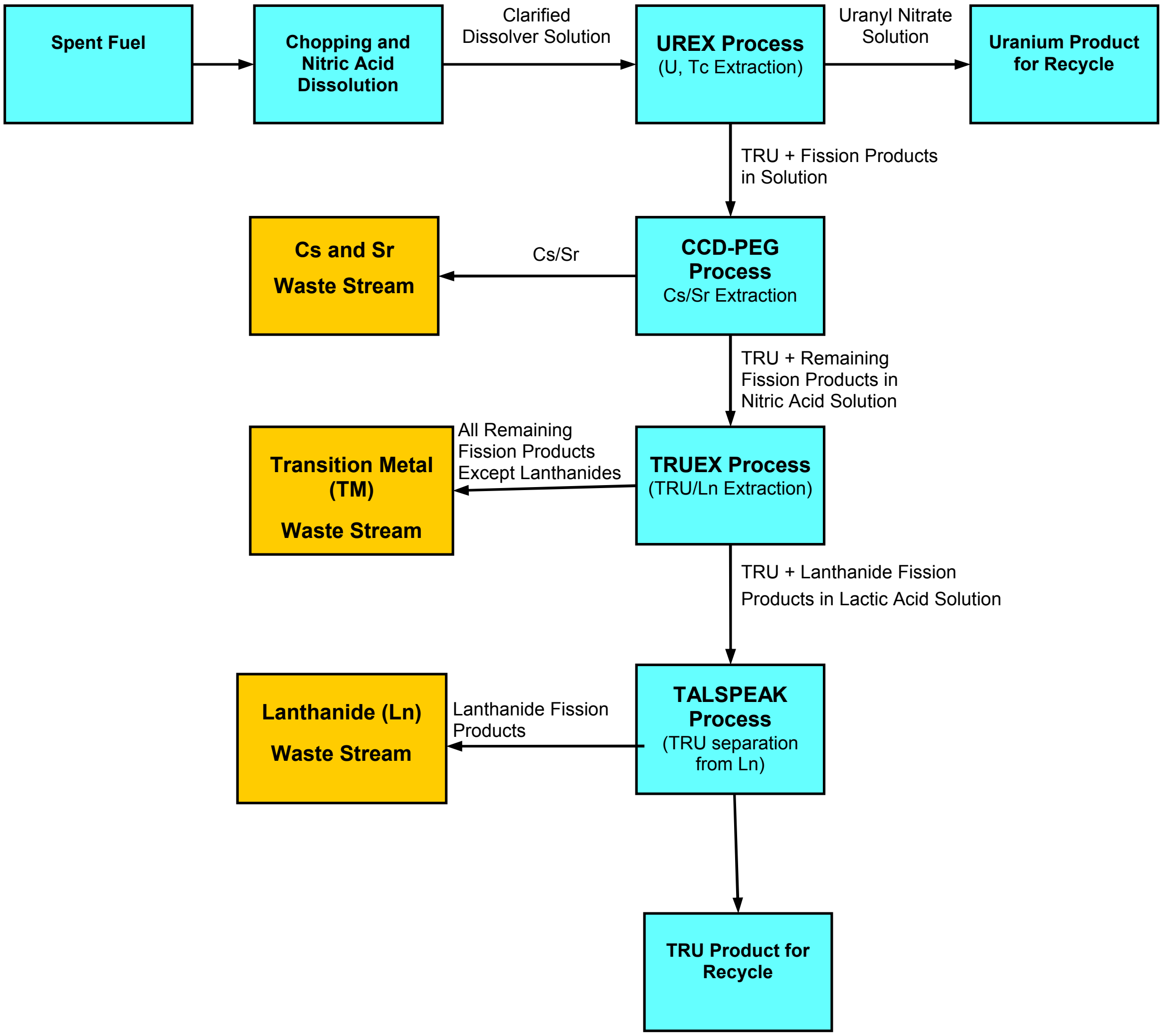

Figure 1. ExampleUREX+ flowheet depicting Cs/Sr, TRUEX and TALSPEAK separations processes and resulting waste streams.

The AFCI baseline technology for immobilization of the Ln/TM wastes is vitrification into a borosilicate glass. Vitrification of the Ln and TM streams have several advantages, including relatively high waste loadings, a proven technology, and similarity in form to waste forms currently accepted for repository disposal. The combination of the separated Cs/Sr wastes and Ln/TM wastes may be a cost effective approach by minimizing the number of waste forms to be fabricated.

