

# Using Polymerization, Glass Structure, and Quasicrystalline Theory to Produce High Level Radioactive Borosilicate Glass Remotely: A 20+ Year Legacy

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Vitrification is currently the most widely used technology for the treatment of high level radioactive wastes (HLW) throughout the world. Most of the nations that have generated HLW are immobilizing in borosilicate glass. One of the primary reasons that glass has become the most widely used immobilization media is the relative simplicity of the vitrification process, e.g. melt a highly variable waste with some glass forming additives such as SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub> in the form of a premelted frit and pour the molten mixture into a stainless steel canister. Seal the canister before moisture can enter the canister (10' tall by 2' in diameter) so the canister does not corrode from the inside out. Glass has also become widely used for HLW is that due to the fact that the short range order (SRO) and medium range order (MRO) found in the structure of glass atomistically bonds the radionuclides and hazardous species in the waste. The SRO and MRO have also been found to govern the melt properties such as viscosity and resistivity of the melt and the crystallization potential and solubility of certain species. The molecular structure of the glass also controls the glass durability, i.e. the contaminant/radionuclide release, by establishing the distribution of ion exchange sites, hydrolysis sites, and the access of water to those sites. The molecular structure is flexible and hence accounts for the flexibility of glass formulations to HLW waste variability. Nuclear waste glasses melt between 1050-1150°C which minimizes the volatility of radioactive components such as <sup>99</sup>Tc, <sup>137</sup>Cs, and <sup>129</sup>I. Nuclear waste glasses have good long term stability including irradiation resistance. Process control models were developed based on the molecular structure of glass, polymerization theory of glass, and quasicrystalline theory of glass crystallization. These models create a glass which is durable, pourable, and processable with 95% accuracy without knowing from batch to batch what the composition of the waste coming out of the storage tanks will be. These models have operated the Savannah River Site Defense Waste Processing Facility (SRS DWPF), which is the world's largest HLW Joule heated ceramic melter, since 1996. This unique "feed forward" process control, which qualifies the durability, pourability, and processability of the waste plus glass additive mixture before it enters the melter, has enabled ~8000 tons of HLW glass and 4242 canisters to be produced since 1996 with only one melter replacement.

## Introduction

Most nuclear nations have generated high level radioactive wastes from nuclear weapons programs and/or commercial nuclear power generation and most nations store waste materials from a variety of reprocessing flowsheets. The Plutonium and URanium EXtraction (PUREX) process<sup>†</sup> is the baseline for spent fuel reprocessing for most countries with active fuel cycle programs. France and the UK reprocess spent fuel for electric utilities from other countries using the PUREX process to recover uranium (U) and plutonium (Pu). Slight modifications to the PUREX process can be made to recover U, Pu, Np, and Tc (if desired) and a number of countries (e.g., France, Japan, China, etc.) are developing solvent extraction processes to recover the minor actinides (Am and Cm) from spent fuel. Many of these radionuclides can be reprocessed as fuel and some have medical applications.

In the US, a moratorium was placed on reprocessing of commercial spent nuclear fuel in 1977. A 2005 energy bill has revived the potential for reprocessing but currently spent fuel rods (once through) are in storage pools across the US and destined for direct disposal in a deep geological repository. Hence, HLW in the US is primarily defense wastes of which 36 million US gallons (136,275 m<sup>3</sup>) are stored at the Savannah River Site (SRS) in South Carolina and 50 million US gallons (189,270 m<sup>3</sup>) are stored at the Hanford site in Richland, Washington. While Hanford has more waste volume, Savannah River Site waste contains higher curie contents. Prior to the 1977 moratorium, a reprocessing facility had been built and initiated operation in West Valley, New York. The West Valley Demonstration Project (WVDP)

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<sup>†</sup> The PUREX process was developed in the United States in 1950 and the world's first operational full-scale PUREX separation plant, began radioactive operations at the Savannah River Plant in 1954. The process has run continuously at SRP since start-up for defense materials only.

created ~ 0.66 million US gallons (2,500 m<sup>3</sup>) of HLW from commercial nuclear fuel reprocessing using the PUREX and THOREX processes<sup>1</sup>.

The HLW streams are stored either as a neutralized nitric acid stream in mild steel tanks (U.S. and Russia) or as nitric acid streams in stainless steel tanks (France, UK, Japan, Russia). Although borosilicate glasses have become the preferred waste form for the immobilization of HLW solutions in the majority of the nuclear nations, the chemical variability of the wastes from the different reactor and reprocessing flowsheets coupled with the additional variability imposed by neutralization vs. direct storage of acidic wastes has led to a diverse HLW chemistry, e.g. HLW contains about three fourths of the elements in the periodic table (Figure 1).

