IDAHO NATIONAL ENGINEERING AND ENVIRONMENTAL LABORATORY ENVIRONMENTAL MANAGEMENT VITRIFICATION PROGRAM

C. A. Musick, R. R. Kimmit, R. D. Tillotson, B. A. Scholes, K. J. Perry
Idaho Nuclear Technology and Engineering Center, Idaho Falls, ID. 83415

ABSTRACT

The Idaho National Engineering and Environmental Laboratory (INEEL) High Level Waste (HLW) Technology Development Program is tasked with treating approximately 4 million liters of liquid Sodium Bearing Waste (SBW) and 4,400 m^3 of HLW calcine for eventual disposition. The settlement agreement between the State of Idaho, Department of Energy (DOE), and the United States Navy dictates that the SBW must be removed from its current storage tanks by 2012 and the calcine must be retrieved and made road ready for repository storage by 2035. Vitrification, the process of stabilizing a material or waste form into a glass form, may be applied directly or may follow pretreatment processing such as solvent extraction, ion exchange, etc. The vitrification technology development program is currently developing candidate glass formulations and processes that immobilize INEEL wastes. The INEEL waste compositions are unique compared to other DOE sites high level waste, in that Idaho's waste is acidic compared to caustic and contains high amounts of sulfates, fluorides, phosphates, nitrates, and chlorides.

This paper focuses on the methodology and current status of the INEEL vitrification program. The program consists of laboratory scale and pilot scale testing by the INEEL and collaborative partners. Candidate glass formulations are identified through a series of crucible tests that are performed by Pacific Northwest National Laboratory (PNNL), Savannah River Technology Center (SRTC), and INEEL glass formulation scientists. The glass formulation crucible tests are performed to define the primary processability parameters (viscosity and liquidus temperature) and product performance (durability, homogeneity) criteria necessary for waste form qualification. To date these key criteria have all been met at the crucible scale. Additional crucible scale testing is also conducted with varying waste composition parameters to establish the compositional envelope in which acceptable glass products can be made per the key product parameters. Pilot scale testing is conducted in parallel with these variability tests to confirm the ability to make acceptable glass products at the larger scale. Pilot scale melter tests are also performed to identify potential process upsets (corrosion, foaming, off-gas emissions, and redox) and compare product performance (durability) with the crucible test results. SBW glass shows sensitivity to sulfate concentration and oxidation state, which are the focus of near term testing. Much more calcine vitrification work will need to occur to envelop the feed variability. Compositional Variation Study (CVS) work will facilitate investigation through robust prediction models.

INTRODUCTION AND BACKGROUND

As a result of four decades of nuclear fuels reprocessing at the Idaho Nuclear Technology and Engineering Center (INTEC), large volumes of radioactive wastes have been collected. Since 1963 these wastes have been converted to a granular form through fluidized bed calcination. These calcined High Level Wastes (HLW), totaling about 4,400 m^3 in volume, are currently being stored on site in stainless steel bin sets. Figure 1 provides a view of one of the INTEC calcine storage bin sets.

During the span of INTEC operations, secondary radioactive liquid wastes high in alkali nitrates have also been collected and stored. These wastes originate from decontamination, off-gas treatment, and laboratory and fuel storage activities. Collectively, these liquid wastes are known as "sodium bearing wastes (SBW)". Historically SBW has been blended with reprocessing wastes or non-radioactive aluminum nitrate prior to calcination. Because fuel reprocessing is no longer being performed at INTEC, the option of waste blending to deplete SBW inventory is eliminated. Consequently, about 4 million liters of SBW are temporarily stored in stainless steel tanks at INTEC.

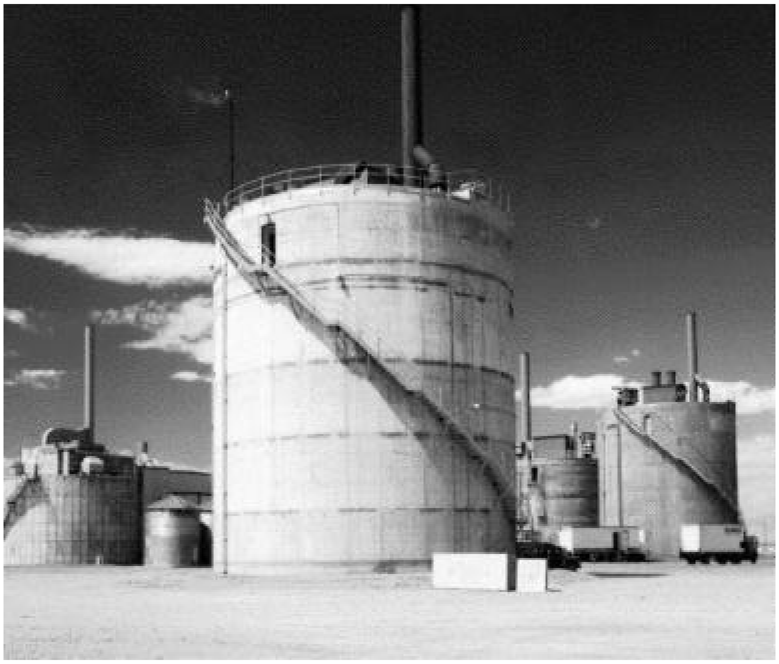

Fig. 1. Empty Calcine Storage Bin Set

A Settlement Agreement was established in August 1995, between the U.S. Navy, the State of Idaho and the U.S. Department of Energy (DOE). The Agreement states that the liquid SBW must be removed from the stainless steel tanks by 2012 and the calcine must be retrieved, treated, and made road ready for repository storage by 2035. Although these dates seem to provide substantial time, the development process must move forward with a steady, productive pace to accomplish the goal of treating these unique waste forms.