EXPERIMENTAL DETAILS

Initial studies concentrated on the development and testing of glasses for the Ln only waste stream (Option 1) and the combined Ln + TM waste stream (Option 2). Recent studies have included the Cs/Sr waste stream to formulate and test a combined Cs/Sr/Ln/TM glass waste form (Option 3).

The testing was conducted in a serial manner where several glass formulations were developed in phases building off of results from the previous phase and incorporation of changes in waste compositions to reflect new knowledge gained from separations flowsheet development and testing. For brevity and illustration purposes, only one or two glass compositions will be discussed for each waste immobilization option.

Waste Compositions

The waste composition of the Ln-only stream is projected to consist of a majority of the lanthanides from the lanthanide series as oxides (Ln_2O_3). The major lanthanide oxides expected to be present are Ce_2O_3, La_2O_3, Nd_2O_3 and Pr_2O_3. Combining the TM stream with the Ln stream adds noble metal fission products (primarily RuO_2, Rh_2O_3 and PdO) to the combined stream. It is expected that a significant amount of ZrO_2 will also be introduced to the combined Ln/TM stream by the introduction of the TM stream.

When the Cs/Sr waste stream is added to Ln/TM combined stream, the main constituents added are Cs_2O, SrO, BaO and MoO_3. The addition of the Cs/Sr stream increases the relative heat load of the waste significantly. Depending on variations in potential flowsheets, the efficiency of the separations processes and the relative partitioning of elements in the waste streams, the combined Cs/Sr/Ln/TM stream was represented by two extremes. One extreme consisted of high MoO_3 content while the other extreme had high noble metal contents. Both MoO_3 and noble metals can have significant impacts on waste loading. It is expected the waste stream compositions will become more definitive as the separations processes mature and are tested. However, at this stage testing extreme levels appeared to be a prudent approach.

Identification of Candidate Glass Forming Systems

Option 1- A lanthanide borosilicate (LaBS) glass was identified as a suitable candidate for immobilization of the lanthanide waste stream, because the waste stream consists mainly of rare earth elements.

Option 2- An alkali borosilicate glass was identified as a suitable candidate for the immobilization of the combined Ln and TM waste stream, because of the complex chemical makeup of the waste.

Option 3 – Alkali borosilicate glass systems were identified as likely candidates for immobilization of the combined Cs/Sr/Ln/TM waste stream, because of the complex chemical makeup of the waste and high variability of MoO_3, noble metals, and ZrO_2.

Glass Fabrication

Each test matrix glass was prepared from the proper proportions of reagent-grade metal oxides, carbonates, H_3BO_3, and salts to produce sufficient glass for the associated testing (typically 200 grams). In general, the raw materials were thoroughly mixed and placed into platinum-alloy crucibles (Pt, Pt/Rh, or Pt/Au). In the case of glasses containing high levels of noble metal oxides (RuO_2, Rh_2O_3, PdO, Ag_2O, etc.), the batch materials were melted in alumina or silica crucibles in order to prevent undesired reactions with the glass and platinum-alloy crucibles during melting. The well mixed batches were placed into electrically heated, high-temperature furnaces at melting temperatures between 1250°C and 1400°C. After an isothermal hold at the targeted melting temperature for nominally 2 hours, the crucibles were removed from the furnaces, and the glasses were poured onto a clean stainless steel plate and allowed to air cool (quenched). In some cases the glass was removed from the furnace and allowed to air cool while remaining in the crucible. The glass pour patties were used as the sampling stock for the various property measurements (e.g. product consistency test [PCT], liquidus temperature [T_L], X-ray diffraction [XRD] and chemical composition).

Durability as Defined by Product Consistency Test (PCT)

The PCT was performed in triplicate on quenched samples of glasses to assess chemical durability using the ASTM C-1285 Method A Procedure [1]. Also included in the PCT testing sets were the Environmental Assessment (EA) glass, the Approved Reference Material (ARM) glass, and blanks. The resulting solutions (leachates) were analyzed via ICP-AES for Si, B, Na, and Li concentrations. Normalized release rates were then calculated based on target and measured compositions using the average of the common logarithms of the leachate concentrations.