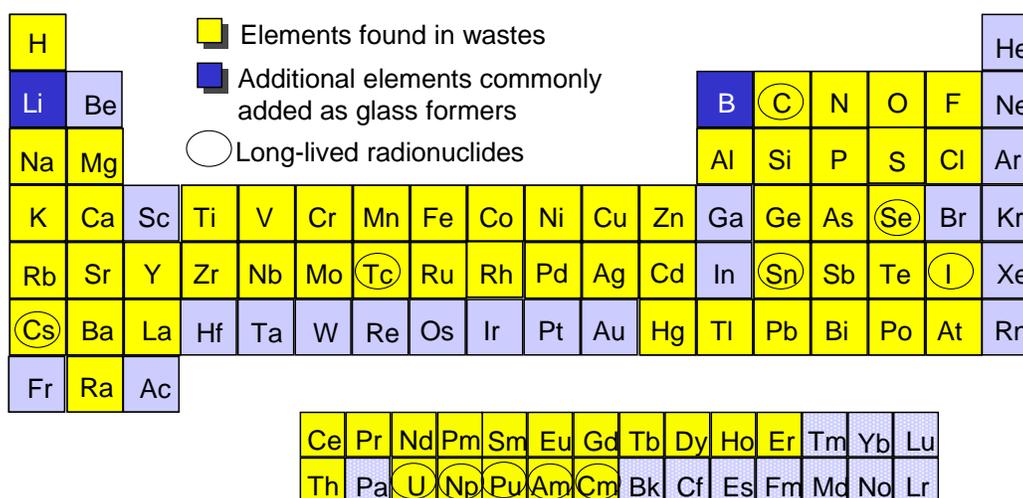
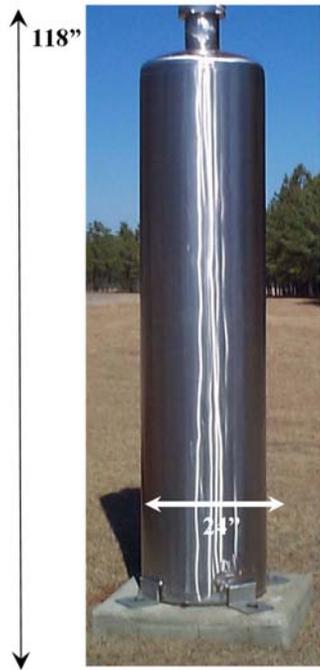


Figure 1. Elements in US HLW Defense Waste Glass.

The manufacture of window glass ( $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ ) and Pyrex glass ( $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ ), is easy compared to the manufacture of HLW glass, because (1) the glass chemist knows the glass forming regions in the simple three component oxide systems, (2) sacks of raw materials have known compositions, and (3) the raw materials are not radioactive. With HLW glass manufacture, (1) a glass forming region had to be defined based on variable input streams, (2) the incoming waste mixture is highly variable and poorly characterized, (3) all processing must be performed remotely due to the high radiation fields. In addition, due to the radioactivity a waste glass cannot be recycled to the front part of the process for re-processing and once a HLW glass is poured into the tall narrow canisters (10' x 2') with a narrow neck so they can be hoisted by a grappling hook (Figure 2), re-processing is impossible. In addition, melter replacement (Figure 3) and repair must be done remotely due to the radioactivity and so the glass processing window must not only be defined but be accurate to the 95% confidence level. One more important consideration is to maximize the amount of HLW waste per canister so that the minimum disposal volume (smallest number of total canisters) is achieved. Disposal costs in a yet to be sited geologic repository are expensive on a per canister basis.



**Materials:** 304L Stainless Steel  
**Empty Weight:** 1150 lbs.  
**Glass Weight:** 3800 lbs.



**Canister Inspection  
Prior to Usage**

Figure 2. HLW Glass Canister Geometry Used at DWPF (Courtesy of Savannah River Site).

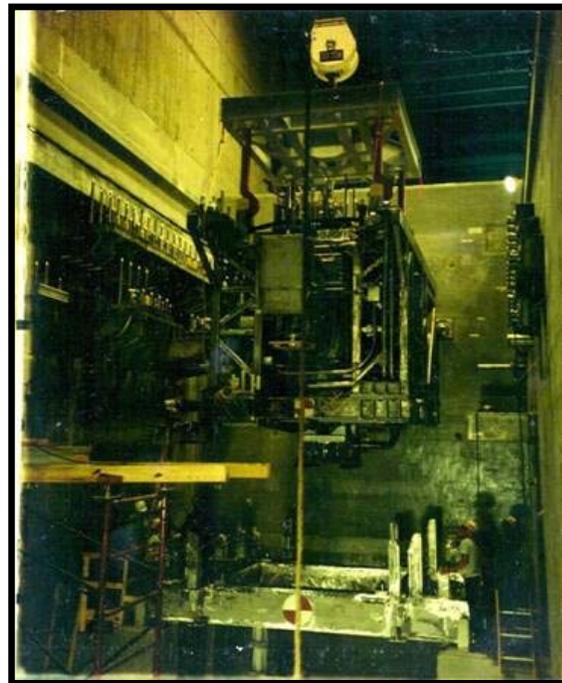


Figure 3. DWPF melter #1 being disposed of after 9 years of operation. Melter was emptied through emergency bottom drain and lifted out of the melt cell into a waste box for storage and eventual disposal (Courtesy of Savannah River Site).

## Theory

Glass has been found to be very flexible and bond many of the HLW constituents (both radioactive and non-radioactive components) atomistically. Borosilicate waste glasses and melts possess short-range order (SRO; radius of influence  $\sim 1.6\text{-}3\text{\AA}$ ) around a central atom, e.g. polyhedra such as tetrahedral and octahedral structural units and medium range order (MRO) which encompasses second- and third-neighbor environments around a central atom (radius of influence  $\sim 3\text{-}6\text{\AA}$ )<sup>2</sup>. The MRO in glasses have distributions exhibiting polymerization into rings and chains and allow glass structures to accommodate the wide range of species existing in HLW wastes compared to crystalline (ceramic or mineral) waste forms in which one must more rigorously know what crystalline structure each HLW waste component will reside in.

In glass, the more highly ordered regions of MRO, referred to as clusters or quasicrystals, often have atomic arrangements that approach those of crystals<sup>2,3</sup>. These clusters or quasicrystals, in conjunction with the octahedral site preference energies<sup>4,5</sup>, govern what waste constituents have poor solubility in borosilicate glass<sup>6,7,8,9</sup> and what crystalline species may form at the liquidus or during cooling of the vitrified waste form<sup>4,5</sup>.

