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**PNL Vitrification Technology
Development Project Glass
Formulation Strategy for LLW
Vitrification**

**D. Kim
P. R. Hrma
J. H. Westsik, Jr.**

March 1996

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest National Laboratory
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Pacific Northwest National Laboratory
Richland, Washington 99352

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SUMMARY

This Glass Formulation Strategy describes development approaches to optimize glass compositions for Hanford's low-level waste vitrification between now and the projected low-level waste facility start-up in 2005. The objectives of the glass formulation task are to develop optimized glass compositions with satisfactory long-term durability, acceptable processing characteristics, adequate flexibility to handle waste variations, maximize waste loading to practical limits, and to develop methodology to respond to further waste variations.

The Glass Formulation Strategy addresses the near-term needs driven by TPA milestones to select a reference melter technology and reference glass formulation by June 1996. The Strategy also addresses the longer term needs to develop and verify glass formulations based on evolving waste characterization information, vitrification system design, and disposal system requirements. Initial glass formulations for the high-sodium LLW wastes are being developed from the alumino-silicate glass family. The glasses will be characterized and selected based on their long-term chemical durability and their processing behavior. The Strategy also includes verification of the glass formulations through 1) testing in small- and pilot-scale melter systems to confirm processability and to support design and 2) radioactive testing with actual wastes and formulations to validate simulants and models. Glass property models will be developed/adapted to aid the formulation effort and as process control tools.

Implementation of this strategy requires testing of glass formulations spanning a number of waste loadings, compositions, and additives over the range of expected waste compositions. The resulting glasses will then be characterized and compared to processing and performance specifications yet to be developed.

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1.0 INTRODUCTION

The recently renegotiated Tri-Party agreement (TPA 1994) among the Washington State Department of Ecology, the U.S. Environmental Protection Agency, and the U.S. Department of Energy specified vitrification as the immobilization technology for Hanford's low-level waste. All of the tank wastes stored at Hanford are to be separated into high-level waste (HLW) and low-level waste (LLW) fractions and vitrified for disposal.

Immobilization of the low-level tank waste, which is characterized by a high content of Na_2O , averaging about 80 wt% on an oxide basis, necessitates the development of durable high-sodium glasses. The overall objectives of the glass formulation effort are to develop optimized glass compositions containing the maximum fraction of waste while maintaining satisfactory long-term durability, acceptable processing characteristics, and adequate flexibility to handle waste variations, and to develop a methodology to respond to waste variations. The purpose of optimizing glass compositions through waste loading maximization is to achieve reduction of final glass product volume and processing cost without adversely affecting glass durability and requiring more elaborate disposal systems, and thus to minimize the overall vitrification and disposal costs.

In a previous report (Kim 1994), the literature on the short-term durability of high-sodium silicate glasses was reviewed to select glass systems suitable for LLW vitrification. Recommended base systems were silicate glasses containing a relatively high concentration of Al_2O_3 (9 to 12 wt%) along with B_2O_3 and/or CaO . A preliminary glass formulation strategy presented in the report by Kim (1994) was based on glass durability and possible effects of minor components on glass processing.

The present report expands and updates the glass formulation strategy previously proposed using experience accumulated during FY-94 LLW glass formulation studies. It describes the near-term glass formulation work leading to establishing a reference formulation to meet a June 1996 TPA milestone, the long-term strategy for optimized glass development up to the projected LLW vitrification facility start-up in 2005 and beyond, and the approach to glass composition development. The glass formulation work will be closely

coordinated with other activities in the Pacific Northwest Laboratory (PNL) Vitrification Technology Development (PVTD) project, especially the performance assessment and the process chemistry development tasks, the HLW vitrification glass formulation task, and the Tank Waste Remediation System (TWRS) LLW Immobilization program. The glass formulation strategy will be updated periodically to include new information obtained during the course of the program.

2.0 GLASS FORMULATION STRATEGY

Figure 1 shows the major elements of the glass formulation strategy from the present through the projected LLW vitrification facility start-up in 2005 and into plant operations. These glass formulation activities are tied to major TPA milestones; vitrification system evaluation, design and operation; disposal system design; and performance assessment. Success of the strategy requires significant coordination among the strategy elements. This coordination is implicit in Figure 1 but is not shown.

As this strategy is being developed, the initial activities are already underway as shown in Figure 1. Melter technologies are being evaluated by WHC via testing at seven melter vendor facilities. The glass formulation team is developing representative glass formulations that the vendors could select for their tests. For those vendors developing their own formulations, the glasses are being characterized to confirm that they meet minimum requirements. In parallel with the melter technology evaluation, glass formulation activities are underway to develop a reference glass formulation in order to meet a June 1996 TPA milestone to select a reference melter and establish a reference LLW glass formulation (M-60-02). Also, long-term durability testing has been initiated at Argonne National Laboratory to support the performance assessment effort and to provide feedback to glass formulation development.

The initial glass formulation work uses simulants based on limited knowledge of tank contents, tank retrieval sequences, pretreatment flowsheets, and LLW vitrification flowsheets. Thus, as this information becomes better defined, the range and variability in the low-level wastes to be vitrified will become better known. Also, the design of the LLW disposal system is not known at this time so the specific performance requirements that the glass must meet are not yet defined. Therefore, the glass formulation strategy anticipates that the glass formulations will continue to evolve as our knowledge of the wastes, the vitrification flowsheet, and the requirements of the disposal system increases.