Liquidus Temperature (T_L)

The liquidus temperature (T_L) of glasses were determined using an isothermal liquidus determination method [2]. In this method, a glass sample was subjected to a set temperature for nominally 24 hours. The sample was then evaluated using optical microscopy and/or quantitative XRD. For optical microscopy, the sample was thin-sectioned and examined for the presence of crystals. The isothermal heat treatments were continued until the T_L was identified as the temperature between the highest temperature at which a heat-treated sample contained crystals and the lowest temperature without crystals. For XRD, the sample was ground to a fine powder and spiked with known about of CaF_2 (internal standard) to identify crystalline phase type(s) and concentration(s) of the unknown crystalline phase(s) present within the sample. Crystal fraction results were collected for a range of temperatures below T_L. Results are then plotted as mass % crystallinity vs. temperature and a linear fit is used to extrapolate to T_L.

RESULTS AND DISCUSSION

Glass Compositions

The targeted glass compositions that were tested are shown in Table I. Two glasses are discussed for the Ln only waste with the compositions differing significantly in the relative concentrations of Al_2O_3 and B_2O_3. Both compositions resulted in homogeneous glasses with total lanthanide loadings of about 60 wt % (on a calcined oxide basis). Glass Ln-01-2008 was formulated for the Ln only waste stream in the first series of glasses based on LaBS glass data from previous studies [3-5]. Glass Ln-X-SUB was based on a LaBS glass compositions previously developed for actinide disposition [6].

The waste loading for the Ln/TM glass was constrained to result in a total noble metal loading of 2 wt % noble metals in the glass. As noted above, an alkali borosilicate glass was selected for this waste composition.

The Cs/Sr/Ln/TM-1-2.5 glass was formulated with a constraint of a total MoO_3 content of 2.5 wt % in the glass. The Cs/Sr/Ln/TM-2-3.0 glass was limited to 3.0 wt % total noble metal oxide content in the glass. The noble metal content was increased in this composition based on the previously performed Option 2 testing.

Table I. Targeted Glass Compositions for Option 1) Lanthanides, Option 2) Lanthanides + Transition Metal Fission Products, Option 3) Cs + Sr + Lanthanides + Transition Metal Fission Products

Component Wt %	**Ln-X-SUB**	**Ln-01-2008**	**Ln+TM-Fe**	**Cs/Sr/Ln/ TM-1-2.5**	**Cs/Sr/Ln/ TM-2-3.0 ***
Ag_2O	-	-	0.03	0.07	0.11
Al_2O_3	8.79	15.75	4.81	5.95	6.53
B_2O_3	11.43	6.50	9.62	5.00	5.16
BaO	-	-	-	1.41	2.20
CaO	-	-	4.81	7.00	5.16
CdO	-	-	0.07	0.07	0.11
Ce_2O_3	13.82	14.20	1.78	1.98	3.09
Cs_2O	-	-	-	1.84	2.87
Eu_2O_3	0.80	0.82	0.10	0.11	0.17
Gd_2O_3	0.94	0.93	0.12	0.10	0.16
La_2O_3	7.05	7.24	0.91	1.01	1.58
Li_2O	-	-	2.41	4.02	3.21
MoO_3	-	-	0.22	2.50	0.78
Na_2O	-	-	8.42	7.00	7.22
Nd_2O_3	23.27	23.91	3.00	3.36	5.22
PdO	-	-	0.80	0.01	0.02
Pr_2O_3	6.43	6.60	0.83	0.93	1.44
Rb_2O	-	-	-	0.27	0.42
Rh_2O_3	-	-	0.19	0.05	0.07
RuO_2	-	-	1.01	0.13	0.18
Sb_2O_3	-	-	0.01	-	-
SeO_2	-	-	0.02	0.05	0.08
SiO_2	17.58	16.10	57.36	53.03	49.94
Sm_2O_3	4.88	5.02	0.63	0.69	1.07
SnO_2	-	-	0.07	0.04	0.07
SrO	2.20	-	-	0.63	0.98
TeO_2	-	-	0.31	0.42	0.65
Y_2O_3	2.81	2.88	0.36	0.40	0.63
ZrO_2	-	-	2.12	1.91	0.87

* Waste loading at 3 wt % noble metal oxide content but noble metal oxides only added at levels where there were expected to be soluble

PCT Results

The PCT results for Option 1 – Ln glass formulations are shown in Table V. Similar to values reported in previous LaBS glass studies, the PCT release values were extremely low (<0.08 g/L) [6-7]. This is compared to the baseline reported value for repository acceptance of EA glass at an average normalized boron release of 16.695 [8]. In almost all cases for Option 1, normalized elemental releases were below the measurement detection limit. PCT results for the Option 2 glass are also reported in Table V. All of the measured PCT normalized elemental releases were also at least an order of magnitude below that of EA, though slightly higher than the Option 1 glasses. PCT results for the Option 3 glasses were comparable and normalized releases were better than an order of magnitude lower than the EA glass for both glasses.