Most of the calcine now in storage resulted from calcination of the liquid waste from the reprocessing of a variety of nuclear fuel types. This explains the significant variability in calcine composition. This issue is discussed in more detail below in the section on calcine vitrification. All of the liquid waste from reprocessing has been converted to calcine.

The SBW, although not the direct product of reprocessing, has a similar degree of variability in its composition. This variability is due to the numerous processes by which these liquid wastes were generated such as decontamination, off-gas treatment, and laboratory and fuel storage activities. From the early days of reprocessing to the present, all liquid wastes have been evaporated to reduce the volume of waste stored. The amount of volume reduction varies due these chemistry differences, thus increasing the variability of the SBW wastes that will be vitrified.

The waste treatment situation becomes even more complex given the variety of potential processing options for calcine. Separations entail the use of various chemicals and solvents to strip out the high activity waste (HAW) to both reduce the volume of waste high in radionuclide content, and to reduce the radiation field of the bulk waste to minimize handling difficulty. In that event, the HAW portion of the waste would be vitrified. That waste stream will not only contain the concentrated radionuclide sources, but also the by-products of the separation's process, which may include solvents and organic species. The variability in waste composition and possible up front treatment processes result in a challenging waste treatment task. This variation demands a robust treatment process that has been engineered to encompass as much waste variability as possible.

Currently, the baseline path forward for treatment of the liquid SBW is direct vitrification. The INEEL HLW program and DOE partners developed a SBW treatment roadmap. The roadmap lists all the technology development activities that must be completed to resolve the key uncertainties for SBW disposition. This roadmap schedule was developed based on a prioritization of uncertainties and the development activities required for resolution. The development activities that resolve the high impact uncertainties comprise the scope of work in FY-01. Each development activity being performed has been scoped to meet requirements that fulfill one or more these needs or issues. The goal of technology development is to complete a mass balance and process flow diagrams prior to initiating conceptual design. Once this is completed, technology development will then begin to validate the medium to low assumptions identified in the roadmap.

A technology roadmap has also been used for defining the three alternative calcine treatment and disposal paths that may be used to support the calcine treatment technology decision. These alternatives include two separations paths followed by vitrification and grout and one direct vitrification path. The activities necessary to reach a recommendation for a single technology are estimated to be complete by the end of fiscal year 2005. Due to budget limitations, technology development efforts in FY-01 have been directed toward treatment of the SBW. Most of the technology development activities needed to support a 2005 calcine alternative decision are scheduled to start in FY-02.

COMPOSITION VARIATION STUDY

One of the most important aspects of the INEEL vitrification development program is the Composition Variation Study (CVS). The CVS is comprised of a statistically designed series of experiments that produces several glass samples that are analyzed for key glass properties. Figure 2 shows a typical glass being poured from a crucible. The data from these analyses are then used to develop a mathematical relationship between these glass properties and the composition of INEEL wastes. Where lab scale and pilot scale testing endeavor to understand the operational aspects of producing acceptable glass forms, the CVS examines the potential effect of variations in waste composition on the glass properties.