The HLW glass formulations, which had to be defined before HLW glass processing could begin, were driven by the need to simultaneously optimize<sup>10,11,12</sup> multiple product/ process (P/P) constraints such as waste component solubility, melt viscosity, melt corrosivity, melt volatility, liquidus and glass product durability (Table I). A given HLW glass must simultaneously optimize all of the P/P constraints and not just have superior chemical durability while having poor thermal or mechanical stability or while being corrosive to all known melter materials of construction. In other words, one must look at the entire process, a “systems approach,” e.g. how does this waste form react during processing and how will the product produced react with the disposal environment and meet the regulatory requirements of the disposal system? Most P/P properties, other than melt temperature, cannot be measured directly. The waste streams are often highly variable and difficult to characterize. Therefore, P/P models are used to relate glass composition to a given property, e.g. durability, viscosity, liquidus which ensures the glass is durable, pourable and will not crystallize in the melter. The “systems approach” ensures that the final product safeguards the public, and that the production process used is safe to operate.

TABLE I. HLW Glass Product/Process (P/P) Constraints

Product Constraints	Process Constraints
chemical durability	melt viscosity
glass homogeneity	liquidus
thermal stability	waste solubility
regulatory compliance	melt temperature/corrosivity
mechanical stability	radionuclide volatility
	REDuction/OXidation (REDOX)*

\* controls foaming and thus improves melt rate and controls and metal nodule formation and thus improves melter longevity

## Results and Discussion

### Glass Quality: Feed Forward Process Control

When processing HLW glass, a production facility cannot wait until the melt or waste glass has been made to assess its acceptability, since by then no further changes to the glass composition and acceptability are possible. Therefore, the acceptability decision is made on the upstream process, rather than on the downstream *melt* or glass product. That is, it is based on “feed forward” statistical *process* control (SPC)<sup>†</sup> rather than statistical *quality* control (SQC).<sup>††</sup> In SPC, the feed composition to the melter is controlled *prior* to vitrification. In SQC, the glass product is sampled *after* it is vitrified. In addition, in the US, the P/P constraints must be satisfied to a very high degree of certainty (>95%) as rework (remelting) of the product impossible. With feed forward process control, individual property models are used to transform constraints on the melt and product properties into constraints on the feed composition, e.g. the melter is treated as a “black box” and the glass quality in the canister is controlled at 95% confidence from the incoming feed composition.

The successful “systems approach” used at the Savannah River Sites HLW Defense Waste Processing Facility (DWPF) since 1996 is based on “feed forward statistical process control.” A confirmatory glass sample is taken only when the feed tank composition changes, e.g. once every 0.5-3 years. The feed composition is used to calculate the P/P properties of a melter feed from mechanistic P/P models that relate the melt composition to the P/P properties<sup>10, 11</sup>. The P/P models depend on known relationships between glass bonding, thermodynamics, and glass structure. These models are the foundation of the SPC system used to monitor and control glass composition for HLW (Product Composition Control System)<sup>13</sup>. Since 1996, over 8000 metric tons (Table II) of HLW glass has been successfully processed to stringent constraints (95% confidence) without any rework.

TABLE II. Summary of DWPF Production Data (as of September 2016)

	Melter # 1	Melter # 2	Total*
<b>Years Operated</b>	8.5 y (6.5 yrs rad op) (05/94 to 11/02) (03/96 to 11/02 rad)	>14 y (03/03 to Present)	>18.5 yrs (rad)
<b>Canisters Produced</b>	1,339 rad. + 80 non- rad.	2903 rad	4242 (rad)
<b>Glass Produced (kgs)</b>	2.83E+05	6.92E+06	7.20E+06
<b>Curies Processed</b>	1.03E+06	5.584E+07	5.95E+07

The mechanistic models can be extrapolated well outside the glass composition range for which they were developed<sup>14</sup> because they are based on known mechanisms. Therefore, mechanistic models allow more flexibility for process control than empirical models, e.g. empirical models are restricted to the compositional region over which they were developed. The P/P models presented below can, therefore, be directly applied to other types of HLW wastes and borosilicate waste glasses. Changes to mechanistic models are easily facilitated as long as the mechanism that oxide plays in the glass structure are known<sup>15,16</sup>.

† This controls the Slurry Feed to the Melter *prior* to vitrification.

†† Which would adjudicate product release by sampling the glass *after* it's been made.

## Glass Durability and Homogeneity

The durability of a waste glass is the single most important variable controlling release of radionuclides and/or hazardous constituents. The intrusion of groundwater into, and passage through, a waste form burial site in which the waste forms are emplaced is the most likely mechanism by which constituents of concern may be removed from the waste glass and carried to the biosphere. Thus it is important that waste glasses be stable in the presence of groundwater.

For homogeneous borosilicate HLW glasses, acceptable performance is defined as an acceptably low dissolution rate, which is controlled by maintaining the glass composition within an acceptable range. The approach can be represented in terms of linking several relationships:

process control ↔ composition control ↔ dissolution rate control ↔ performance control ↔ acceptable performance

This linkage is appropriate for HLW waste glasses because the radionuclides are incorporated within the glass structure and are released congruently as the glass dissolves. In general, for any waste form it must be established that control of performance in a laboratory test predicts acceptable control of performance in a disposal system based on performance tests and modelling.

In the United States the durability and phase stability of vitrified HLW must be assessed during production<sup>17</sup> because the repository is interested in knowing and being able to predict the “maximum radionuclide release.” These glass composition and durability are tied together by the linking relationships shown above as the process and/or composition control translates into acceptable performance. The “product quality constraint” on the HLW glass requires that the waste form producer demonstrate control of the waste form production by comparing production samples or process control information, separately or in combination to a benchmark glass standard<sup>18,19</sup> using the Product Consistency Test (ASTM C1285-08)<sup>20</sup>.

