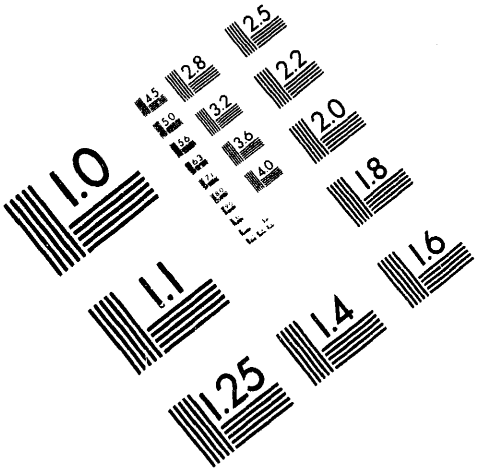

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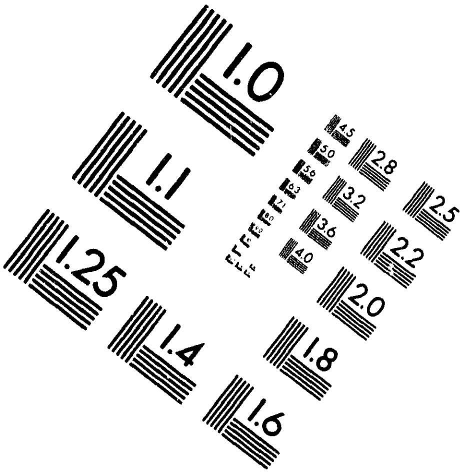

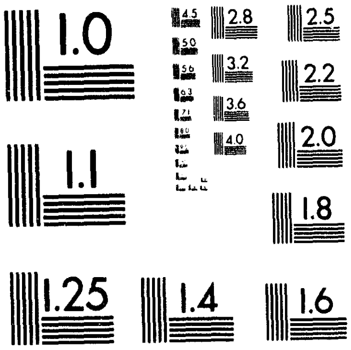

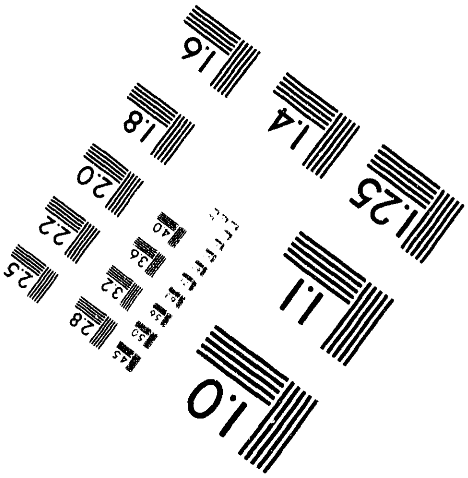

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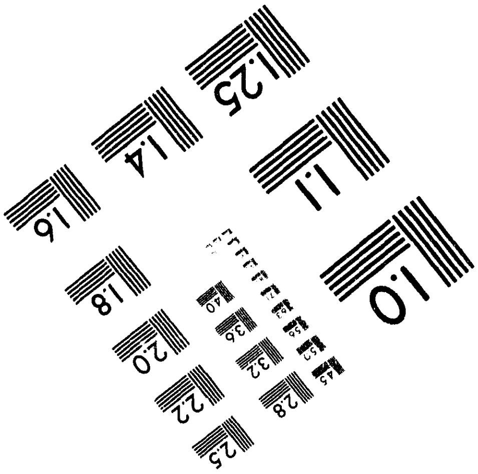

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# VITRIFICATION OF LOW LEVEL AND MIXED (RADIOACTIVE AND HAZARDOUS) WASTES: LESSONS LEARNED FROM HIGH LEVEL WASTE VITRIFICATION

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# VITRIFICATION OF LOW LEVEL AND MIXED (RADIOACTIVE AND HAZARDOUS) WASTES: LESSONS LEARNED FROM HIGH LEVEL WASTE VITRIFICATION

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## ABSTRACT

Borosilicate glasses will be used in the USA and in Europe to immobilize radioactive high level liquid wastes (HLLW) for ultimate geologic disposal. Simultaneously, technologies are being developed by the US Department of Energy's (DOE) Nuclear Facility sites to immobilize low-level and mixed (radioactive and hazardous) wastes (LLMW) in durable glass formulations for permanent disposal or long-term storage. Vitrification of LLMW achieves large volume reductions (86-97 %) which minimize the associated long-term storage costs. Vitrification of LLMW also ensures that mixed wastes are stabilized to the highest level reasonably possible, e.g. equivalent to HLLW, in order to meet both current and future regulatory waste disposal specifications. The technologies being developed for vitrification of LLMW rely heavily on the technologies developed for HLLW and the lessons learned about process and product control.