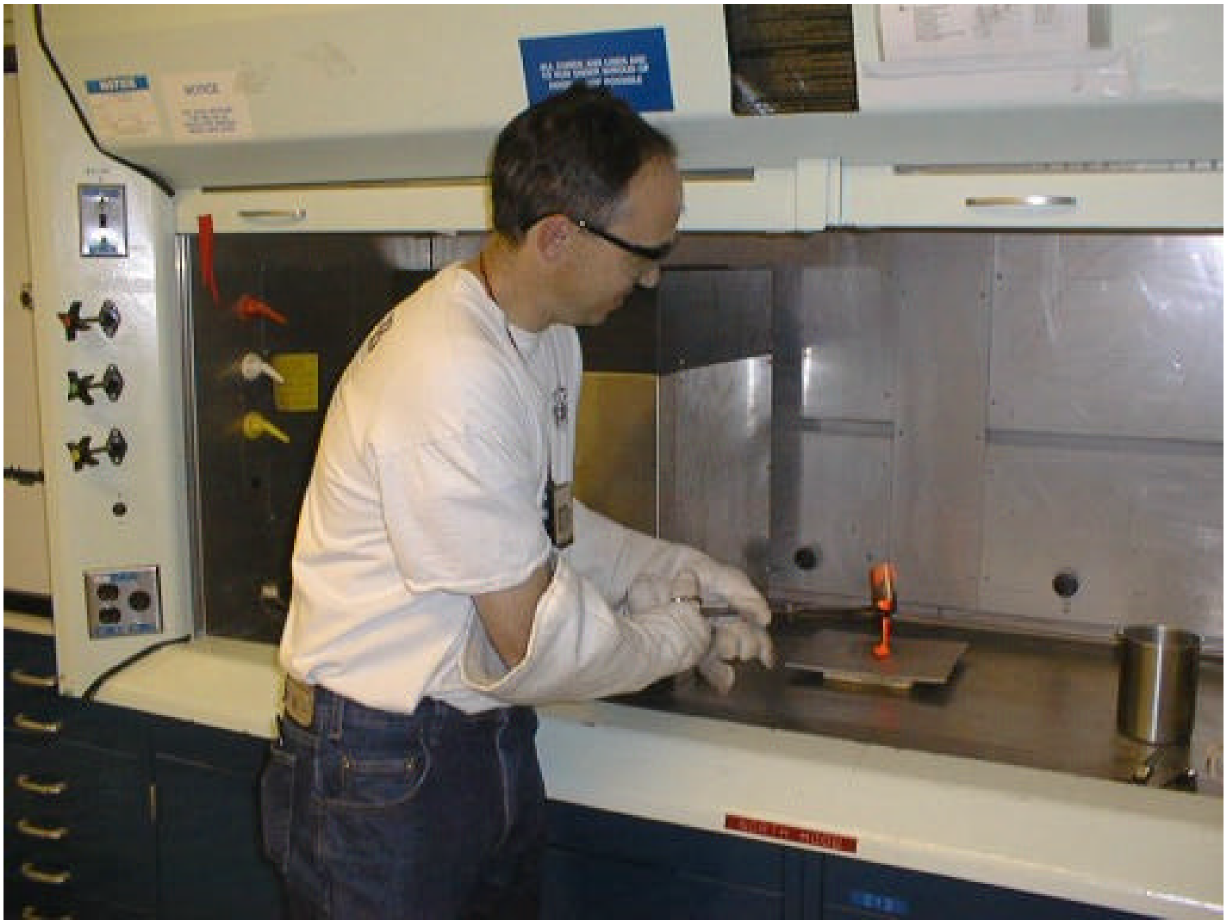

Fig. 2. Pouring glass from a crucible

The probability of a significant degree of variability within SBW and calcine waste is high. The CVS allows the development team to define quantitative relationships between waste composition and the glass properties of interest. These relationships are then employed in the design of a vitrification process, as well as glass formulations, that will produce acceptable glass products within this waste variability envelope. The CVS is critical to the development of a waste qualification program and to the development of a qualified glass production process.

The glass properties that affect the qualification of the waste form are chemical composition, product durability, and phase stability. The chemical composition is not a parameter to be controlled, but rather to be measured and reported accurately. Product consistency embodies the durability of the glass product. Durability is measured through the Product Consistency Test (PCT), which evaluates leachate from crushed glass samples, and is standardized by comparison to PCT results from a known standard glass composition (1). The standard used is called Environmental Assessment (EA) glass (2). Phase stability is accomplished by defining and controlling viscosity, electrical conductivity, liquidus temperature, redox, volatilization, phase separation, and precipitation (3). Viscosity (η) as a function of temperature is obtained on the CVS glasses using a method consistent with ASTM standard procedure C965-95 (4). The liquidus temperature is defined as the maximum temperature at which equilibrium exists between a molten glass and its primary crystalline phase. The liquidus temperature is measured on all single-phase glasses using the uniform temperature method described by Vienna et al. (1998) (5). A CVS shows how these properties are impacted by the varying input waste compositions, and it shows that an acceptable glass form can be produced within a specified envelope of waste variation.

The INEEL CVS has been developed with input from experts at PNNL and SRS based on their experience in developing these processing envelopes for waste at their sites. The development team decided to initiate a phased approach for the various studies. This approach allows for most recent characterization data to be used in defining the waste composition input parameters. Phase 1 of the CVS was performed using only current HAW estimates based on the preliminary separations flowsheet. Phase 1 was completed, and its results were presented in March, 1999 (6). Phase 2 was performed to evaluate the potential for developing formulations for the direct vitrification of INTEC calcined wastes in addition to the vitrification of HAW. The results of the Phase 2 CVS were reported in February, 2000 (7). Phase 3 of the INTEC CVS was developed to improve the coverage of the composition-region studied in CVS Phase 2 glasses and thereby expand the understanding of glass composition-property relationships. Results of the Phase 3 CVS were reported in December, 2000 (8).

In fiscal year 2001, the CVS work is addressing SBW. The study is important in providing data to the ongoing work on the development of waste qualification and certification efforts. The solubility of troublesome components such as sulfate and certain metals are of interest in the SBW CVS. This activity will involve evaluation of more than 60 glass compositions. These results will impact waste loading targets and glass formulations, as well as provide input to the other lab and pilot scale testing within the development program.

VITRIFICATION DEVELOPMENT WORK TO DATE

Sodium Bearing Waste - Feed Preparation and Bench Scale Tests

Glass formulation development for INEEL SBW crucible studies were performed at PNNL and SRTC during the fiscal year of 1999 (9). Empirical models were used to identify candidate glass formulations suitable for the average liquid waste composition. The models included predictions for viscosity-temperature profile and durability. One major concern in vitrifying SBW is the potential for nepheline crystallization. This material has been shown to reduce glass durability. The models were not able to predict either liquidus temperature or homogeneity; therefore, additional constraints were imposed on glass composition. For example, alkali metal oxide content was limited to 25%. To reduce the potential for nepheline formation the sum of SiO_2, Al_2O_3, and Na_2O was limited to 60%. Limits were also placed on Al_2O_3 (10%), Fe_2O_3 (8%), and TiO_2 (2%) to avoid high liquidus temperatures. Based on the modeling work, the frit and glass compositions shown in Table I were selected for testing.

To formulate the feed materials, three feed composition variations were prepared from oxides, salts, and boric acid. These were chosen to evaluate the impacts on glass performance of sulfate, chloride, and fluoride in the feed. For example, chloride was included in SBW but omitted from the SBW-a and SBW-b formulations. Fluoride and sulfate were not included in SBW-a, but were in the other two mixtures. A small amount of iodide was added to only to the SBW feed mixture. See Table II for specific feed compositions.