For a glass to be acceptable, the mean concentrations of lithium, sodium, and boron in the leachate, after normalization for the concentrations in the glass, must be less than those of the benchmark glass. For congruent dissolution, the rate of release of a radionuclide from the waste form is proportional to both the dissolution rate of the waste form and the relative abundance of the radionuclide in the waste form<sup>21</sup>. Thus for borosilicate glass <sup>99</sup>Tc is the radionuclide released at the fastest rate (<sup>137</sup>Cs is released at a somewhat slower rate). However, extensive testing<sup>22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32</sup> demonstrated that Tc<sup>99</sup> is released at the same rate, congruently, as Na, Li and B. This enables the Na, Li, and B to be measured in a glass durability test and be equated to the “maximum radionuclide release.” These elements are not sequestered in precipitates that participate in surface alteration reactions, and are also not solubility limited.

In HLW glasses, the molecular structure controls dissolution (contaminant release) by establishing the distribution of ion exchange sites, hydrolysis sites, and the access of water to those sites<sup>33</sup>. Thus the durability model, known as the Thermodynamic Hydration Energy Reaction Model (THERMO™)<sup>34, 35</sup>. THERMO™ estimates the relative durability of silicate and borosilicate glasses based on their compositions. THERMO™ calculates the thermodynamic driving force of each glass component to hydrate based on the mechanistic role of that component during dissolution, e.g. ion exchange, matrix dissolution, accelerated matrix dissolution, surface layer formation, and/or oxidative dissolution. The

overall tendency of a given glass to hydrate is expressed as a preliminary glass dissolution estimator, e.g. the change in the free energy of hydration of a glass ( $\Delta G_p$ ) based solely on its composition. The  $\Delta G_p$  is correlated to the response of a 7 day ASTM C1285 (Product Consistency Test). For glasses that undergo accelerated matrix dissolution, an accelerated hydration free energy,  $\Delta G_a$ , can be calculated from known strong base [SB] weak acid [WA] equilibrium. The  $\Delta G_a$  term is additive to  $\Delta G_p$  such that the overall durability of the glass, expressed as the final hydration free energy ( $\Delta G_f$ ), can be predicted, e.g.  $\Delta G_f = \Delta G_p + \Delta G_a$ . The more negative the  $\Delta G_f$  the more readily the hydration reaction will occur and the less durable the glass.

To ensure that borosilicate HLW glasses do not exhibit glass-in-glass phase separation, a minimum  $\text{Al}_2\text{O}_3$  limit (wt% in the glass) is applied.<sup>§</sup> The effect of insufficient  $\text{Al}_2\text{O}_3$  was first hypothesized by French researchers<sup>36</sup> who determined that many glass durability models were non-linear, e.g., glasses had release rates far in excess of those predicted by most models, in regions corresponding to low  $\text{Al}_2\text{O}_3$  and in excess of 15 wt%  $\text{B}_2\text{O}_3$  and this was later confirmed independently by Jantzen, et al.<sup>34, 35, 37</sup> The low  $\text{Al}_2\text{O}_3$  was also shown to a cause of glass-in-glass phase separation in  $\text{Al}_2\text{O}_3$ - $\text{Fe}_2\text{O}_3$ - $\text{FeO}$ - $\text{Na}_2\text{O}$ - $\text{SiO}_2$  natural basalt systems<sup>37</sup>.

### Glass Viscosity and Resistivity

The viscosity of a waste glass melt as a function of temperature is the single most important variable affecting the melt rate and pourability of the glass. The viscosity determines the rate of melting of the raw feed, the rate of glass bubble release (foaming and fining), the rate of homogenization, and thus, the quality of the final glass product. If the viscosity is too low, excessive convection currents can occur, increasing corrosion/erosion of the melter materials (refractories and electrodes) and making control of the waste glass melter more difficult. Waste glasses are usually poured continuously into steel canisters or cans for ultimate storage. Glasses with viscosities >500 poise do not readily pour. Moreover, too high a viscosity can reduce product quality by causing voids in the final glass. Therefore, a range of viscosities between 20 and 110 poise at  $T_{\text{melt}}$ , are currently being used for Joule heated waste glass melters.

The approach taken in the development of the viscosity and resistivity process models<sup>11, 38, 39</sup> was based on glass structural considerations, expressed as a calculated non-bridging oxygen (NBO) term. This NBO parameter represents the amount of structural depolymerization in the glass (Equation 1). Oxide species were expressed in mole fraction and related to the viscosity-temperature dependence of the Fulcher equation<sup>40, 41</sup> also known as the Vogel-Fulcher-Tammann (VFT)<sup>‡</sup> equation. The VFT relates the viscosity ( $\eta$ ) of a glass to temperature (Equation 2) for Newtonian fluids.

$$\text{Equation 1} \quad \text{NBO} \equiv \frac{2(\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Cs}_2\text{O} + \text{Li}_2\text{O} + \text{Fe}_2\text{O}_3 - \text{Al}_2\text{O}_3) + \text{B}_2\text{O}_3}{\text{SiO}_2}$$

<sup>§</sup> In glasses the competition for dominant tetrahedral role can cause one or more of the  $(\text{SiO}_4)^{-4}$ ,  $(\text{BO}_4)^{-5}$ ,  $(\text{PO}_4)^{-3}$  SRO tetrahedral units to phase separate and contaminants/radionuclides can partition to the more soluble of the two or more glassy phases created. However, the presence of  $(\text{AlO}_4)^{-5}$  tetrahedra in glass contract the glass structure and inhibit phase separation.