## I. INTRODUCTION

Technologies are being developed in the US to stabilize low-level and mixed wastes for permanent disposal. One of the alternative stabilization technologies is vitrification. The Environmental Protection Agency (EPA) has declared vitrification the Best Demonstrated Available Technology (BDAT) for high-level radioactive waste[1] and produced a Handbook of Vitrification Technologies for Treatment of Hazardous and Radioactive Waste.[2]

Vitrification of HLLW waste sludge into a durable glass produces volume reductions of ~77 wt% at waste loadings of ~28 wt% on a dry oxide basis. Vitrification of LLMW sludges and incinerator wastes into a durable glass produces volume reductions up to 97% at waste loadings of 50-75 wt% on a dry oxide basis.[3-4] These large reductions in final waste form volume minimize long-term storage costs making vitrification cost effective on a life cycle basis.

Hazardous and radioactive species are atomistically bonded in the glass waste form structure during vitrification allowing glass to have a high potential to meet the EPA characteristically hazardous and/or listed Land Disposal Restrictions (LDR's). Vitrified waste forms, therefore, have the highest probability of being "delisted," which would allow for final disposal into a low level burial ground rather than in hazardous/mixed waste vaults. Delisting a waste form, therefore, provides for additional life cycle cost savings.

The US DOE Savannah River Site (SRS), is currently investigating vitrification for disposal of various low-level and mixed wastes.[3,4] The vitrification technologies being developed for LLMW rely heavily on the lessons learned from vitrification of HLLW.

## II. SYSTEMS APPROACH

Glass formulation optimization for HLLW[5] and LLMW wastes[3-4] has included examination of the following process and product constraints:

- product control
  - chemical durability
  - homogeneity
  - thermal stability
- process control
  - viscosity
  - liquidus
  - volatility
  - melt temperature
  - melt corrosivity
  - waste solubility

This "systems approach" requires that parameters affecting product performance and processing considerations be optimized simultaneously. The "systems approach" ensures that the final product safeguards the public, and that the production process used is safe to operate.

First principles process and product quality models were developed for vitrification of HLLW at SRS.[6] These process/product models directly relate process and product parameters to glass and/or feed composition.[6] This simplifies the fabrication of HLLW waste glass while ensuring processability and product quality. These models are the foundation of the statistical process control system used to monitor and control glass composition for HLLW (the Product Composition Control System).[7,8]

## III. PRODUCT CONTROL

### A. Chemical Durability Model

The most important glass product property is the glass durability.[5,6] 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 repository 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.

The chemical durability of glass is a complex phenomenon that depends on the following:

- homogeneity (phase separation, crystallization)
- test parameters including
  - temperature (T)
  - length of time (t) glass contacts solution
  - exposed surface area (S) of the glass
  - volume (V) of the solution
  - composition of the solution
  - glass surface (natural, ground, etc.)
- glass composition

A model, the Thermodynamic Hydration Energy Reaction MOdel (THERMO) has been developed to relate glass composition to glass durability test response.[6,9] THERMO is based on the calculation of the thermodynamic hydration free energy from the glass and/or feed composition. The model expresses the thermodynamic tendency of species (components) in a glass to hydrate. Individual thermodynamic hydration equations are written for each compositional species. The components of a glass are chosen as the reactants for the individual thermodynamic hydration equations. The hydrated product species for each reaction are chosen to be consistent with the equilibrium phases predicted from known solution (Pourbaix or Eh-pH ) stability diagrams or from the experimentally determined role of certain species in glass leached surface layer formation.