Table I. Sodium Bearing Waste, Frit, and Glass Composition in Mass Fraction Oxides and Halides

Oxide	Waste	Frit	Glass
Al_2O_3	0.2734		0.0956
B_2O_3	0.0065	0.1426	0.0950
CaO	0.0223		0.0078
Cl	0.0104		0.0036
Cr_2O_3	0.0025		0.0009
Fe_2O_3	0.0155	0.1131	0.0790
F	0.0098		0.0034
I	0.0002		0.0001
K_2O	0.0792		0.0277
Li_2O		0.0267	0.0173
MgO	0.0005		0.0002
MnO	0.0078		0.0027
MoO_3	0.0013		0.0005
Na_2O	0.5005		0.1750
NiO	0.0055		0.0019
P_2O_5	0.0119		0.0042
PbO	0.0031		0.0011
RuO_2	0.0004		0.0002
SO_3	0.0373		0.0130
SiO_2	0.0018	0.6869	0.4474
SnO	0.0002		0.0001
TiO_2		0.0308	0.0200
ZrO_2	0.0100		0.0035
Total	1.0000	1.0000	1.0000
Loading	0.35	0.65	1.0000

Table II. Target Compositions of Different SBW Waste Simulants in Mass Fractions of Oxides and Halides

Oxide	SBW	SBW-a	SBW-b
Al_2O_3	0.0956	0.0975	0.0959
B_2O_3	0.0950	0.0969	0.0953
CaO	0.0078	0.0079	0.0078
Cl	0.0036	0.0000	0.0000
Cr_2O_3	0.0009	0.00092	0.0009
Fe_2O_3	0.0790	0.0806	0.0793
F	0.0034	0.0000	0.0034
I	0.0001	0.0000	0.0000
K_2O	0.0277	0.0283	0.0278
Li_2O	0.0173	0.0177	0.0174
MgO	0.0002	0.0002	0.0002
MnO	0.0027	0.0028	0.0027
MoO_3	0.0005	0.0005	0.0005
Na_2O	0.1750	0.1786	0.1756
NiO	0.0019	0.0019	0.0019
P_2O_5	0.0042	0.0042	0.0042
PbO	0.0011	0.0011	0.0011
RuO_2	0.0002	0.0002	0.0002
SO_3	0.0130	0.0000	0.0130
SiO_2	0.4474	0.4564	0.4490
SnO	0.0001	0.0001	0.0001
TiO_2	0.0200	0.0204	0.0200
ZrO_2	0.0035	0.0036	0.0035
Total	1.0000	1.0000	1.0000

The product glass from the SBW feed included a yellow layer of salt. The salt was rinsed off the glass, analyzed, and was composed primarily of sodium sulfate. Small amounts of alkali-chromate, -phosphate, and –halide salts were also present. The mass of salt in the yellow layer was less than 2% of the related salts included in the feed material. Figure 3 shows a sample of glass with this sodium sulfate salt layer.

Fig. 3. Glass sample with sodium sulfate salt layer evident

All three glasses performed well in the PCT. Release rates for boron, silica, sodium, and lithium were well below those for the EA glass standard. Results are shown in Table III.

Table III. PCT Results for the SBW Glasses and EA Glass

Glass	r_B	r_{Si}	r_{Na}	r_{Li}	**pH**
SBW	0.735	0.216	0.689	0.496	11.16
SBW-a	0.390	0.185	0.395	0.255	10.98
SBW-b	0.520	0.195	0.540	0.335	11.13
EA	8.937	2.156	7.314	4.940	11.84
Note r_x = normalized leach rate, g/m^2					

The viscosity-temperature profile of the SBW glass was measured. The glass viscosity was 5 Pa·sec at the nominal melter operating temperature of 1150°C.

The SBW glass was heat treated at 1050°C for 24 hours, then evaluated for the presence of crystalline phases. Only a small amount of sodium sulfate salt was observed using SEM; therefore, the liquidus temperature glass is no higher than 1050°C. This met another goal that the liquidus temperature be at least 100°C below the nominal melter operating temperature.

A final glass sample was made using a liquid SBW simulant. This simulant contained about 7 molar nitrate. Activated carbon was added to some batches as a reducing agent at about 1.3 moles carbon per mole of nitrate. NiO was added to determine if nickel would be reduced to elemental metal. Crucible tests showed that carbon addition reduced foaming, but did not cause the formation of elemental metal.

Tests on liquid SBW simulant were also performed at INEEL using a small laboratory-scale melter. The melter was designed to hold up to 130 cubic centimeters of molten glass and allow periodic/continuous addition of feed material. During test, the liquid boiled rapidly and a crust of undissolved material was formed. This crust precluded establishment of a steady feed rate.

Tests performed on the laboratory-scale melter glass were comparable to those obtained from crucible glass. However, viscosity-temperature curve was above that for crucible glass, probably due to the presence of excess SiO_2 when part of a quartz feed tube broke off and fell into the melt.