<sup>‡</sup> Fulcher derived this expression to model viscosity of inorganic glasses in 1925. In 1921 Vogel (Phys. Zeit., 22, 645-646) derived a similar expression for the viscosity of water, mercury, and oils and Tammann and Hesse generated a similar equation for organic liquids in 1926 (Z. Anorg. Allg. Chem. 156, 245-257). So all three are credited with the derivation of the mathematical expression and it is often referred to as the VFT equation.

Equation 2

$$\log_{10} \eta = A + \frac{B}{T - T_0}$$

In Equation 2,  $\eta$  is viscosity (poise or  $\text{d}\cdot\text{Pa}^*$ ),  $T$  is temperature in  $^{\circ}\text{C}$ , and  $A$ ,  $B$ , and  $T_0$  are fitted constants. It is well documented that the overall fit of the Fulcher equation is excellent for glasses but that it also overestimates viscosity at lower temperatures in the range of viscosities  $>10^{10} \text{ Pa}\cdot\text{s}^{42}$ .

Calculation of the NBO term from molar composition was combined with quantitative statistical analyses of response surfaces to express glass viscosity and resistivity as a function of melt temperature and glass composition (Figure 4). The DWPF glass viscosity model is given by

Equation 3

$$\log \eta(\text{poise}) = -0.61 + \left( \frac{4472.45}{T(^{\circ}\text{C})} \right) - (1.534 * \text{NBO})$$

with an  $R^2 = 0.976$ .

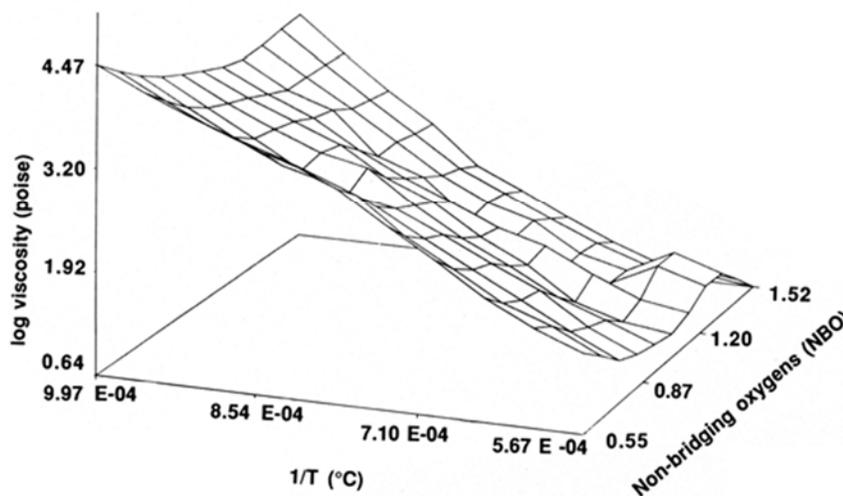


Figure 4. DWPF viscosity model showing the relationship between composition (NBO), viscosity and temperature.

\* The unit of viscosity is the dyne second per square centimetre which is called the poise. The SI unit for viscosity is the Newton second per square meter, or pascal second; one of these units equals 10 poise.

The DWPF viscosity model assumes that a pure SiO<sub>2</sub> glass is fully polymerized; i.e. there are no NBO and 4 BO bonds per Si. In the DWPF viscosity model it is assumed that each mole of alkali oxide added creates two non-bridging oxygen bonds by forming metasilicate (Na<sub>2</sub>SiO<sub>3</sub>) structural units, thus depolymerizing the glass. While the exact number of non-bridging oxygen atoms depends on the molar ratio of all of the species in a waste glass to SiO<sub>2</sub>, most DWPF glasses have a O<sup>2-</sup>/ Si<sup>4+</sup> ratio of 2.6 to 3.3 which implies that disilicate and metasilicate structural units predominate for the alkali species in the waste glasses. Calculation of the O<sup>2-</sup>/ Si<sup>4+</sup> ratio for DWPF glasses included contributions from Na, K, Li, and Cs alkali species and a Si<sup>4+</sup> concentration that was depleted by the amount associated with B<sub>2</sub>O<sub>3</sub> structural units.

The DWPF viscosity model further assumes that each mole of Al<sub>2</sub>O<sub>3</sub> creates two bridging oxygen bonds (polymerizes the glass structure) by creating tetrahedral alumina groups that bond as NaAlO<sub>2</sub> structural groups. In Al<sub>2</sub>O<sub>3</sub> and/or SiO<sub>2</sub> deficient glasses, Fe<sub>2</sub>O<sub>3</sub> can take on a tetrahedral coordination and polymerize a glass by forming NaFeO<sub>2</sub> structural groups. However, if sufficient Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> are present in a glass such as DWPF waste glasses that typically contain >3 wt% Al<sub>2</sub>O<sub>3</sub> and >40 wt% SiO<sub>2</sub>, then Fe<sub>2</sub>O<sub>3</sub> is octahedral and creates two non-bridging oxygen bonds, i.e. it depolymerizes the glass matrix as assumed in the DWPF viscosity model (Equation 1). This is consistent with the work of Mysen<sup>1</sup> who demonstrated that high iron magmas (iron silicate glasses) that contained levels of 10 wt% Fe<sub>2</sub>O<sub>3</sub> decreased the melt viscosity. He concluded that NaFeO<sub>2</sub> structural groups were not incorporated into the silicate network to the same degree as NaAlO<sub>2</sub> structural groups<sup>43</sup>. Therefore, Fe<sub>2</sub>O<sub>3</sub> is considered a network modifier and depolymerizer in the DWPF viscosity model. Since FeO is also known to act as a glass network depolymerizer, there is no need for a separate FeO term and all the iron in a given glass is calculated as if it were Fe<sub>2</sub>O<sub>3</sub>.