The glass formulation effort will continue after the selection of the reference melter and formulation. Development and vitrification of glass formulations will continue based on evolving waste characterization data,

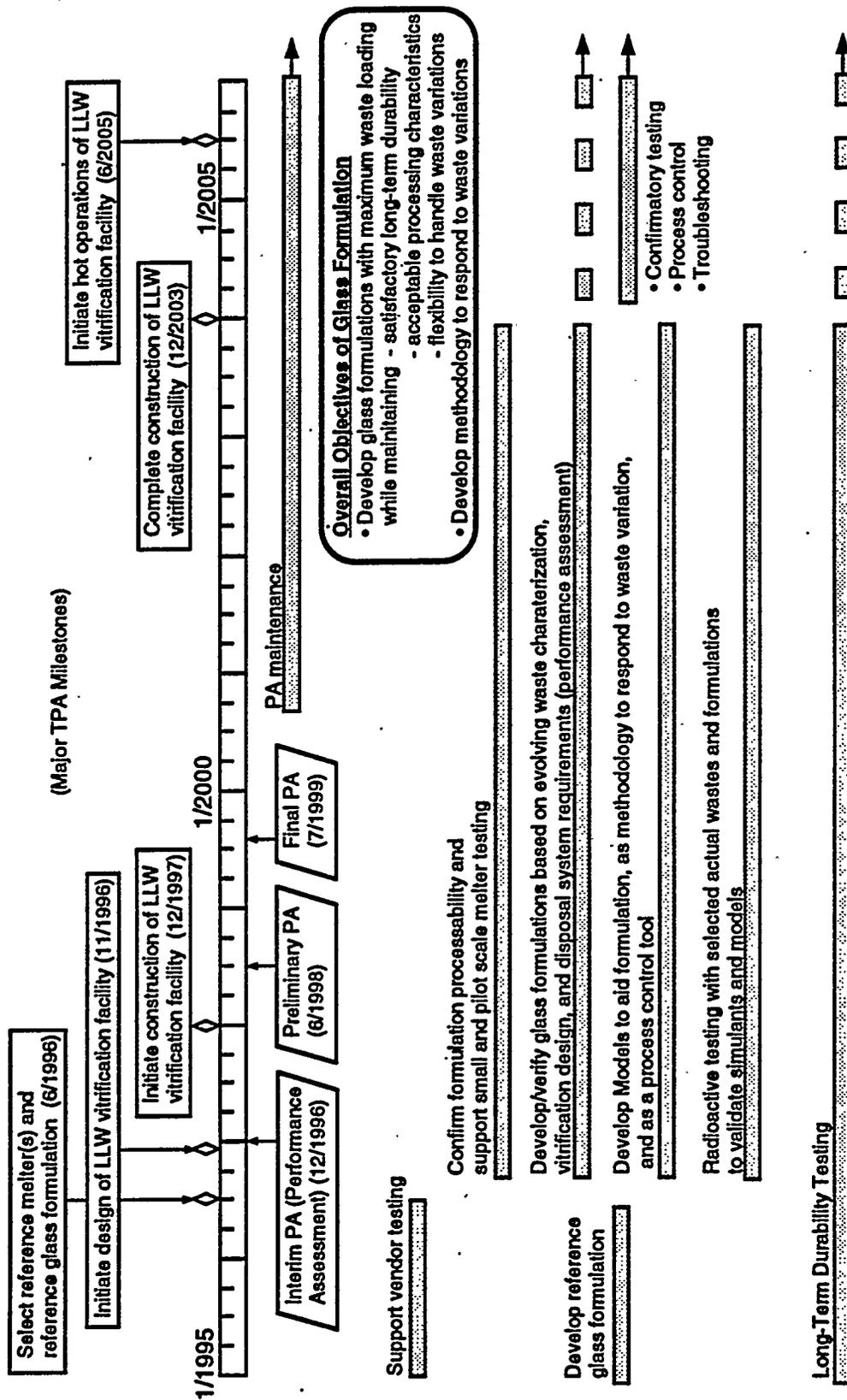


FIGURE 1. A Simplified Logic Diagram for Glass Formulation Strategy

vitrification system design, and disposal system requirements. Small- and pilot-scale vitrification system testing will be conducted to confirm processability and to support the design of the vitrification system. Radioactive testing with selected actual wastes and formulations will be conducted on a laboratory and small scale to confirm the results obtained with simulants in the laboratory. As data on glass formulations and their characteristics become available, development of models will be initiated to aid the formulation effort, as a methodology to respond to waste variation, and as a process control tool. Long-term durability testing will continue in order to support the formulation effort and the disposal system performance assessment. It is expected that these activities will be required at some level through start-up of the LLW vitrification facility. Once the LLW vitrification facility is in operation, the glass formulation effort will be primarily devoted to confirmatory testing, process control, and troubleshooting.

The strategies for formulating glasses for melter vendor testing, developing reference glass, and developing optimized glass compositions based on waste variations and model development are discussed in Sections 2.1 to 2.3. Glass process testing and testing of radioactive glasses are discussed in Sections 2.4 and 2.5.

2.1 Glasses for Melter Vendor Tests

Various glass melting technologies are available in the commercial glass industry and more have been developed for waste vitrification. Until recently, melters for nuclear waste vitrification have utilized Inconel™ for electrodes and/or melter lining. These melters are limited to melting temperatures of $\leq 1150^{\circ}\text{C}$. Glasses for this temperature range can be based either on borosilicate glass developed for HLW (Hrma, Piepel, et al. 1994) or an iron-phosphate glass. High temperature ($\geq 1250^{\circ}\text{C}$) melters have only recently been developed for nuclear waste glass. These melters attempt to match commercial glass melters in their capability to process glass at a high melting rate and to reduce waste volume by allowing the waste loading to increase above that of the low temperature glass.

The large variety of melter designs precludes development of any single glass composition that could be recommended as a common composition for all

melter technologies. The development of a series of glasses to cover a wide range of temperatures has not been attempted because such an undertaking would be unrealistic considering the time limitations, and, more importantly, it could compromise glass performance and waste loading by imposing requirements that are not compatible with volume minimization and high durability of the product. Because of the complexity of different constraints imposed on the glass and the need to deliver glass compositions within a short time, the glass development effort is currently focused on compositions with optimized durability at the level of 20 wt% Na₂O. Only existing test methods (those used for HLW glasses) have been employed to assess the durability.

Five candidate vendor glasses at 20 wt% Na₂O level were formulated and tested to support WHC's melter system evaluation (Wilson 1994) while the study on FY-94 test matrix LLW glasses (Langowski et al. 1994) was in progress. The melting temperature of these glasses was >1250°C. Melter vendors could select one of the five candidate glasses for testing or they were free to develop and use their own glass, provided the Na₂O level was 20 wt% and sodium release as measured in the 7-day PCT (Product Consistency Test, Jantzen et al. 1991) was acceptable [$<7 \text{ g}/(\text{m}^2 \cdot 7\text{-day})$].* Glasses formulated by prospective vendors were also tested at PNL to verify the required properties. Support for melter system evaluation will continue, providing glass formulation and glass property testing as necessary. Additional glass formulations may be required to support the more extensive and challenging testing associated with long-term performance of the glasses.