Pilot Scale Tests

Pilot testing was conducted using the Envitco-designed EV-16 melter at the Clemson Environmental Technology Center (CETL) in Anderson, SC. The unit has a cross-sectional area of 2100 cm^2 and a depth of 40 cm. Figure 4 shows the EV-16 melter in operation, where the thin, light looking strip is actual glass being poured from the melter. Electrical power is applied to the melter through a 100-kVA power supply, which uses a Scott-T transformer to convert the three-phase power to a balanced two-phase input to the furnace. The applied power is controlled through two Silicon Control Rectifier (SCR)/secondary transformer sets, which are adjusted to the desired power level through a common potentiometer control. Power is applied to the bath through four 32-mm diameter molybdenum electrodes that enter the melter horizontally through each of the four sides of the melt chamber. A variable-speed tubing pump delivered the feed to the melter through a 6.35-mm stainless steel feed tube. The feed was drawn from a agitated feed tank located on the mezzanine at the backside of the EV-16. The feed tube entered the melter from a penetration in the rear face of the hood and is manually positioned to deposit the feed in the desired location in the melter.

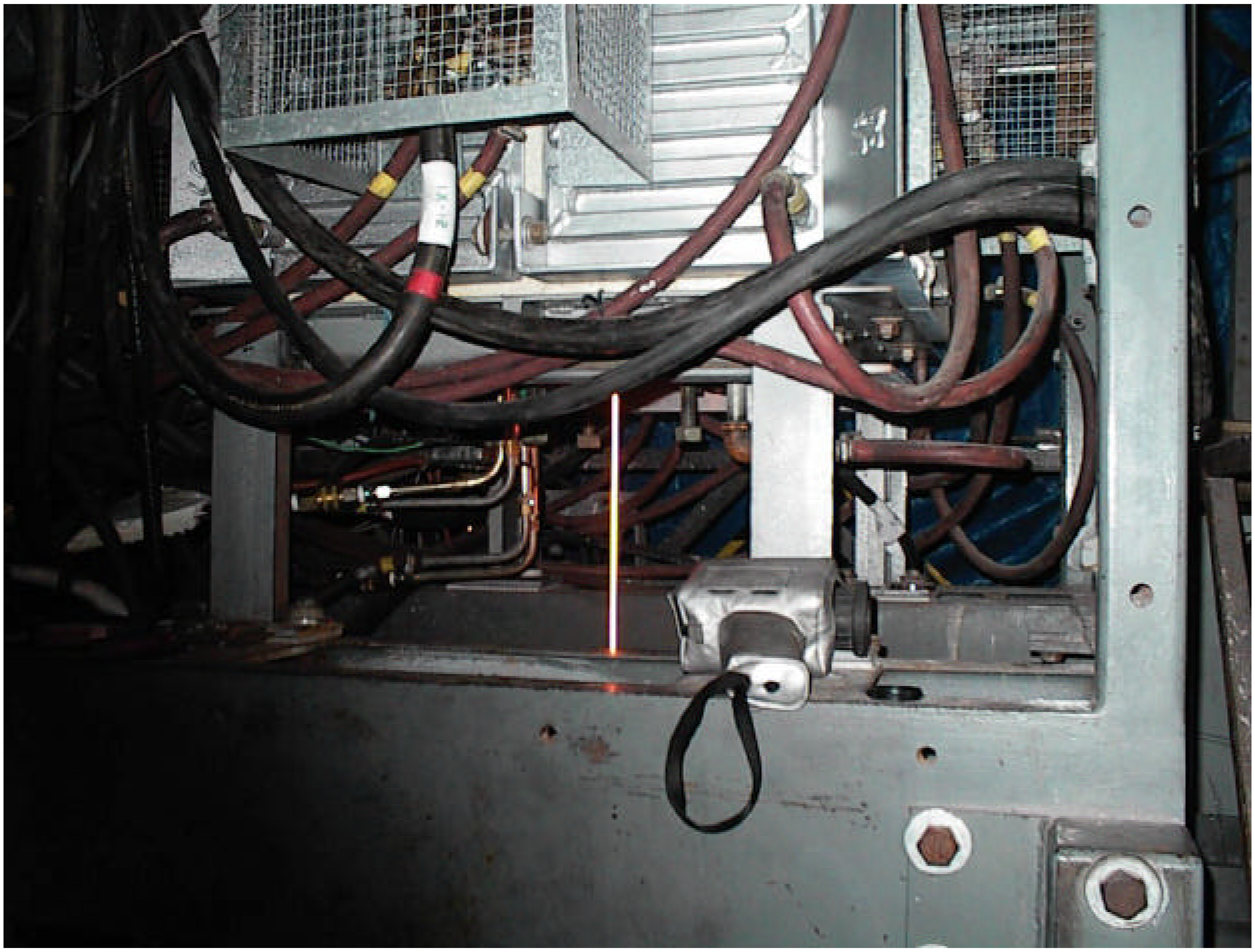

Fig. 4. EV-16 melter pouring glass

The off-gas scrubbing system for the EV-16 melter includes a quench chamber, steam venturi, cyclone separator, packed bed scrubber, and demister.

The melter was operated for 3 days during which approximately 185 kg of glass was poured, including 30 kg of ground glass used as a starting material. A total of 450 liters of slurry feed was added during this time. Glass samples from this melter test were fully characterized. Glass produced at CETL was analyzed at PNNL and SRTC. Table IV compares the target to the measured compositions for the SBW pilot melter glass.