Lastly, the DWPF viscosity model assumes that each mole of B<sub>2</sub>O<sub>3</sub> creates one non-bridging oxygen bond. This is based on data by Smets and Krol<sup>44</sup>, and Konijnendijk<sup>45</sup> who demonstrated that for sodium silicate glasses with low B<sub>2</sub>O<sub>3</sub> content the B<sub>2</sub>O<sub>3</sub> enters the glass network as BO<sub>4</sub><sup>-</sup> tetrahedral. At higher B<sub>2</sub>O<sub>3</sub> concentrations these tetrahedra are converted into planar BO<sub>3</sub><sup>-</sup> groups. Tetrahedra BO<sub>4</sub><sup>-</sup> contributes no NBO while planar BO<sub>3</sub><sup>-</sup> groups contribute one non-bridging oxygen atom<sup>46</sup>.

Uranium was shown to have no impact on glass viscosity since it has about equivalent BO and NBO bonds that cancel each other out. While, ThO<sub>2</sub> at <1 wt% had no impact on glass viscosity<sup>39</sup>. Therefore, the viscosity model does not include any radioactive species. The viscosity model has been validated over composition and temperature regions (800-1500°C) well outside of the regions for which it was developed because it is based on known glass structural mechanisms. This affords the ability to use the viscosity model for the broader composition ranges of LLW\*, TRU†, and mixed wastes.

The electrical resistivity of a waste glass melt as a function of temperature is the single most important variable affecting the establishment of Joule heating for electrically heated melters. The electrical resistivity controls the rate of melting after the establishment of Joule heating. At low temperatures, glasses are good insulators, while at high temperatures they conduct electric current relatively well. The current is transferred by ion migration: the modifying ions mobility is much higher than that of network formers at all temperatures. The concentration of alkali ions contributes the most to the electrical conductivity. During passage of direct current through a glass melt, the alkali ions migrate to the cathode while the glass close to the anode is enriched with SiO<sub>2</sub> and the resistivity locally increases. These

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\* LLW = Low level waste.

† TRU = transuranic waste.

polarization effects are eliminated by the use of alternating current as used in JHM's. However, the chemical composition of a melt thus has a significant effect on the electrical properties<sup>47</sup> and the melt rate at the melt temperature.

The same melt polymerization model used for glass viscosity can be used for glass resistivity as the NBO,  $1/T(^{\circ}\text{C})$ , and NBO form a three dimensional plane that can be modeled similar to the viscosity correlation shown in Figure 4. The equation of the three-dimensional regression plane for resistivity is given in Equation 4

Equation 4

$$\log \rho(\Omega \text{ cm}) = -2.48 + \left( \frac{4399.57}{T(^{\circ}\text{C})} \right) - (0.45 * \text{NBO})$$

with an  $R^2 = 0.92$ .

### Glass Liquidus

A liquidus temperature model prevents melt pool or volume crystallization during operation. Volume crystallization needs to be avoided because it can involve almost simultaneous nucleation of the entire melt pool as volume crystallization can occur very rapidly. Furthermore, once iron spinel crystals are formed (the most ubiquitous liquidus phase occurring in US defense HLW), these crystals are refractory and cannot easily be redissolved into the melt pool. The presence of either the spinel or nepheline liquidus phases may cause the melt viscosity and resistivity to increase which may cause difficulty in discharging glass from the melter as well as difficulty in melting via Joule heating. Once a significant amount of volume crystallization has occurred and the resulting crystalline material has settled to the melter floor, melting may be inhibited and the pour spout may become partially or completely blocked making pouring difficult.

The crystal-melt equilibria were modeled based on quasicrystalline concepts<sup>4, 5</sup>. A pseudobinary phase diagram between a ferrite spinel (an incongruent melt product of transition metal iron rich acmite) and nepheline was defined. The pseudobinary lies within the  $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-Na}_2\text{O-SiO}_2$  quaternary system that defines the crystallization of basalt glass melts (note that the basalt glass system is used as an analogue for waste glass durability, liquidus, and the prevention of phase separation). The liquidus model developed based on these concepts has been used to prevent unwanted crystallization in the DWPF HLW melter for the past six years while allowing  $>10$  wt% higher waste loadings to be processed. The liquidus model (Equation 5) and the pseudobinary (Figure 5) are shown<sup>4, 5</sup> to be consistent with all of the thermal stability data generated on DWPF HLW glasses. The model ranges developed on 105 different glass compositions and validated over wider ranges (161 glasses)<sup>14</sup>.

Equation 5

$$\begin{aligned} \frac{1}{T_L(K)_{\text{spinel}}} &= -0.000260 \ln(M_2) - 0.000566 \ln(M_1) - 0.000153 \ln(M_T) - 0.00144 \\ &= \ln \left\{ (M_2)^{-0.000260} (M_1)^{-0.000566} (M_T)^{-0.000153} \right\} - 0.00144 \end{aligned}$$

where

$$\Sigma_{\text{MT}} \equiv \phi_{\text{T,SiO}_2} Z_{\text{SiO}_2} + \phi_{\text{T,Al}_2\text{O}_3} Z_{\text{Al}_2\text{O}_3} + \phi_{\text{T,Fe}_2\text{O}_3} Z_{\text{Fe}_2\text{O}_3}$$