No attempts were made to formulate low-temperature glasses for vendors, because experience with the development of HLW glasses that melt at approximately 1150°C shows that durable LLW low-temperature glasses are less likely to be obtained. The main reason is that alumina, which is necessary for making durable high-alkali glasses, strongly increases glass viscosity. This in turn requires higher melting temperatures. However, development of low-temperature glasses will be needed if melters using Inconel™ electrodes are

* This PCT acceptability limit was preliminary for melter vendor test Phase I only. See Section 2.2 for the current preliminary specification.

selected as a reference system. Glasses for this temperature range can be based on borosilicate glasses developed for HLW (Hrma, Piepel, et al. 1995) (see Section 3.2).

At this initial stage of glass development, a higher priority was placed on high quality glass as compared to the technology concerns with regard to different melter types. This approach is in accordance with the tradition and practice of commercial glass makers, who formulate the glass first and then choose or design an appropriate melter. Compromises between glass formulation and melting technology are made at later stages and only when absolutely necessary. The existence of high temperature melters both in the commercial glass industry and in waste glass technology allows formulation of highly durable glasses and makes compromises less likely.

2.2 Reference Glass Formulation

The Tri-Party Agreement specifies that a reference LLW glass formulation that meets complete system requirements be established by June 1996. Initial glass formulation efforts have been and continue to be focused on providing data to support the selection process. Selection of the reference glass will be dictated primarily by long-term durability and performance requirements, as well as by processing concerns.

Recently, a preliminary durability specification for Hanford LLW glass was proposed.* The corrosion rate as determined by a single-pass flow-through test at 20°C and pH 12 be less than 10^{-3} g/(m²·d). This proposed test method is particularly aggressive relative to what the glass should see in a disposal environment. The final specification must be supported by test methodology development and thorough performance assessment analysis.

Importantly, the low dissolution rate must be sustainable for long periods of time, on the order of 10⁴ years. This requirement makes a crucial cross-link between performance assessment and glass formulation. Glass formulation requires testing of a large number of compositions within a reasonable time scale whereas performance analysis represents a substantial effort that can be

* Workshop, Development of Preliminary Durability Specification for Hanford LLW glass, Park City, UT, November, 1994.

undertaken for only a limited number of glasses. Glass formulation, therefore, works with quick test methods.

Consequently, the selection of test methods must be a focus of both glass formulation and performance analysis to create a reliable interface between these two activities. More appropriate test methods will translate into a more realistic ordering of glasses of different compositions according to their long-term durability. This will allow formulation of a reference glass in a manner that will best serve its purpose for technology testing and provide a base for final glass optimization.

Secondary criteria for reference glass selection are melt viscosity and the ability to incorporate troublesome minor components. As mentioned in the previous section, a wide range of melter technologies are available that allow operating at different temperatures to obtain an optimal operating viscosity range. Therefore, the melt viscosity of a reference glass does not need to be determined by the melter type. However, extremely refractory glasses that melt at very high temperatures ($>1550^{\circ}\text{C}$) will not be considered because of the difficulties caused by excessive volatilization of high-alkali glasses at high temperatures. Also, as explained in Section 2.1, low-viscosity glasses are not targeted because they are less likely to achieve high performance characteristics.

Minor components may restrict the base glass composition because some may interact unfavorably with major components used as additives to the waste. For example, F interacts with CaO to precipitate CaF_2 and with B to increase volatilization. Phosphorus may generate water soluble phosphates, etc. If future pretreatment development tends to increase the fraction of minor components in glass, these components must be considered in the reference glass selection process. At the presently anticipated level (Section 3.1), minor components are not of a primary concern for the reference glass.

Candidate reference glass systems include alumino-borosilicate glasses, borosilicate glasses containing zirconia, iron-borosilicate glasses, iron-phosphate glasses. These systems are currently being tested to determine whether they should be considered as candidates for the reference glass – see Section 3.2.

2.3 Optimized Glass Formulation

Following the selection of a reference melter system and reference glass by June 1996, the glass formulation for vitrification of various LLW compositions will focus on

- (1) optimization (maximization of waste loading) in terms of long-term durability linked to performance assessment,
- (2) processing flexibility within a temperature range defined by the reference melter system, and
- (3) volatilization (especially of radioactive components).

A durability specification, mentioned in Section 2.2, has been proposed and will be revised based on future results from short- and long-term durability testing and performance assessment analyses. The reference melter system is still to be determined. Although volatilization can be minimized by the melter design and operation, melt volatility is an area in which glass formulation and melter design must integrate.

The optimized glass composition for a given LLW type should also be developed with the flexibility to accommodate the variation in waste stream composition. Therefore, the development of models for major glass and melt properties as functions of glass composition are essential for formulating optimized glass compositions and operating the vitrification facility efficiently. Strategies for handling waste variations and property model development related to glass optimization are discussed in the following subsections.

2.3.1 Waste Variations

At this early stage in the program, the range of waste compositions and the expected compositional variability are not defined with a desirable precision. The glass formulation strategy, therefore, must provide the flexibility to develop glass formulations to accommodate the waste variability and/or develop a methodology to quickly formulate glasses in response to waste variation definitions.

Because waste loading is currently based on a Na_2O limit, any limitation by other components in the waste can be determined by its ratio to Na_2O . Al_2O_3 is

the only additive which is simultaneously a major waste component. Its fraction in the waste is the second largest, Na_2O being the first (see Table 1 in Section 3.1). The glass formulation in terms of major components will not be affected by the waste composition if the ratio of Al_2O_3 to Na_2O in the waste does not increase above that which is required for the glass. The minimum concentration of Al_2O_3 in the glass is given by the alumina content in the waste. This minimum must be considered in discussing the impact of alumina in glass on long-term durability and formation of aluminosilicates during the glass corrosion process.

A major effort in the study of waste variations on glass formulation will focus on the incorporation of troublesome components (see Section 3.5). Minor components may restrict the base glass composition because some may interact unfavorably with major components used as additives to the waste. For example, fluorine interacts with CaO to precipitate CaF_2 and with B to increase volatilization. Phosphorus may generate water soluble phosphates, etc. If the concentration of a troublesome component, such as P, F, Cl, S, or Cr, in the glass exceeds the limits that the glass can incorporate, the following options should be considered:

- (1) blend wastes to dilute the troublesome components,
- (2) lower the waste loading, or
- (3) in extreme cases, change the glass system.