The hydration equations calculated for each of the component species are partial thermodynamic molar functions. Partial molar functions are additive so that the summation of the individual component hydration reactions provides an expression of the overall tendency of a given glass to hydrate based on its composition. THERMO provides a more accurate additive thermodynamic model than those previously developed because it mechanistically predicts the following known glass-solution reactions:

- ion exchange, matrix dissolution, and protective layer formation
- pH dependence of ion exchange
- pH dependence of accelerated matrix dissolution
- pH dependence of the leach layer formation
- oxidative dissolution
- in-situ formation of clays as glass reaction products in the glass-solution reaction zone
- structural effects on glass dissolution
- the response of homogeneous and phase separated glasses

The relationship between the thermodynamic and kinetic aspects of glass durability modeling was shown to be a function of the relative contributions of glass composition and imposed test conditions.[10] The kinetic contribution to glass dissolution was shown to be governed by the test geometry. Test parameters such as exposed glass surface area (SA), solution volume (V), test duration (t), and test temperature (T) were shown to alter the kinetic contribution to glass dissolution. The thermodynamic contribution, which represents the long-term glass stability, was shown to be governed by the glass composition. The glass durability test response forms a three dimensional response surface as a function of the kinetic test parameters (Figure 1). The relation between the kinetic and thermodynamic aspects of glass durability modeling will allow THERMO to be applied to other glass durability test geometries important to the performance assessment of LLMW, e.g. the EPA Toxic Characteristic Leach Procedure (TCLP).

### B. Glass Homogeneity

During the development of glass formulations for HLLW, known alkali borosilicate phase diagrams were compiled to determine the homogeneous glass composition envelope.[11] The composite diagram is shown in Figure 2. Glasses in the region of phase separation form two separate glass phases, e.g. glass-in-glass phase separation. One phase is usually borate rich and is more soluble and the second phase is usually silicate rich and more insoluble. The durability of phase separated glasses is always poorer than that of homogeneous glasses because the durability test response is dominated by whichever glass phase is more soluble.

The durability of waste glasses formulated in the region of known homogeneity give consistent durability test response. Glasses incorrectly formulated in the region of phase separation give inconsistent PCT test response because phase separation is usually inhomogeneously distributed in the glass and is highly dependent on cooling rate. The presence of phase separation in glass, therefore, complicates glass durability modeling and should be avoided.

Glass durability can also be adversely affected by crystallization. Crystallization can sometimes cause accelerated leaching.[12] However, some isometric[1] crystals such as spinel do not disturb the glass matrix and do not cause accelerated leaching.[12]

### C. Thermal Stability Considerations

Crystallization in glass can be eliminated, if desired, by defining the regions of thermal stability for the glass. This can be accomplished by determining the time-temperature-transformation (TTT) diagrams for the waste glass. The TTT diagrams define the time-temperature regimes which will cause a glass to crystallize (Figure 3).[12-13] Avoiding the time and temperature conditions that cause crystallization during processing and storage will eliminate concerns about the thermal stability and crystallization of the glass.

## IV. PROCESS CONTROL

### A. Glass Viscosity (and Resistivity) Model[6]

The viscosity of the 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 melter more difficult. The lowest glass viscosities should, therefore, be conservatively set at ~20 poise at the melt temperature, $T_{melt}$, as done for HLLW glass.

Waste glasses are usually poured continuously into steel canisters or cans for ultimate storage. Glasses with viscosities above 500 poise do not readily pour. Moreover, too high a viscosity can reduce product quality by causing voids in the final glass. A conservative range of 20-100 poise at the melt temperature, $T_{melt}$, is recommended as optimal as established for HLLW waste glass.

Although, electrical resistivity of waste glasses is not a process model constraint, the electrical resistivity of a glass is highly correlated with its viscosity. The ability to predict the electrical resistivity of a glass from its composition, or alternatively from its viscosity, is important to startup and/or restart of Joule-heated electric melters. At low temperatures, glasses are good insulators, while at high temperatures they conduct electric current relatively well so that the glass melt may be heated by direct passage of electric current. The electrical resistivity is, therefore, the single most important variable affecting the establishment of Joule heating in an electric melter.