Table IV. Glass Composition in mass fraction from SBW Pilot Melter Test

Oxide	**Target Composition, Mass Fraction**	**Measured Composition, Mass Fraction**
Al_2O_3	0.0956	0.1100
B_2O_3	0.0950	0.0841
CaO	0.0078	0.0143
Cl^-	0.0036	0.0034
Cr_2O_3	0.0009	0.0018
Fe_2O_3	0.0790	0.0501
F^-	0.0034	0.0033
I^-	0.0001	ND
K_2O	0.0277	0.0275
Li_2O	0.0173	0.0162
MgO	0.0002	0.0003
MnO	0.0027	0.0033
MoO_3	0.0005	0.0006
Na_2O	0.1750	0.1690
NiO	0.0019	<0.0100
P_2O_5	0.0042	0.0059
PbO	0.0011	0.0004
RuO_2	0.0002	ND
SO_3	0.0130	0.0057
SiO_2	0.4474	0.4760
SnO	0.0001	ND
TiO_2	0.0200	0.0190
ZrO_2	0.0035	0.0004
Total	1.0000	0.9912
ND: Not Determined		

In addition to composition, standard waste glass parameters were measured from the sample taken from the third crucible. Viscosity was higher than expected, but within the desired 10 Pa·sec upper limit at 1175°C. Results of PCT, shown in Table V below, indicate that leach resistance is greatly superior to the reference EA glass.

Table V. Normalized PCT Release Values (based on measured compositions)

Glass	**r_B (g/m^2)**	**r_{Si} (g/m^2)**	**r_{Li} (g/m^2)**	**r_{Na} (g/m^2)**	**pH**
SBW-3rd Crucible	0.107	0.089	0.130	0.164	10.60
EA Reference	8.35	3.922	4.78	6.67	11.85

As part of the liquidus temperature test, glass samples were subjected to heat treatment according to the Canister Centerline Cooling (CCC) protocol (10). This procedure is intended to simulate the cooling regime of glass in the center of a waste canister, where the greatest potential exists for crystallization. Only 3% crystallization was observed.

Direct Vitrification of Calcine - Feed Preparation

The calcine waste currently in storage at INEEL varies widely in chemical composition. About one-fourth of the material contains more than 85% alumina. Most of the remaining three-fourths of the calcine contains about 15% zirconia and 45% calcium fluoride. A small amount of the calcine is high in sodium.

Since most of the calcine is of the "zirconia" type, the bulk of the testing to date has been with this type of feed material. Unfortunately, the databases and predictive tools developed for work at Hanford, SRS, and West Valley were not suitable for INEEL zirconia calcine chemistry. Because of this, a series of scoping tests were performed to determine the solubility range of calcium and fluoride in borrosilicate glasses (11). The results indicated that CaO concentrations up to about 12% and fluoride levels up to 6% produced glass with acceptable durability and viscosity. These test results, combined with existing models, led to the development of six initial glass formulation candidates. These are shown in Table VI. All are based on 35 wt% waste loading (oxide basis) for zirconia calcine. The formulations were prepared using non-radioactive pilot-plant calcine from INEEL.

Table VI. Glass Compositions Targeting a 35 mass % Waste Loading (of unblended Run 78 calcine), mass fraction

Oxide	**Frit-1-78a-35**	**Frit-2-78a-35**	**Frit-3-78a-35**	**Frit-4-78a-35**	**Frit-5-78a-35**	**Frit-6-78a-35**
Al_2O_3	0.0693	0.0693	0.0693	0.0693	0.0693	0.0693
B_2O_3	0.0634	0.1234	0.1234	0.1234	0.0534	0.0613
CaO	0.1259	0.1259	0.1259	0.1259	0.1259	0.1259
F^-	0.0599	0.0599	0.0599	0.0599	0.0599	0.0599
Fe_2O_3	0.0300	0.0300	0.0600	0.0025	0.0298	0.0610
TiO_2	0.0000	0.0000	0.0000	0.0300	0.0000	0.0000
K_2O	0.0024	0.0024	0.0024	0.0024	0.0024	0.0024
Li_2O	0.0425	0.0600	0.0300	0.0600	0.0600	0.0325
MgO	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Na_2O	0.1405	0.0830	0.0630	0.0604	0.1132	0.1317
P_2O_5	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
SiO_2	0.4000	0.3800	0.4000	0.4000	0.4200	0.3900
ZrO_2	0.0506	0.0506	0.0506	0.0506	0.0506	0.0506
Others	0.0150	0.0150	0.0150	0.0150	0.0150	0.0150
Others = 0.0014 Cr_2O_3, 0.0003 Cl^-, 0.0005 MnO, 0.0003 NiO, 0.0001 PbO, and 0.0124 SO_3^{-2}						

When quenched samples of these glasses were prepared, only three were found to be homogeneous. When subjected to the CCC cooling regime, only the frit 5 feed showed limited crystallization.

It was understood that fluoride content affects the viscosity of the melt. However, the volatility of fluorine-containing species was not known. Three additional feeds were prepared from oxides and salts and based on the frit 5-78a-35 formulation. In these materials, the fluoride content was varied from2.4% to 6%. As expected, the higher the fluoride content, the lower the viscosity was at any given temperature. It is interesting to note that, for all of these glass formulations, the operating temperature must be lowered to around 1050oC to obtain viscosity in the desired range of 2-10 Pa sec.

The liquidus temperatures of these glasses were measured and are shown in Table VII. All liquidus temperature (TL) values were more than 100 degrees below the lower operating temperature.