$$\begin{aligned} \Sigma_{M1} &\equiv \phi_{M1,Al_2O_3} Z_{Al_2O_3} + \phi_{M1,Fe_2O_3} Z_{Fe_2O_3} + \phi_{M1,TiO_2} Z_{TiO_2} + \phi_{M1,Cr_2O_3} Z_{Cr_2O_3} + \phi_{M1,ZrO_2} Z_{ZrO_2} \\ &\quad + \phi_{M1,NiO} Z_{NiO} + \phi_{M1,MgO} Z_{MgO} + \phi_{M1,MnO} Z_{MnO} \\ \Sigma_{M2} &\equiv \phi_{M2,NiO} Z_{NiO} + \phi_{M2,MgO} Z_{MgO} + \phi_{M2,MnO} Z_{MnO} + \phi_{M2,CaO} Z_{CaO} \\ &\quad + \phi_{M2,K_2O} Z_{K_2O} + \phi_{M2,Li_2O} Z_{Li_2O} + \phi_{M2,Na_2O} Z_{Na_2O} \\ \Sigma_{T1} &\equiv \phi_{T1,SiO_2} Z_{SiO_2} + \phi_{T1,Al_2O_3} Z_{Al_2O_3} + \phi_{T1,Fe_2O_3} Z_{Fe_2O_3} + \phi_{T1,TiO_2} Z_{TiO_2} \\ \Sigma_{N1} &\equiv \phi_{N1,K_2O} Z_{K_2O} + \phi_{N1,Li_2O} Z_{Li_2O} + \phi_{N1,Na_2O} Z_{Na_2O} \end{aligned}$$

and

$$M_2 \equiv \frac{\Sigma_{M2}}{\Sigma}, M_1 \equiv \frac{\Sigma_{M1}}{\Sigma}, M_T \equiv \frac{\Sigma_{MT}}{\Sigma}, \text{ and } \Sigma \equiv \Sigma_{M2} + \Sigma_{M1} + \Sigma_{MT} + \Sigma_{T1} + \Sigma_{N1}$$

and  $R^2 = 0.89$ . The details of the modeling are given elsewhere<sup>48</sup>.

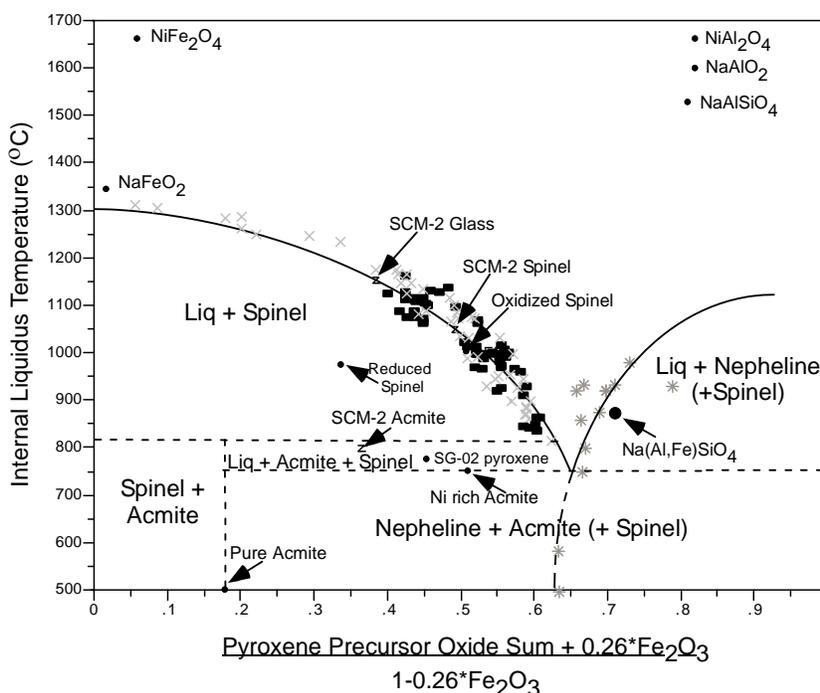


Figure 5. Pseudobinary between Spinel and Nepheline derived from the DWPF liquidus model and data<sup>4, 5</sup>.

### Glass REDOX

Control of the REDUction/OXidation (REDOX) equilibrium in the DWPF melter is critical for processing high level liquid wastes. Foaming, cold cap roll-overs, and off-gas surges all have an impact on pouring and melt rate during processing of HLW waste glass. All of these phenomena can impact waste throughput and attainment. These phenomena are caused by gas-glass disequilibrium when components in the melter feeds convert to glass and liberate gases such as steam, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, NO<sub>x</sub>, and/or N<sub>2</sub>. In order to minimize gas-glass disequilibrium a REDOX strategy is used to balance feed reductants and feed oxidants while controlling the REDOX between  $0.09 \leq Fe^{2+}/\Sigma Fe \leq 0.33$ . A  $Fe^{2+}/\Sigma Fe$  ratio  $\leq 0.33$  prevents metallic and sulfide rich species from forming nodules that can accumulate on the floor of the

melter. Control of foaming, due to deoxygenation of manganic species, is achieved by converting oxidized  $MnO_2$  or  $Mn_2O_3$  species to  $MnO$  during melter preprocessing. At the lower REDOX ratio of  $Fe^{2+}/\sum Fe \sim 0.09$  about 99% of the  $Mn^{+4}/Mn^{+3}$  is converted to  $Mn^{+2}$  and foaming does not occur. Nominally a  $Fe^{2+}/\sum Fe$  of  $\sim 0.2$  in the mid-range of 0.09-0.33 is targeted in the melt pool.