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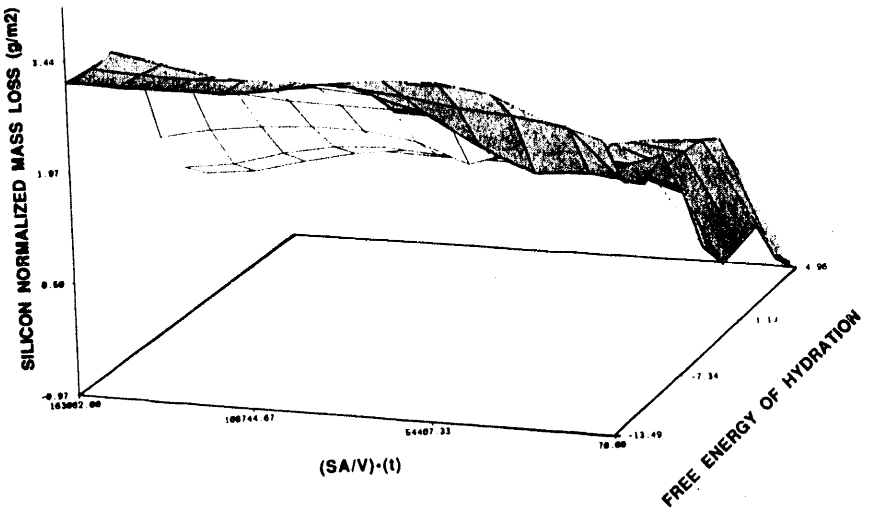
[1] that system of crystals in which the forms are referred to three equal mutually perpendicular axes.



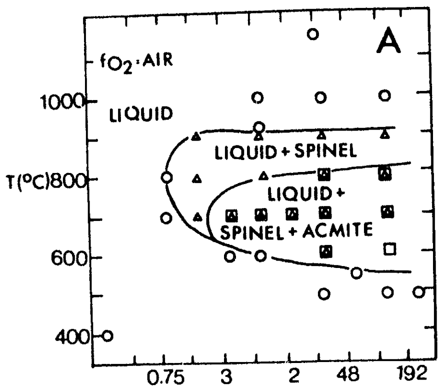
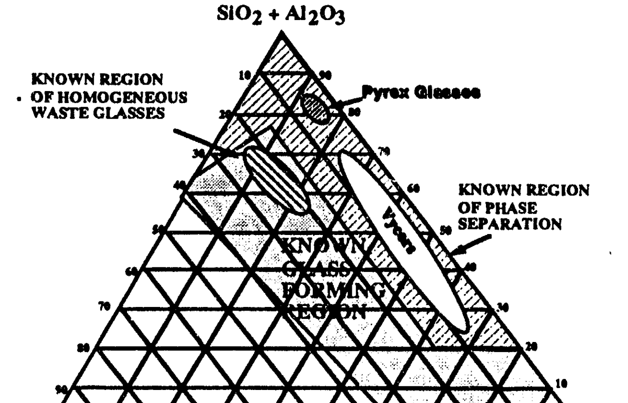


Figure 1. Response surface relating glass durability (Si release from glass in ppm) to glass composition (free energy of hydration) and test geometry (surface area of glass, volume of solution, and test duration). The response surface demonstrates the relation between the thermodynamic and kinetic aspects of glass durability.[10]

Figure 3. Example of time-temperature-transformation (TTT) diagrams. The TTT diagram can be used to determine the time-temperature regions to avoid so that a glass does not crystallize.[12,13]



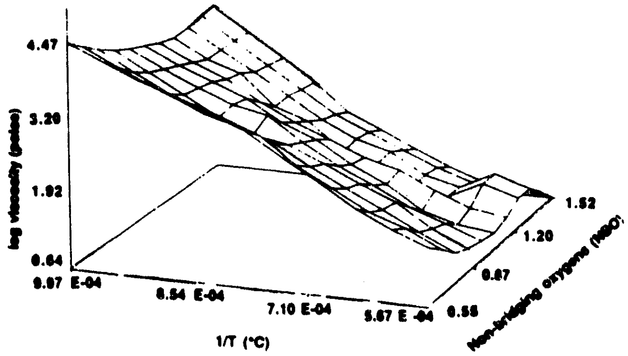


Figure 2. Composite diagram of the alkali-borosilicate system indicating regions where homogeneous and inhomogeneous waste glasses form.[5, 11]

Figure 4. Response surface relating glass viscosity to glass composition (expressed as a non-bridging oxygen term, NBO) and to 1/T (°C).[6]

The approach taken in the development of the viscosity process model was a first principles approach based on glass structural considerations, expressed as a calculated non-bridging oxygen (NBO) term. This NBO parameter is representative of the amount of structural depolymerization in the glass. Calculation of the NBO term from the glass composition (Equation 1) was combined with quantitative statistical analyses of response surfaces to express glass viscosity as a function of melt temperature and glass composition (Figure 4).