Table VII. T_L and Primary Phase as a Function of F^- Concentration

ID	**F^- conc., wt. %**	**T_L (°C)**	**Primary Phase**
Frit-5-78a-35	5.81	870	CaF_2
Frit-5-78b-35	4.7	868	CaF_2
Frit-5-78c-35	2.35	879	Sodalite group

Because of the anticipated good performance of the frit 5 glass, testing with higher waste loadings was desired. A second round of bench-scale tests was initiated, targeting 38% waste loading. The higher fluoride level led to a concern about homogeneity, especially under CCC conditions. New frit formulations were developed using La_2O_3 as compared to Fe_2O_3 to increase viscosity during cooling and limit devitrification. After evaluating 20 glasses for homogeneity under CCC conditions, two formulations (frit's 9 and 10) provided both acceptable durability and limited crystallization. Table VIII shows the calcine, frit, and glass compositions associated with frit 5 (35 % waste loading), frit's 9 and 10 (38 % waste loading). These formulations were all tested using a pilot-scale melter.

Table VIII. Comparison of Nominal Compositions for Frit-5-78-35, Frit-9-78b-38, and Frit-10-78b-38 Recommended for Pilot-Scale Melter Testing, mass fraction

	Run 78-D	**Frit-5**	**Frit-5-78d-35**	**Frit-9**	**Frit-9-78b-38**	**Frit-10**	**Frit-10-78b-38**
Al_2O_3	0.2471		0.0865		0.0939		0.0939
B_2O_3	0.0192	0.0680	0.0509	0.1050	0.0724	0.1050	0.0724
CaO	0.3344		0.1170		0.1271		0.1271
Cl^-	0.0011		0.0004		0.0004		0.0004
Cr_2O_3	0.0038		0.0013		0.0014		0.0014
F^-	0.1346		0.0471		0.0511		0.0511
Fe_2O_3	0.0077	0.0420	0.0300	0.0000	0.0029	0.0400	0.0277
K_2O	0.0041		0.0014		0.0016		0.0016
La_2O_3	0.0000		0.0000	0.0400	0.0248	0.0000	0.0000
Li_2O	0.0000	0.0923	0.0600	0.1000	0.0620	0.1000	0.0620
MnO	0.0036		0.0013		0.0014		0.0014
Na_2O	0.0438	0.1516	0.1139	0.1460	0.1072	0.1460	0.1072
NiO	0.0009		0.0003		0.0003		0.0003
P_2O_5	0.0336		0.0118		0.0128		0.0128
PbO	0.0000		0.0000		0.0000		0.0000
SiO_2	0.0082	0.6461	0.4228	0.5930	0.3708	0.5930	0.3708
SO_3^{-2}	0.0226		0.0079		0.0086		0.0086
SrO	0.0000		0.0000		0.0000		0.0000
ZrO_2	0.1353		0.0474	0.0160	0.0613	0.0160	0.0613
Total	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

Pilot Scale Tests

The EV-16 melter at the CETL was used for the calcine tests. A screw-type feeder was used to deliver the dry powdered feed to the melter. For tests involving frit's 5 and 9, pilot plant calcine was combined with frit components. However, the supply of pilot-plant calcine from INEEL was limited, and frit 10 testing was done with a surrogate material composed of oxides and salts. Because the calcine contains about 7% sodium nitrate, it was decided to add about 1.2 wt. % powdered activated carbon to the feed to limit oxidation of the molybdenum electrodes in the EV-16 melter.

The test with feed based on frit 5 lasted 29 hours. A total of 320 kg of glass was produced. The glass was subjected to the CCC regime, then evaluated by optical microscopy, X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) for homogeneity. Less than 1 vol. % crystallization was observed. The crystals present were determined to be iron and nickel sulfides. Other properties of the glass were measured and are summarized in Table IX.

Table IX. Frit 5 Glass Product Performance Assessment

Performance Criteria	**Target/Objective**	**Frit 5 Demonstration Results**	**Notes**
Viscosity	2-10 Pa·s at processing temperature (1050 ± 25°C)	1.2-2.8 Pa·s	Note (b)
PCT	Less than 1 g/m^2 for r_B	0.192 g/m^2 (avg.)	Excellent
	Less than 1 g/m^2 for r_{Na}	0.354 g/m^2 (avg.)	Excellent
	Less than 1 g/m^2 for r_{Li}	0.315 g/m^2 (avg.)	Excellent
Phase Stability	Less than 2 vol. % crystallinity[(a)] (after CCC heat treatment schedule)	1-2% typical 5–10% observed	Note (c)
Liquidus Temperature	$T_L \leq T_M - 100^oC$	T_L not Measured	Note (d)

(a) Glass formulation development was based on a conservative goal of less than 2 vol. % crystallinity formed during simulated CCC. This served as a temporary guideline. Follow-on work is required to determine an acceptability limit for crystallinity of the glasses.

(b) Fluoride volatility was much less than expected, resulting in F- levels in the glass in excess of the target. Subsequent formulations were based on higher anticipated F- retention with adjusted formulations to better meet the target viscosity (η) range.

(c) Variation in the crystallinity is assumed to be due to the variation in composition of the glass samples. It is important to note that 1) the 2 vol. % crystallinity served as a target for the glass formulation development and is not a waste acceptance limit, and 2) the crystallinity had no observable affect on the glass PCT performance.

(d) Processing temperatures are discussed in the Melter Demonstration observations.

The condition of the melter was observed at the end of the test, after residual glass was mined out. The electrodes and refractory showed no degradation over the test period. Some nodules were observed in the bottom of the melter. These were not analyzed, but were assumed to be iron and nickel sulfides. Their presence indicates that the reducing agent added was in excess of the optimum concentration.

While all of the frit 5 feed material was made using pilot plant calcine, there was not enough calcine for later runs. A portion of the feed based on frit 9 and all of the feed based on frit 10 was made using oxides and salts to simulate the calcine.