The REDOX model relates the  $Fe^{2+}/\sum Fe$  ratio of the final glass to the molar concentrations of the oxidants and reductants in the melter feed. The REDOX model is based on Electron Equivalents (EE) that are exchanged during chemical reduction (making an atom or molecule less positive by electron transfer) and oxidation (making an atom or molecule more positive by electron transfer). Therefore, the number of electrons transferred for each REDOX reaction can be summed and an Electron Equivalents term for each organic and oxidant species defined<sup>49, 50, 51</sup>. The model accounts for reoxidation of the manganese by nitrate salts in the cold cap and takes the form

Equation 6

$$\frac{Fe^{2+}}{\sum Fe} = f \left[ \left( 2[F] + 4[C] + 4[O_T] - 5[N] - 5[Mn] \right) \frac{45}{T} \right] = f[\xi]$$

where

$f$	=	indicates a function
[F]	=	formate (mol/kg feed)
[C]	=	coal (carbon) (mol/kg feed)
[O <sub>T</sub> ]	=	oxalate <sub>Total</sub> (soluble and insoluble) (mol/kg feed)
[N]	=	nitrate + nitrite (mol/kg feed)
[Mn]	=	manganese (mol/kg feed)
T	=	total solids (wt%)

$$\xi = \left( 2[F] + 4[C] + 4[O_T] - 5[N] - 5[Mn] \right) \frac{45}{T}$$

$$\text{and } \frac{Fe^{2+}}{\sum Fe} = 0.2358 + 0.1999\xi$$

A model that also includes sugar as a reductant can be found in reference **Error! Bookmark not defined.**

### Product Composition Control System (PCCS) and Process Limits

While the individual P/P models are based on glass structural concepts of SRO, MRO and quasicrystalline theory, the process limits are set for a given melter type and geometry by experience with non-radioactive pilot scale melters. Multivariate statistical theory was used in conjunction with the P/P models to control within multi-dimensional composition space<sup>12, 13</sup>. The application of the combined P/P model is known as the Product Composition Control System (PCCS).

PCCS incorporates modeling error, errors in analytic feed measurement, sampling and measurement systems. These errors must be accounted for in order to achieve 95% confidence in the property predictions. In DWPF, a composition measurement is a vector of measurements taken for several

constituents simultaneously.‡ Thus the description of compositional uncertainty requires multivariate statistical techniques. The concentrations of the individual constituents in the DWPF composition measurements are assumed to be multivariate Gaussian with a covariance matrix  $\Sigma_m$  and the solution can be solved with a student's t-test for all product and processing constraints incorporating all relevant constituent elements measured in the glass. The confluence of the regions described by the t-tests for all property constraints forms a Measurement Acceptable Region (MAR) for HLW glass formulation which includes all measurement and sampling errors including tank transfer errors.

HLW glass formulations falling inside the MAR are durable and processable within 95% confidence. The ternary representation of the PCCS system demonstrates the flexibility to blend two different types of waste: a radionuclide rich stream that comes from the removal of these components from the salt supernates (waste I) and the sludge (waste II). This allows the waste glass formulations on lower boundary of the MAR (Figure 6) which maximizes waste sludge component loadings instead of waste glass formulations in the middle of the qualified MAR region. At the same time, it provides the basis for knowing, to within 95% confidence, that a given melter feed will be pourable, will not crystallize inside the melter, and will be durable and acceptable to the geologic repository. By being able to define all the sources of error, waste loadings can be maximized at the edges of the region defined by the MAR as indicated by the circle inside the MAR on Figure 6. Thus satisfying both 95% confidence and maximum waste loading in a glass. The use of empirical models would have entailed operations in the center of a glass qualified region had the PCCS multivariate statistical approach and mechanistic modeling not been adopted as the error analysis is virtually impossible to perform.

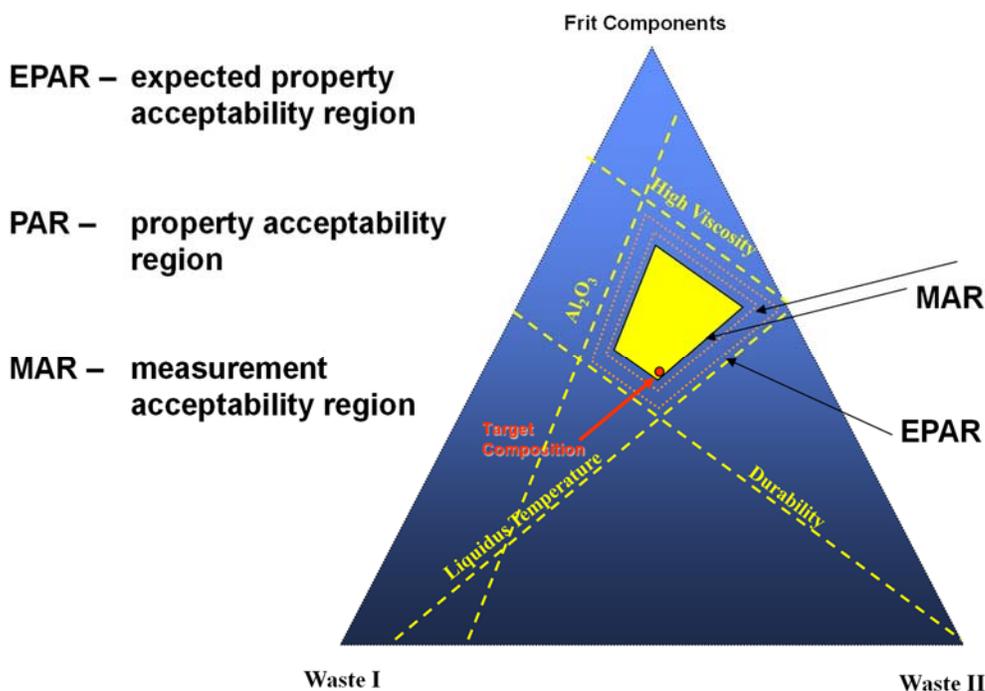


Figure 6. The HLW Glass Melter Product Composition Control System (PCCS)

‡ At least, these measurements are taken very close together in time and by consequence may be considered simultaneous.

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