The second and third options involve a change of glass composition. Studies are underway and will continue addressing minor component effects on glass processing and performance.

To facilitate the proper response to the waste variations in the future vitrification plant, computerized formulation tools such as OWL (Optimal Waste Loading) and TWEAT (Ternary Waste Envelope Assessment Tool) will be adapted to LLW glasses. These tools will use property models, minor component limits, and other information pertinent to glass processing and performance.

2.3.2 Property Models Development

Glass-property models are needed to aid and direct the glass formulation effort. The models also provide a tool for responding to variations in waste entering the vitrification facility and for process control. Empirical models will be developed for viscosity, electrical conductivity (as long as the Joule-heated melters are not excluded), glass transition temperature, thermal expansion coefficients, and liquidus temperature. The composition range to be covered by these models will be determined based on the results from current glass formulation studies and updated periodically as new information on the waste compositions and performance requirements become available.

Empirical models generally provide better prediction within the composition range covered than any models based on *a priori* assumptions related to structure or thermodynamic properties of glass. However, empirical models may not predict well outside their validity range. They require an appropriately sized data base that must be developed experimentally. Semi-empirical models that incorporate structural and thermodynamic information combined with empirical fitting need fewer data points and, therefore, are less expensive to develop. However, their lower accuracy makes their engineering value problematic. Both empirical and semi-empirical approaches for modeling glass properties will be investigated, but it is expected that empirical models will be more accurate and have better precision.

Glass property models will be developed using experimental data collected over the feasible LLW glass composition region. Statistical experimental design techniques as well as knowledge of LLW glass systems will be used to select glass compositions for experimental testing. This will result in efficiently and adequately exploring the feasible LLW glass composition region, which will support development of accurate and precise property models. Statistical methods will also be used to quantify the uncertainty in each glass property model developed, and such uncertainties will be accounted for in formulating optimal LLW glass compositions.

For an effective glass formulation, models that predict values resulting from durability tests, such as PCT and MCC-1, which have been developed for

HLW glasses (Hirma, Piepel, et al. 1994), are a necessity. For LLW glasses, empirical models predicting PCT elemental releases and flow-through dissolution rates need to be developed. These models are mathematical functions relating durability characteristics to glass compositions. They allow computerization of glass optimization, parametric studies, applications of TWEAT and OWL tools, etc. These models contain higher-order terms (usually second-order), which are prominent in LLW glasses because of their highly non-linear behavior (Kim 1994).

Semi-empirical models exist which are based on correlations between glass properties and results from standard durability tests, such as PCT and MCC-1. The hydration model is a typical example of such an approach (Jantzen 1992). This model estimates the hydration energy of glass as a weighted sum of hydration energies of silicates and oxides, in terms of which the glass composition is mathematically expressed. According to Paul (1990), glass durability increases as the hydration energy decreases. Jantzen (1992) indicates that the logarithm of normalized elemental loss as determined by either MCC-1 test or PCT is a linear function of the free energy of hydration. Savannah River Laboratory is investigating the application of this model to LLW glasses.

Hydration and other models based on *a priori* coefficients and linear correlation are of academic value, but require further development for application to glass formulation and engineering application. They should include the thermodynamics of solution, gel layer formation, and kinetic factors such as reaction rates and transport phenomena.

Model development will use the CVS (Composition Variation Study) data base and models for HLW glasses as much as possible. However, CVS models can not be extended to LLW glasses because of different composition region (e. g. low boron and no lithium) and temperature range. Therefore, the basic approach will initially define the composition region for LLW glasses and test limited number of glasses within that region, and then compare with HLW glass models, determine compositional overlap, and decide which approach to use from the followings:

- (a) completely separate models for LLW,

- (b) separate models based on data from all LLW and selected HLW glasses (the extent of HLW data use can be different for each property), or
- (c) combined models from all LLW and HLW glasses.

The main focus of glass formulation will be on matching glass formulation with performance assessment. Currently, no tools are available to apply the information obtained from performance assessment model development directly to glass formulation. The methodology to investigate the effect of glass composition on the product performance and to apply the results to future formulation of glass composition should be developed.

2.3.3 Critical Issues in Glass Optimization

Glass formulation is a key activity which interfaces with three of the major TWRS/LLW vitrification activities:

- (1) waste characterization and pretreatment,
- (2) melter technology, and
- (3) performance assessment.

The glass formulation must be tailored to the waste composition and/or provide sufficient flexibility to accommodate the waste variability. Waste characterization plus understanding pretreatment flowsheets provides information about the waste composition. Issues connected with the high sodium content of LLW were discussed in Section 2.3:1 and troublesome components are discussed in Section 3.5. Advanced pretreatment methods may result in a wider range and larger concentrations of non-radioactive components to LLW that would otherwise go to HLW. This would reduce HLW glass volume, but it may complicate glass formulation of LLW. However, because of much higher volume of LLW compared to HLW, the troublesome components will be diluted and thus be of lesser concern.

Although innovations in the vitrification flowsheet are expected, the overall melter technology for LLW glass will probably not deviate significantly from commercially available technologies except that these technologies have not been developed for high-sodium glasses. This places on melter vendors a burden

of being sensitive to glass composition development. As has been stressed in Section 2.1, this is not new in the glass-making tradition. Melter technologies allow for some variation in glass composition. However, sensitive issues, such as volatilization, must be addressed by glass formulation with respect to compositional alternatives and their impact on glass performance.

As stated in Section 2.3, the long-term performance of glass is a key element in optimizing glass composition. This implies that there is a pressing need for glass formulation criteria based on the short-term properties that are measured in the laboratory, which can be related to long-term performance. Significant steps toward this end have already been made. The MCC-1 test has been abandoned and replaced by the flow-through test performed at pH 12 for all LLW glasses. In addition, vapor hydration tests are being performed for selected glasses to a greater extent than has been done so far.