The glass produced with the frit 9 formulation was clear green with streaks of white crystalline material. Cuspidine and CaF2 were the major crystalline species present. Total crystallinity varied from about 2 vol. % in two of the glass samples to more than 25 vol. % in the third sample. This variability was due to the lack of homogeneity in the glass and some subjectivity in the sampling process. Despite the lack of homogeneity, the performance of all glass samples was within the desired ranges. Durability was significantly better than the reference EA glass, and viscosity was within the desired range at operating temperatures. Table X summarizes these results.

Table X. Frit 9 Glass Product Performance Assessment

Performance Criteria	**Target/Objective**	**Frit 9 Demonstration Results**	**Notes**
Viscosity	2-10 Pa·s at processing temperature (1000 ± 25°C)	2.0-4.0 Pa·s	Good[(b)]
PCT	Less than 1 g/m^2 for r_B	0.194 g/m^2 (avg.)	Excellent
	Less than 1 g/m^2 for r_{Na}	0.330 g/m^2 (avg.)	Excellent
	Less than 1 g/m^2 for r_{Li}	0.290 g/m^2 (avg.)	Excellent
Phase Stability	Less than 2 vol. % crystallinity[(a)] (after CCC heat treatment schedule)	1-2% typical 25–50% observed	Note (c)
Liquidus Temperature	$T_L \leq T_M - 100°C$	T_L not measured	

(a) Glass formulation development was based on a conservative goal of less than 2 vol. % crystallinity formed during simulated canister centerline cooling (CCC) heat treatment. This served as a temporary guideline. Follow-on work is required to determine an acceptability limit for crystallinity of the glasses.

(b) Viscosity levels are within range, but tended toward the lower end. Fluoride levels in the glass in excess of the target, and may have been responsible for lower than desirable viscosity (η).

(c) Variation in the crystallinity is assumed to be due to the variation in composition of the glass samples. It is important to note that a) the 2 vol. % crystallinity served as a target for the glass formulation development and is not a waste acceptance limit, and b) the crystallinity had no observable affect on the glass PCT performance. Higher levels of devitrification were noted in the calcine blend glass samples, which contained F^- in excess of the target concentration.

Because no pilot-plant calcine was available for the frit 10 test, the feed material was prepared using oxides and salts. Unfortunately, one of the chemical containers was mislabeled, and this resulted in lower than expected concentrations of calcium and fluoride in the feed. Nevertheless, the results of this test can be compared to frit 5 and frit 9 results to demonstrate the impact of high calcium and fluoride expected in the actual calcine.

Because metallic deposits were seen in the bottom of the melter at the end of the frit 5 test, only 0.34 wt % of powdered activated carbon was added to frit 10 feed. All glass samples from this test showed less than 1 vol. % crystallization. This was expected, given the lower calcium and fluoride levels when compared to frit 9 feed. The lack of fluoride had a significant impact on viscosity. This parameter was much higher than was observed with frit 9. The overall glass properties are summarized in Table XI.

Table XI. Frit 10 Glass Product Performance Assessment

Performance Criteria	**Target/Objective**	**Frit 10 Demonstration Results**	**Notes**
Viscosity	2-10 Pa·s at processing temperature (1000 ± 25°C)	8.0-15.0 Pa·s	Note (b)
PCT	Less than 1 g/m^2 for r_B	0.240 g/m^2 (avg.)	Excellent
	Less than 1 g/m^2 for r_{Na}	0..301g/m^2 (avg.)	Excellent
	Less than 1 g/m^2 for r_{Li}	0..360 g/m^2 (avg.)	Excellent
Phase Stability	Less than 2 vol. % crystallinity$^{(a)}$ (after CCC heat treatment schedule)	~1 vol. % typical	Note (c)
Liquidus Temperature	$T_L \leq T_M - 100°C$	T_L not measured	

(a) Glass formulation development was based on a conservative goal of less than 2 vol. % crystallinity formed during simulated canister centerline cooling (CCC) heat treatment. This served as a temporary guideline. Follow-on work is required to determine an acceptability limit for crystallinity of the glasses

(b) Viscosity levels exceed the limit, but this is due to the low Ca and F^- in the glass.

(c) Variation in the crystallinity is assumed to be due to the variation in composition of the glass samples. It is important to note that a) the 2 vol. % crystallinity served as a target for the glass formulation development and is not a waste acceptance limit, and b) the crystallinity had no observable affect on the glass PCT performance. Higher levels of devitrification were noted in the calcine blend glass samples, which contained F- in excess of the target concentration.

PATH FORWARD

Based on the SBW direct vitrification testing to date, the technology development team members and DOE partners are confident that quality glass can be produced with SBW. However, the product is sensitive to sulfate concentration and oxidation state of the melt during processing. High waste loadings will produce a secondary molten salt phase, with its attendant production management problems. Also, without adequate control of oxidation, insoluble sulfides or elemental metal phases may form, thus resulting in an unpredictable and less robust process. Other challenging work that is in progress includes waste characterization, off-gas cleanup, secondary waste treatment, and feed preparation. The technology development currently being performed will resolve the uncertainties and provide a process basis that will be utilized to initiate conceptual design.

For calcine, the data that have been collected from the CVS and pilot scale melter testing with surrogate calcine indicate that direct vitrification of calcine and one of the separation processes are viable alternatives. However, only a fraction of the range of calcine compositions have been tested, thus requiring more data to complete the process flow diagrams and mass balance. The calcine roadmap identifies the remaining scope of work that is needed to make a single path decision.

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