$$NBO = \frac{2(M_2O + Fe_2O_3 - Al_2O_3) + B_2O_3}{SiO_2} \quad (1)$$

where $M_2O = Na_2O + K_2O + Cs_2O + Li_2O$

The equation of the response surface is, therefore,

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

$$R^2=0.976 \quad (2)$$

Equation 2 can be used to predict glass viscosity at $T_{melt}$ or to determine a melt temperature from the waste plus glass former composition.[4]

A similar three dimensional response surface can be generated to relate the glass resistivity, $\log\rho$, to 1/T (°C) and glass composition (NBO). Therefore, another response surface can be generated to relate the glass resistivity, $\log\eta$, to the glass viscosity, $\log\rho$, and glass composition (NBO) for all temperatures.

### B. Glass Liquidus Model[6]

The approach taken in development of the liquidus process model was to identify the theoretical and experimental relationship of the liquidus[2] temperature with the glass composition. The first principles approach used for the liquidus process model was based on the free energy of formation of the liquidus phases, spinel and nepheline. The model assumes a precipitation reaction for these species at 1050°C. For HLLW at SRS $Fe_2O_3$ and $Al_2O_3$ are major waste components which are diluted by frit constituents such as $SiO_2$. The following assumptions were made in order to write the reaction occurring at the liquidus as a precipitation (solubility) reaction:

- amorphous $SiO_2$ is the predominant solvent in borosilicate waste glass
- $Fe_2O_3$ is considered as the limiting species for spinel precipitation
- $Al_2O_3$ is considered as the limiting species for nepheline precipitation

The precipitation reaction modeled is as follows:

$$\text{Glass} \xrightarrow{1050^\circ C} \text{NiFe2O4} \downarrow \quad (3)$$

where the glass is considered a mixture of silicate and oxide species and the predominant solvent in the glass is considered to be amorphous $SiO_2$ depleted by the amount of $SiO_2$ needed to form $NaAlSiO_4$. The competition between the solvent ($SiO_{2(amorphous)}$-$NaAlSiO_4$) and the spinel precipitation can then be represented as a pseudo-equilibrium constant

$$k = \frac{NiFe_2O_4}{(SiO_{2(amorphous)}-NaAlSiO_4)} \quad (4)$$

A similar approach can be used for any type of waste glass once the liquidus phases are identified.

### C. Species Volatility/Melt Temperature Limits

Waste glasses formulated for LLMW with radioactive or hazardous volatile species should be optimized at the HLLW glass melt temperature of 1150°C or below in order to minimize volatility. Wet slurry feeding of the LLMW wastes, as is done for HLLW, is recommended rather than dry feeding since the pyrohydrolysis reactions that govern the off-gas chemistry limit volatilization of hazardous species compared to pyrolysis reactions that occur during dry waste feeding or incineration. Pyrohydrolysis reactions necessitate

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[2] the maximum temperature at which equilibrium exists between a molten glass and its primary crystalline phase

the presence of steam and $SiO_2$ and can effectively help dechlorinate wastes.[3] Dry feeding and/or incineration (pyrolysis) in the absence of steam causes volatilization of hazardous species and creation of tertiary waste streams which is undesirable.

### D. Melt Corrosivity and Waste Solubility Considerations

For HLLW vitrification, finely reactive glass forming "frits" have been developed as the glass forming additives in order to maximize glass homogeneity, simplify process control, and lower melt temperatures in order to minimize volatility. For LLMW wastes, a Reactive Additive Stabilization Process (RASP) which uses and/or accommodates spent filter aids such as diatomaceous earth and/or perlite, precipitated silica, pyrolyzed rice husk ash, and/or alkali or alkaline earth carbonates was developed.[3,4] Reactive high surface area silica, as a waste form additive, was determined to greatly enhance the solubility and retention of hazardous, mixed and heavy metal species in glass.[3,4] Highly reactive silica was found to increase the solubility and tolerance of Soda($Na_2O$)- Lime(CaO)-Silica($SiO_2$) glass (SLS) and borosilicate ($B_2O_3$-$SiO_2$) glass formulations to atomistically bond the waste species. Highly reactive silica lowers glassification temperatures, increases waste loadings which provides for large waste volume reductions, and produces EPA acceptable glasses.

## V. CONCLUSIONS

The lessons learned and the process/product models developed for HLLW have been shown to be directly applicable to LLMW vitrification.

## ACKNOWLEDGEMENTS

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