On the perennial issue of the relationship between performance assessment requirements and practical short term testing constraints, there are two alternatives to consider: (1) Develop the best glass possible with reasonable waste loading, etc. and use the performance assessment to determine if matrices or barriers are needed to meet disposal system performance objectives. (2) Develop confidence in long-term reaction path modeling for LLW glass compositions by combining selected experimental data with modeling to define a long term leach rate or leachate composition envelope that meets performance objectives. Then demonstrate by experiment and theory that short term tests are conservative with respect to the long term envelope projections.

2.4 Glass Processing

The long-term glass formulation strategy includes testing in small- and pilot-scale equipment to confirm the processability of the selected glass formulation(s). This process testing will identify any difficulties with the formulation such as phase separation or excessive volatility that may not be evident in laboratory-scale testing. It will also provide data to support the design of the vitrification system.

2.5 Radioactive Testing

The long-term glass formulation strategy includes testing with actual wastes. Radioactive testing is required to

- (1) assure that the simulants used in glass formulation development provide results representative of the actual wastes,
- (2) provide data on radioactive species that cannot be obtained from non-radioactive simulants,
- (3) validate the process and product models developed using simulants,
- (4) assess the radiation effects on glass performance, and
- (5) assess the effect of minor components that are deleted from simulants.

If the simulants used in the product and process development are not validated, the vitrification plant and/or the glass product may not function as designed because the chemistry of the waste feed to the plant could be different due to process history, chemical history, and/or minor differences in composition. Moreover, the repository performance of radioactive glasses may be different from that of the simulated glass.

3.0 GLASS COMPOSITION DEVELOPMENT APPROACH

Waste compositions and variability, melter type, and performance requirements are the major issues that need to be determined before the optimized glass composition is finalized. Still, glass formulation work most proceed in order to help resolve these issues and to provide a foundation for the reference formulation selection and formulation optimization. This section describes approaches to develop an optimized glass composition based on waste composition, candidate glass systems, chemical durability, crystallization, troublesome components, viscosity and other glass properties. The current approaches discussed in this section allow sufficient flexibility to meet future processing and performance requirements.

3.1 LLW Waste Compositions

Table 1 shows two simulated LLW compositions (in terms of components that end up in glass). The candidate additives (SiO_2 , B_2O_3 , CaO , and Al_2O_3) and major waste oxides (Na_2O , Al_2O_3) comprise the group of the major glass components, while the Others group consists of the minor waste components. Both compositions shown in Table 1 have been used in glass formulation studies. The Nominal LLW feed composition represents the average composition of all tank wastes except those included in the Double-Shell Slurry Feed (DSSF). The simulated Nominal LLW stream has been used in major PNL glass formulation activities. Simulated DSSF, which is spiked with several minor components, was used in the formulations of candidate melter vendor glasses to support melter system evaluations (Wilson 1994).

Unsatisfactory processing conditions can result from troublesome waste components (P_2O_5 , SO_3 , Cr_2O_3 , F, Cl) if they are present at high concentrations. It is possible that actual LLW streams may contain a large fraction of some of these components. Therefore, the impact of troublesome components on glass and melt behavior must be addressed. Possible effects of troublesome components are discussed in Section 3.5.

TABLE 1. Compositions of Simulated Nominal LLW Stream and Double-Shell Slurry Feed (DSSF)

Component	Nominal (wt%)	DSSF (wt%)
SiO ₂	0.03	
B ₂ O ₃		
Na ₂ O	84.42	76.05
CaO	0.01	0.01
Al ₂ O ₃	6.19	12.20
Others	9.35	11.74
Total	100.00	100.00

Others Component	(wt%)	(wt%)
Bi ₂ O ₃	0.06	
Cr ₂ O ₃	0.15	0.15
Cs ₂ O		0.56*
Fe ₂ O ₃	0.02	0.01
K ₂ O	1.38	5.54
MgO		0.01
MnO	0.03	0.01
MoO ₃		0.57*
Nd ₂ O ₃	0.05	
SrO		0.40*
ZrO ₂	0.02	
P ₂ O ₅	5.01	0.72
SO ₃	1.35	0.82
Cl	0.39	1.33
F	0.90	1.12
I		0.50*
Subtotal	9.35	11.74

* Cs, Mo, Sr, I in DSSF waste are spiked to increase the concentration of these elements so that mass balance across the melter during melter evaluation tests can be determined.

3.2 Candidate Glass Systems

The following aluminosilicate systems are being considered for the formulation of LLW glasses:

$\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$

$\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{CaO} - \text{SiO}_2$

$\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{CaO} - \text{SiO}_2$

Glasses formulated in FY94 were confined to 20 wt% Na_2O to determine the effect of Al_2O_3 , B_2O_3 and CaO concentrations on the short-term and long-term durability. Small additions (up to 6 wt%) of ZrO_2 , MgO , Fe_2O_3 , and any other components that may improve the long-term durability of glass will be investigated starting in FY95. A comprehensive study on the incorporation of troublesome components (P_2O_5 , SO_3 , Cr_2O_3 , F, Cl) has begun on a glass from the $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{CaO} - \text{SiO}_2$ system.

Iron oxide and zirconia have important potential benefits. Zirconia has generally a positive effect on the long-term durability of glass by allowing a decrease in alumina content. This can prevent the formation of aluminosilicates during long-term dissolution. Precipitation of aluminosilicate minerals causes a substantial increase in glass dissolution rate after a period of slow dissolution (see Section 3.3). Iron may help to minimize or eliminate calcium as an additive without increasing boron content. Calcium oxide has a negative effect on glass durability compared to boron, impairs long-term behavior as demonstrated by vapor hydration tests (Bakel and Ebert 1994), reduces solubility of F and P, and increases liquidus temperature. If calcium oxide is replaced by boron oxide, volatility from the resulting glass increases. Iron is far less volatile than boron and may not impair glass performance.