Table V. Measured PCT Response for AFCI Glasses

Glass ID	**Normalized Release (g/L)**			
	Li	**B**	**Na**	**Si**
LN-X-SUB	N/A	<0.080	N/A	<0.002
LN-01-2008	N/A	<0.081	N/A	0.003
LN+TM-Fe	0.368	0.185	0.089	0.095
Cs/Sr/Ln/TM-1-2.5	0.511	0.214	0.420	0.157
Cs/Sr/Ln/TM-2-3.0	0.486	0.245	0.418	0.149
EA [11]	9.565	16.695	13.346	3.922

Liquidus Temperature (T_L) Results

The measured T_L and primary crystalline phases of the Option 1 glasses are given in Table VI. The optical microscopy method was used for determination of T_L for the option 1 glasses. XRD was used to determine the primary crystalline phases of the Option 1 glasses. Cerianite (LnO_2) structure was identified in LN-01-2008. Lanthanide borosilicate ($Ln_3BSi_2O_{10}$) structure was identified in LN-X-SUB.

The measured T_L and primary crystalline phase for the Option 2 glass are given in Table VI. The crystal fraction method (XRD) was used for measurement of T_L for this glass. This switch in method was made because the noble metals are almost entirely undissolved in the glasses, and at the higher concentration of noble metals in this glass made it difficult to determine if other crystalline phases were present near T_L. The undissolved noble metals don't significantly interfere with identification and quantification of other crystalline phases in the crystal fraction method. XRD was used to determine the primary crystalline phase in the glass. The LN+TM-Fe (Fe_2O_3 removed), had a primary crystalline phase of $Ca_{2.2}Nd_{7.8}(SiO_4)_6O_{1.9.}$

The measured T_L and primary crystalline phase for the Option 3 glasses are shown in Table VI. These liquidus temperatures would support glass processing at a nominal 1250º C processing temperature. The primary crystalline phase, $Ca_2Nd_8Si_6O_{26}$, was the same for both the MoO_3 and noble metal limited glasses.

Table VI. Measured T_L and Primary Crystalline Phases of Option 1 Glasses

GLASS ID	**MEASURED T_L, °C**	**PRIMARY CRYSTALLINE PHASE(XRD)**
LN-X-SUB	1279	$Ln_3BSi_2O_{10}$
LN-01-2008	1315	Cerianite (LnO_2)
LN+TM-Fe	1036(XRD)	$Ca_{2.2}Nd_{7.8}(SiO_4)_6O_{1.9}$
Cs/Sr/Ln/TM-1-2.5	1017	$Ca_2Nd_8Si_6O_{26}$
Cs/Sr/Ln/TM-2-3.0	1128	$Ca_2Nd_8Si_6O_{26}$

CONCLUSIONS

Glass compositions have been developed for the Ln waste steam alone (Option 1), the combined Ln and TM waste streams (Option 2) and the combined Cs, Sr, Ln and TM (Option 3) waste streams generated by the AFCI UREX+ family of processes.

For the Ln only (Option 1) stream, lanthanide loadings in excess of 60% (on a calcined oxide basis) were demonstrated using a lanthanide borosilicate (LaBS) glass system.

- The glasses had excellent relative durability as determined by the PCT.
- The measured T_L ranged from 1315°C to 1279°C for the Option 1 glasses. These values are well below the nominal 1400°C processing temperature for these glass compositions.

For the Ln + TM glasses (Option 2), noble metal solubility will likely limit waste loading. A glass composition was developed and tested that contained 2 wt % noble metals.

- The measured PCT normalized elemental releases for this glass were at least an order of magnitude below that of EA glass.
- The measured T_L was 1036ºC which is sufficiently below the 1250ºC processing temperature for this glass.

For the Cs/Sr/Ln/TM glasses (Option 3), noble metal solubility or Mo solubility are expected to limit waste loading. Waste glasses were fabricated and tested that contained 3 wt % noble metals and 2.5 wt % MoO_3, respectively.

- The measured PCT normalized elemental releases for the glasses were at least an order of magnitude below that of EA glass.
- These measured T_L temperatures (1017 and 1128º C for the MoO_3 and noble metal limited glasses, respectively) would support glass processing at a nominal 1250º C processing temperature.

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