The CVS (Composition Variation Study) for HLW glasses provides a large data base and property-composition models that are valid over broad composition regions. It contains several HLW glasses with high contents of alkali oxides. Table 2 summarizes measured values of normalized releases from 7-day PCT and 28-day MCC-1 (Materials Characterization Center, 1986) tests at 90°C and viscosity at 1150°C of CVS glasses with > 18 wt% Na_2O . Among the four glasses with the 7-day PCT normalized Na release sufficiently low, i.e., < 1 g/(m²·7-day), only CVS2-23 appears to be an acceptable prototype for a low-temperature LLW glass. The other three glasses are not adequate. CVS2-63 contains too low concentration of SiO_2 , making it structurally less stable (i.e., prone to crystallization, etc.). CVS1-16 has a

TABLE 2. Normalized Releases of Sodium and Boron from 7-day PCT and 28-day MCC-1 Tests at 90°C and Viscosity at 1150°C of High-Sodium (Na₂O > 18 wt%) CVS Glasses

Glass	Composition (mass fraction)											Normalized releases				Viscosity at 1150°C (Pa·s)
	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	ZrO ₂	Others	7-day PCT (g/m ² /7-day)		28-day MCC-1 (g/m ² /28-day)			
	Na	B	Na	B	Na	B	Na	B	Na	B	Na	B	Na	B		
CVS2-63	0.3232	0.1717	0.1900	0.0051	0.1000	0.0200	0.1800	0.0100	0.0100	0.0100	0.39	0.33	9.58	9.65	2.38	
CVS1-16	0.4327	0.0500	0.1873	0.0100	0.0800	0.0858	0.1442	0.0100	0.0100	0.54	0.52	16.01	16.85	17.81		
CVS2-23	0.5700	0.0522	0.2000	0.0100	0.0800	0.0200	0.0578	0.0100	0.0100	0.81	0.17	11.63	11.21	9.91		
CVS2-35	0.4200	0.0500	0.2000	0.0428	0.0800	0.0632	0.1340	0.0100	0.0100	0.91	0.32	12.03	11.61	2.82		
CVS2-33	0.4200	0.0544	0.2000	0.0364	0.0800	0.0200	0.0892	0.1000	0.1000	1.61	1.72	13.95	14.51	2.15		
CVS2-27	0.5463	0.0500	0.2000	0.0155	0.0800	0.0200	0.0782	0.0100	0.0100	2.34	3.27	10.98	11.22	14.41		
CVS2-34	0.4200	0.1743	0.2000	0.0369	0.0200	0.1388	0.0100	0.0100	0.0100	2.70	4.34	22.81	29.24	1.79		
CVS2-98	0.4200	0.1743	0.2000	0.0369	0.0200	0.1388	0.0100	0.0100	0.0100	2.80	4.52	25.95	30.44	1.90		
CVS2-28	0.5619	0.0500	0.2000	0.0126	0.0200	0.0555	0.1000	0.1000	0.1000	3.54	5.14	9.98	9.84	13.44		
CVS1-14	0.4200	0.2000	0.1862	0.0100	0.0200	0.0238	0.1300	0.0100	0.0100	5.79	9.85	57.69	73.64	3.42		
CVS2-32	0.5445	0.0500	0.2000	0.0428	0.0200	0.0027	0.1300	0.0100	0.0100	5.90	9.65	16.04	16.62	8.07		
CVS1-13	0.5700	0.2000	0.1862	0.0100	0.0200	0.0038	0.1000	0.0100	0.0100	12.41	14.07	637.31	690.52	3.31		

high MgO content, which is known to decrease durability by precipitating talc from the solution; also, the melting temperature of this glass is $>1150^{\circ}\text{C}$. Finally, CVS2-35 has a high content of Li_2O , which is an unjustified component for high-sodium LLW glasses.

Glass development will proceed as follows:

- (1) glasses showing the best performance in durability tests will be identified at the 20 wt% Na_2O level, and
- (2) the range of Na_2O will be extended to 15 to 35 wt% to determine the effect of waste loading on the long-term durability.

The final decision relative to Na_2O concentration range will depend on long-term durability test results on glasses with 20 wt% Na_2O and performance requirements. In glasses with a high concentration of Na_2O (> 25 wt%), volatilization of sodium may become a limiting factor for waste loading, depending on the melter type.

3.3 Chemical Durability

Long-term reaction of typical silicate glasses in aqueous media progresses in three stages (Bates and Ebert 1994). The initial stage under dilute solution conditions is characterized by a forward reaction rate that depends only on glass composition, temperature, and solution pH. In the intermediate stage, glass reaction rate continually decreases as the concentration of elements released from the glass in the solution increases. The final stage of increased glass dissolution begins when secondary mineral phases precipitate from the concentrated or "saturated" solution. Precipitation of mineral phases causes the solution to become undersaturated with respect to the glass.

The forward reaction rate provides the maximum dissolution rate of the glass, while the low rate in the intermediate stage prior to the formation of secondary phases represents the minimum dissolution rate attainable. According to Bates and Ebert (1994), the long-term performance of glass may be best described by the dissolution rate in the presence of secondary phases. The rate of glass dissolution could be close to the minimum rate of the intermediate stage or similar to the forward reaction rate, depending on the secondary phases formed.

However, it needs to be verified that the secondary phases can form in the LLW glass disposal environments at 20°C. In the recent LLW workshop,* it was agreed that the forward reaction rate determined by single-pass flow-through tests provides the most conservative measure of the glass corrosion rate at a given pH.

Durability of candidate glasses for LLW vitrification will be assessed based on flow-through tests, vapor hydration tests, and long-term PCT. Flow-through tests provide information on the initial forward rate. Vapor hydration tests help identify the mineral phases that may form in the final stage of glass dissolution. Long-term PCT defines the dissolution process through the intermediate and final stages.

The forward rate will be used for ranking the glasses, not directly but by glass dissolution modeling. This information must be provided by disposal system source-term modeling. The current glass formulation and performance assessment source-term modeling efforts are being coordinated to assure free exchange of information.

The temperature dependence of glass corrosion rate is

$$\ln(k) = A - B/T \quad (6)$$

where k is the forward dissolution rate coefficient [$\text{g}/(\text{m}^2\cdot\text{d})$], A a constant, B the activation energy (K), and T the absolute temperature (K). The pH dependence of glass corrosion rate (McGrail and Olson 1992) is described by

$$\log(k) = \log(k') + C [\text{pH}] \quad (7)$$

where k' and C are constants. Joining the two above equations, we obtain

$$\ln(k) = A' - B/T + 2.303 C [\text{pH}] \quad (8)$$

Values typical for borosilicate waste glass are $B = 1 \times 10^4$ K and $C = 0.214$ in the neutral-to-basic pH range (McGrail and Olson 1992). Constant C depends on the glass type, but the dependence is mild: for a highly durable in-situ vitrification glass (McGrail and Olson 1992), $C = 0.321$. The forward rate of glass LD6-5412

* Workshop, Development of Preliminary Durability Specification for Hanford LLW glass, Park City, UT, November, 1994.

containing 20 wt% Na₂O was 3×10^{-3} g/(m²-d) at 50°C and pH 8. Formula (8) predicts that its forward rate at 20°C and pH = 12 is 9×10^{-4} g/(m²-d). Therefore, glass LD6-5412 is likely to be better than the proposed preliminary durability specification (forward rate < 10^{-3} g/(m²-d) at 20°C and pH = 12).

Laboratory tests to determine secondary phases formed and their effects on the dissolution rate of candidate LLW glasses are being conducted at ANL using long-term static tests and vapor hydration test methods (Bates and Ebert 1994). Additional laboratory tests are being conducted at PNL to provide thermodynamic data and intrinsic dissolution rate constants required for long-term durability estimation through modeling of the glass dissolution kinetics (McGrail 1994). The single-pass flow-through test, under controlled chemical conditions, allows key kinetic rate constants to be obtained (McGrail and Olson 1992). The experimental tests to obtain thermodynamic data on glass reaction equilibrium starts in FY-95.

Because glass formulation development demands testing many glasses in a short time, it is not practical to conduct long-term durability testing on every glass. Only the standard 7-day PCT and single-pass flow-through test for forward rate determination will be performed for each glass composition. Considering the current durability specification, the glass development will primarily focus on minimizing the forward rate, while obtaining supporting information by 7-day PCT and vapor hydration tests (performed for selected glasses).

Selected LLW glasses, which represent different compositions within aluminosilicate systems and a broad range of short-term durability, are subjected to long-term durability testing. Glasses with a broad range of short-term durability including some poor performers and the best are tested for long-term durability to determine the relation between short-term and long-term durabilities. The information obtained by comparing short-term and long-term results can be used to develop new test method(s) with a greater potential to anticipate the long-term durability.

3.4 Crystallization and Its Effect on Chemical Durability

Glasses can devitrify during cooling from the melting temperature depending on the cooling rate and glass composition. The chemical durability of a

devitrified glass may increase or decrease according to the type and fraction of crystals formed. In glasses developed and tested for HLW vitrification, formation of nepheline ($\text{NaAlSi}_3\text{O}_8$) after treatment according to the simulated Canister Centerline Cooling (CCC) history resulted in a significant decrease in glass durability. Table 3 presents the HLW glasses that precipitated nepheline after CCC and compares their 7-day PCT normalized Na releases in as-melted (untreated) and CCC samples, showing that the latter was up to 15 times higher than the former.

Table 3 also shows that nepheline formed in glasses containing high concentrations of Na_2O and Al_2O_3 . This suggests that the LLW glasses containing high Al_2O_3 may form nepheline during slow cooling and thus decrease durability. The significant decrease of glass durability in glasses with precipitated nepheline

TABLE 3. PCT Normalized Na Releases in CVS HLW Glasses That Precipitated Nepheline after Simulated Canister Centerline Cooling (CCC) Treatment

Glass	PCT Na (g/m ² /7-d)		Crystallinity after CCC (volume %)
	Untreated	CCC	
CVS1-16	0.54	8.85	Nepheline (15-18%), Spinel (<1%)
CVS2-33	1.61	7.41	Nepheline (~15%)
CVS2-35	0.91	10.38	Nepheline (~10%), Gehlenite (~7%), SiO ₂ (~2%)
CVS2-63	0.39	2.16	Nepheline (~15%)
CVS2-85	0.75	18.34	Nepheline (~33%), Li ₂ SiO ₃ (~30%)
CVS2-86	0.25	0.30	Nepheline (~5%)

Glass	Composition (wt%)									
	SiO ₂	B ₂ O ₃	Na ₂ O	Li ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	ZrO ₂	Others
CVS1-16	43.27	5.00	18.73	1.00		8.00	8.58	14.42		1.00
CVS2-33	42.00	5.44	20.00	3.64		8.00	2.00	8.92		10.00
CVS2-35	42.00	5.00	20.00	4.28	8.00		6.32	13.40		1.00
CVS2-63	32.32	17.17	19.00	0.51	10.00		2.00	18.00		1.00
CVS2-85	44.00	6.00	18.00	7.00	0.50	2.00	0.50	17.00	0.50	4.50
CVS2-86	47.64	6.00	18.00	1.36	4.00	0.50	0.50	17.00	0.50	4.50

may be mainly attributed to the decrease in durability of the residual glass. Crystallization of nepheline removes Al_2O_3 from the residual glass (much less Na_2O is removed from the glass compared to Al_2O_3). To illustrate this effect, the predicted PCT Na release from the residual glass after varying degrees of nepheline crystallization was calculated using the HLW first-order model (Hrma, Piepel, et al. 1994) in glass L6-5412 (Langowski et al. 1994) and shown in Figure 2. Volume % and wt% are similar because the density of nepheline is close to that of glass at $\sim 2.6 \text{ g/cm}^3$. Considering possible concentration gradients around the crystals that may form during precipitation and chemically induced internal stresses, the effect may be even larger.

The cooling rate the glass undergoes after melting depends on the size of the

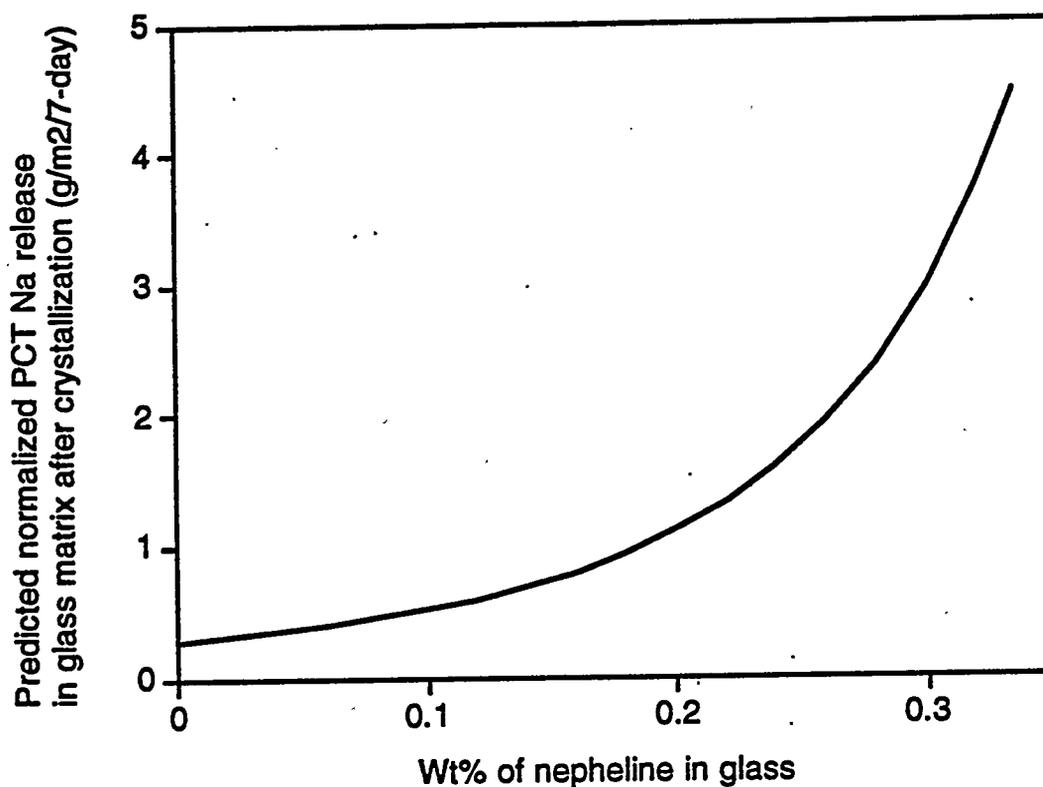


FIGURE 2. Predicted Effect of Nepheline Crystallization on the Normalized Release of Na Determined by 7-Day PCT in Glass L6-5412

glass product. Crystallization in candidate LLW glasses and its impact on durability will be investigated in detail as soon as the decision on the physical form of glass is made and, thus, the cooling rate can be accurately predicted. If the LLW glass is produced as a small-sized cullet or marble, which is currently being used for performance assessment modeling, no need for detailed crystallization study is expected. For the time being, a limited study on LLW glass crystallization, such as gradient furnace testing, will be conducted.

3.5 Troublesome Components

Some minor components (P_2O_5 , SO_3 , Cr_2O_3 , F, Cl) in various Hanford low-level wastes may affect LLW vitrification. These troublesome components may form phase segregated layers (P_2O_5 , SO_3 , Cr_2O_3 , Cl), lead to crystallization (P_2O_5 , Cr_2O_3 , F), or volatilize (F, Cl, SO_3) causing processing problems. The Nominal LLW stream does not contain excessive concentrations of troublesome components, but some individual tank wastes can. Therefore, attention must be given to the potential effects of troublesome components on glass formulation. The information resulting from the troublesome component study may be used for developing a blending strategy.

Investigating the effects of troublesome components will include the following activities:

- (1) Determine the maximum concentration of each (single) troublesome component that can be incorporated into the glass without causing unsatisfactory processing problems (as a function of melting temperature) using one of the candidate LLW glasses.
- (2) Determine possible interactive effects of troublesome components that might result in other problems unexpected from the study of single component effects.
- (3) Determine the effect of major glass components on the incorporation of troublesome components.

- (4) Determine possible mitigation effects of other minor components (not troublesome components) on the incorporation of the limiting components.

Investigation of the activities mentioned above will depend on the following factors: maximum projected concentrations of troublesome components in various LLW types, the limiting concentrations of these components in glass, and the maximum waste loading that will be primarily determined from the chemical durability of glass and performance requirements. For example, if the maximum concentration of a troublesome component in any of the LLW types does not result in a limiting concentration in glass at the estimated maximum waste loading, activities (3) and (4) may not be required. Spectroscopic methods will be used to determine the interaction of troublesome components with the glass structure. This information will help glass formulation in identifying composition regions in which troublesome components can be incorporated safely.

3.6 Viscosity

Information regarding the viscosity of the glass melt is important for successful operation of the glass melter. At glass melting temperatures, a low viscosity may cause excessive corrosion of melter walls and electrodes (Joule-heated melters) and increase volatilization. A high viscosity causes a slow melting rate and difficulty in pouring glass from the melter. Laboratory glass is usually melted at ~ 10 Pa-s. Various large-scale melters may require different optimum viscosities to control corrosion, volatilization, and processing conditions. This may require the use of different melting temperatures even for the same glass composition.

The models for viscosity developed for HLW glasses (Hrma, Piepel, et al. 1994) have not provided sufficiently accurate predictions for LLW glasses because of the differences in composition and melting temperature ranges. The development of a viscosity model for the LLW glass composition and temperature range is, therefore, necessary.

3.7 Other Glass/Melt Properties

Information on the following glass/melt properties are needed to support glass processing including melter operation and glass characterization for disposal.

- Electrical conductivity
- Glass transition temperature
- Thermal expansion coefficients
- Liquidus temperature
- Redox

Because there is not sufficient overlap between the CVS composition region for HLW and LLW glass composition region, it is important to test these properties within the projected LLW glass composition region. Also, CVS models are not validated for LLW glass composition and melting temperature range.

Electrical conductivity data are needed to determine the design parameters of the power supply system for Joule-heated melter types. Glass transition temperature (T_g) characterizes the transformation from an equilibrium melt to a "frozen" glassy state. At T_g , thermal expansion, heat capacity, and other properties change abruptly. Thermal expansion coefficients of solid ($<T_g$) and molten glass ($>T_g$) are obtained as by-products of the T_g measurement. Thermal expansion of molten glass affects convection currents in the melter, which control heat transfer from the molten glass to the cold cap in typical batch-top melting. Thermal expansion of solid glass determines the extent of internal stress development during cooling and, if applicable, crystallization. Data on liquidus temperature of glass will provide information on possible crystallization during melter operation, which might cause processing problems depending on the crystal types formed and the melter system design. Redox data are useful for incorporation of multivalent species, such as chromium and iron, into glass.

Measurements of viscosity, electrical conductivity, glass transition temperature, thermal expansion coefficients, liquidus temperature, and redox will be made using the same test methods that were used in developing HLW glasses (Hrma, Piepel, et al. 1994).

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